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*Review*

# Symmetries, Conserved Properties, Tensor Representations, and Irreducible Forms in Molecular Quantum Electrodynamics

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Received: 13 June 2018; Accepted: 11 July 2018; Published: 23 July 2018

**Abstract:** In the wide realm of applications of quantum electrodynamics, a non-covariant formulation of theory is particularly well suited to describing the interactions of light with molecular matter. The robust framework upon which this formulation is built, fully accounting for the intrinsically quantum nature of both light and the molecular states, enables powerful symmetry principles to be applied. With their origins in the fundamental transformation properties of the electromagnetic field, the application of these principles can readily resolve issues concerning the validity of mechanisms, as well as facilitate the identification of conditions for widely ranging forms of linear and nonlinear optics. Considerations of temporal, structural, and tensorial symmetry offer significant additional advantages in correctly registering chiral forms of interaction. More generally, the implementation of symmetry principles can considerably simplify analysis by reducing the number of independent quantities necessary to relate to experimental results to a minimum. In this account, a variety of such principles are drawn out with reference to applications, including recent advances. Connections are established with parity, duality, angular momentum, continuity equations, conservation laws, chirality, and spectroscopic selection rules. Particular attention is paid to the optical interactions of molecules as they are commonly studied, in fluids and randomly organised media.

**Keywords:** symmetry; parity; quantum electrodynamics; optics; nanophotonics; chirality; helicity; optical activity; optical angular momentum; dual transform; electromagnetic duality; irreducible tensor; multiphoton process; quantum information

## 1. Introduction

It is a truism that principles of symmetry lie at the heart of modern physics. Indeed, it is perhaps to be expected, when scientific reductionism demands fundamental theory to be valid at every level from the smallest subatomic particle upwards. A well-known illustration is afforded by the symmetry principles associated with spherical geometry, which largely determine the character of electronic transitions in atoms—and thereby the form of each atomic spectrum. By contrast, it might be supposed that in the realm of the larger agglomerations we designate as molecules, with a vast multitude of shapes and structures, the operation of symmetry principles would be less prominent. Yet, a moment's reflection tells us this is not so. Consider, for example, the lowly water molecule: it is only because its three atoms, as a result of their intrinsic electronic structure, form a bent rather than a linear arrangement (Schoenflies point group $C_{2v}$ as opposed to $D_{\infty h}$) that $H_2O$ possesses an electric dipole moment—and every life as we know it could not exist otherwise.

The interactions of light with matter exhibit a range of especially puissant symmetry principles, many owing their origin to the intrinsic features of electromagnetism as one of the four fundamental forces of nature. Just as the atoms in a molecule are primarily held together by electrical forces, molecules engage with light by primarily electrical—and to some extent, magnetic—forms of coupling.

At this level, where the quantum nature of the world is very evident, the one theory that correctly accounts for the optical properties of both molecules and light, in their mutual interactions, is molecular quantum electrodynamics (QED) [1–8]. It draws on principles that operate at the deepest fundamental level; QED is widely known as the most successful theory in physics, unsurpassed in the precision of its agreement with experiment. However, it is not simply quantitative accuracy for which the theory has value; it has a robust character of immense power for determining absolutely the validity, viability, and necessary conditions for optical interactions of a wide-ranging nature, based on principles of structural and mathematical symmetry.

In the concise overview that follows, a range of such principles is drawn out with reference to some of the most recent applications. Connections are established with continuity equations, conservation laws, and spectroscopic selection rules, and particular attention is paid to the optical interactions of molecules in fluids (gas, liquid, or solution phases) or randomly organised media—which together account for most common molecular systems. Although, with relatively little reformulation, almost the same framework has been shown to apply to dielectric solids, quantum dots, and quantum wells, those are excluded from the analysis that follows, simply for the sake of brevity. The article substantially builds upon a recent review of the role of symmetry in the quantum theory of nanoscale optical and material chirality [9]; the expanded scope of the present work more widely addresses optical phenomena in molecular systems, with a particular focus on optical transitions. A differently formulated group theoretical approach is necessary to address non-molecular, effectively continuous materials [10].

The following analysis begins in Section 2 with a brief review of charge-parity-time ($\mathcal{CPT}$) symmetry with conservation laws and electro-magnetic dual symmetry discussed in Section 3. (By happy coincidence, the initials $\mathcal{CPT}$ are shared by three pioneers in this field: Craig, Power, and Thiru (as Thirunamachandran insisted he be called, for ease to Westerners). The three worked together extensively, though seldom publishing as a threesome; they were very well known to both the present author and the editor of this special issue. Sadly, all three have departed this life since the millennium). The subsequent Section 4 introduces the full foundation for a detailed analysis of various forms of photon–molecule interaction—those explicitly involving real quantum transitions in the material medium, with directly associated selection rules. In Section 5, the further development of the theory for multiphoton processes then introduces the construction of a convenient representation for radiation and molecular tensors, whose structure and permutational symmetry receives detailed attention in Section 6. After a focus on the general form of observables in Section 7, Section 8 introduces Cartesian tensors of irreducible form, facilitating identification of the dependencies of multiphoton processes on experimental configurations—such as beam geometries and polarization—and on molecular structure. Here, the group theoretical connection with angular momentum coupling comes to the fore. On this basis, Section 9 develops a symmetry categorisation of transition classes, establishing a connection to information content. Then, in Section 10, it is shown how, as a result of effecting isotropic or axial averaging procedures, dramatic simplification ensues when the theory is further developed for application to measurements on fluids, or indeed any substantially or partially disordered molecular system. To illustrate the application and significance of several principles outlined within this paper, Section 11 provides a concise illustration of how they apply to the elucidation of some interesting dichroic effects in the simple case of single-photon absorption. The paper ends in Section 12 with a brief discussion of recent applications.

## 2. Charge-Parity-Time Symmetry in Molecular Electrodynamics

Symmetry principles are powerfully operative in determining the allowed or forbidden character of optical processes in molecular systems. To fully appreciate the origin of the detailed rules that emerge from such considerations, in each form of interaction, it is necessary to formulate theory that treats both matter and light with full quantum rigour. The wide variety of symmetry types into which molecules fall affords an even greater variety regarding their individual electronic and vibrational quantum states.

The realm of optics and electrodynamics generally addresses mechanisms that fundamentally involve the positions and motions of electrical charges. Accordingly, it is the symmetry laws associated with charge, spatial position, and time that are of primary significance, that is, the operations of charge, space, and time inversion denoted by $\mathcal{C}$, $\mathcal{P}$, and $\mathcal{T}$, respectively [11–13]. Each is formally represented by the Abelian group $Z_2$, whose $\pm 1$ eigenvalues signify even or odd parity. All optical phenomena preserve symmetry under the product operation $\mathcal{CPT}$—a proof of this universality and analysis of its implications has been authoritatively presented in a recent review by Lehnert [12], and a broad spectroscopic perspective on the topic has been given by Lazzeretti [14]. Nonetheless, considerations of charge conjugation symmetry are seldom relevant for conventional electrodynamic phenomena, as the mathematical operation $\mathcal{C}$ is never physically realized; clouds of negative charge always surround positively charged nuclei. Accordingly, in the consideration of optical effects, it is usually sufficient to restrict consideration to the $\mathcal{PT}$ product, which, through the constraints of Lorentz invariance, ensures Hamiltonian operators of Hermitian form. Moreover, $\mathcal{PT}$-symmetric quantum theory has been shown to be exactly equivalent to standard (Hermitian) quantum mechanics in terms of all observables [15].

It is worth emphasizing that applying the symmetry operation of time reversal to any mathematical representation both changes the sign of any explicitly occurring time variable, and it effects Hermitian conjugation—which also subsumes complex variable conjugation. In terms of relativity theory, this is consistent with the four-vector symmetry for Lorentz transformations on the Minkowski space $(ict, x, y, z)$; in the sphere of quantum mechanics, it also ensures, for example, that the Hamiltonian operator $i\hbar\partial/\partial t$ is itself time-even [16,17]. An extensive summary of the properties, physical significance, and interpretation of P and T within the framework of molecular QED is given in the literature [9]. Other issues of non-Hermitian photonics and $\mathcal{PT}$ symmetry, which specifically relate to non-molecular media, and are therefore beyond the scope of the present article, are notably discussed in two other recent references [18,19].

## 3. Dual Symmetry and Conservation Laws in Quantum Electromagnetism

To proceed, it is appropriate to recall that for the constituent fields of electromagnetic radiation, the electric field $\boldsymbol{e}$ is formally of odd parity under $\mathcal{P}$ as well as under $\mathcal{T}$; the converse applies to the magnetic induction field $\boldsymbol{b}$. This symmetry is indeed required by the structure of the Faraday and Ampère Laws. Nonetheless, these and the other two Maxwell's equations also support another well-known, fundamental symmetry, registering a dual complementarity between the electric and magnetic fields of optical radiation in free space. It is a symmetry that is compromised in the presence of electric charge, owing to the asymmetry in existence of electric but not magnetic monopoles; for the electric field, a charge-driven source term accordingly appears in Gauss's Law, but there is no counterpart in the expression for divergence of the magnetic field. Nonetheless, there is sufficient interest and power in the underlying free-space symmetry that there is recurrent attention in electromagnetic duality. Indeed, much of the recent interest—largely centred on structured and singular light, with associated momentum and angular momentum issues—does concern essentially free-space propagation.

In a range of acceptable formulations for the Poynting vector, for example, Berry advocates an 'electric–magnetic democracy' [20]. This is a feature that is evident not only the classical formulation, but also in the operator formulation due to Power and Thirunamachandran;

$$\boldsymbol{p}(\boldsymbol{r},t) = \frac{1}{2}\varepsilon_0[\boldsymbol{e}(\boldsymbol{r},t) \times \boldsymbol{b}(\boldsymbol{r},t) - \boldsymbol{b}(\boldsymbol{r},t) \times \boldsymbol{e}(\boldsymbol{r},t)] \tag{1}$$

which is Equation (3.1) in the literature [21], here recast in SI units: $\boldsymbol{r}$ and $t$ are space and time coordinates. For more general application, it is the transverse electric displacement field $\boldsymbol{d}^{\perp}$ that should feature in (1), rather than the electric field $\boldsymbol{e}$, but in source- and current-free regions, there is no physical distinction (the symbol $\boldsymbol{d}$ is also commonly used in entirely different connections). Here, too, with a view to the microscopic formulation that is appropriate for application to systems on the molecular scale, the standard lower-case symbols are used; the context will generally make it clear if quantum operators are signified. Notably, in the above Equation (1), symmetrisation is necessary to ensure Hermiticity, because of the non-commutativity of the electric and magnetic field operators at a common point in space [4,22]:

$$\left[e_i(\boldsymbol{r}), b_j(\boldsymbol{r}')\right] = \frac{i\hbar}{\varepsilon_0}\varepsilon_{ijk}\frac{\partial}{\partial \boldsymbol{r}'_k}\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{2}$$

here and henceforth, there is implied summation over repeated tensor indices; $\varepsilon_{ijk}$ is the Levi–Civita antisymmetric tensor. Equation (2) immediately exhibits quantum uncertainty in optics, manifested at the photon level; it signifies that the electric and magnetic fields cannot be simultaneously determined at any single position.

Another aspect of the free-space relationship between $\boldsymbol{e}$ and $\boldsymbol{b}$ is manifested in the form of the duality transformation under which Maxwell's source-free equations prove invariant:

$$(\boldsymbol{e},\, c\boldsymbol{b}) \to (\boldsymbol{e}\cos\theta + \boldsymbol{b}c\sin\theta,\ \boldsymbol{b}c\cos\theta - \boldsymbol{e}\sin\theta) \tag{3}$$

where the brackets simply denote the orthogonally paired fields. Here, $\theta$ is an arbitrary pseudoscalar, signifying that it changes sign under spatial parity inversion. The odd parity of the electric field, and the even parity of the magnetic field, both under $\mathcal{P}$, are thus preserved in the transformation; temporal parity is compromised, except in the case of $\theta = \pi/2$ (or, trivially, multiples of $\pi/2$). In anticipation of later details, it is worth noting that casting equations in units such as the commonly used $c = \hbar = 1$ can obscure any connection between the transformation properties under $\mathcal{P}$ and $\mathcal{T}$. For example, in the above equation, every element necessarily has the same units, but $c$ clearly does not change under any such transformation; the $\boldsymbol{e}$ and $\boldsymbol{b}$ fields exhibit different spatial and temporal parities because they have different physical dimensions.

Equation (3), known as a Heaviside–Larmor transformation, has the specific form of a 2D rotation, with symmetry SO(2). In some accounts, it is misleadingly described as a Lorentz boost, because an expression of Lorentz transformation equations in terms of hyperbolic (cosh and sinh) functions of *rapidity* has a similar cast [23], and those functions convert to their trigonometric counterparts when their argument is imaginary. However, the signs in (3) are not consistent with this interpretation; moreover, the Lorentz transform necessarily engages time with one physical dimension. A useful account of the Lorentz transforms of electric and magnetic fields is given by Ivezić [24].

The textbook compartmentalisation of optical angular momentum $\boldsymbol{j}$ into spin and orbital parts, $\boldsymbol{s}$ and $\boldsymbol{l}$, respectively, proceeds along the following lines [25]:

$$\boldsymbol{j} = \int \boldsymbol{r}\times\boldsymbol{p}\, d^3\boldsymbol{r} \equiv \boldsymbol{l} + \boldsymbol{s} \tag{4}$$

$$\boldsymbol{l} = \varepsilon_0 \hat{r}_i \int e_j(\boldsymbol{r}\times\nabla)_i a_j d^3\boldsymbol{r} \tag{5}$$

$$\boldsymbol{s} = \varepsilon_0 \hat{r}_i \int (\boldsymbol{e}\times\boldsymbol{a})_i\, d^3\boldsymbol{r} \tag{6}$$

where $\varepsilon_0$ is the vacuum permittivity and $\boldsymbol{a}$ is the vector potential field. Quite apart from the gauge-dependence of $\boldsymbol{a}$, it is well known that this separation is beset with problems; the spin operator $\boldsymbol{s}$ does not satisfy the necessary commutation relations amongst its Cartesian components, to be acceptable as a true quantum mechanical operator [26]. As pointed out by Barnett et al., the same conclusion therefore necessarily applies to the counterpart orbital angular momentum $\boldsymbol{l}$, as the sum of the two does constitute a mathematically correct formulation of the orbital momentum from the vector product $\boldsymbol{r}\times\boldsymbol{p}$. [27]. Their work nonetheless exhibits the dual transformation as essentially consistent, within the paraxial approximation, to the rotations generated by treating $\boldsymbol{l}$ and $\boldsymbol{s}$ as infinitesimal angle generators.

In an incisive analysis by Cameron et al. [28], it has been shown how, through application of Noether's theorem [29] to the appropriate symmetries of Maxwell's equations, it is possible to secure a refined form of angular momentum conservation laws, revealing a subtle interplay of spin and orbital angular momentum features. Further manipulation of the Maxwell equations in terms of vector and scalar potentials, exploiting dual symmetry, has also been shown to reveal a cascade of mathematically equivalent formulations, [30] though with a caveat that application in the presence of charge will introduce complications. For any non-paraxial beam, it is possible to secure exact, self-consistent operator descriptions of the spin and orbital angular momenta in both quantum and classical energy-flow formulations [31]. The ultimately incomplete separability of spin and orbital angular momenta for structured light is essentially connected to the spatial variation of momentum flux, which undermines canonical separation [32]. Accordingly, there is a host of optical phenomena that manifest optical spin-orbit coupling, as shown and summarised in a commendable review [33]. Not surprisingly, the extent and nature of such coupling is compounded when knotted fields are entertained [34].

Bliokh et al. have highlighted problems with exploiting electromagnetic duality in standard electromagnetic field theory, as its association with an incontrovertibly non-dual Lagrangian [35] leads to conflicts in the associated conservation laws. Of course, for any dynamic system, the Lagrangian is not unique; observables relate to equations of motion that are at least invariant to the addition to the Lagrangian of any total time-derivative. However, by recasting the formulation in terms of a dual field tensor, Bliokh's work has shown how it is possible to resolve the issues, and also to afford a more robust method for separately identifying spin and orbital parts of the angular momentum. The analysis engages another field vector with a significant symmetry role, now usually known as the Riemann–Silberstein vector $\boldsymbol{f}$ [36–38]:

$$\boldsymbol{f}(\boldsymbol{r},t) = \boldsymbol{e}(\boldsymbol{r},t) + ic\boldsymbol{b}(\boldsymbol{r},t) \tag{7}$$

together with its Hermitian conjugate, this field also serves as a suitable basis for representing electromagnetic fields. Fernandez-Corbaton and Molina-Terriza favour the Riemann–Silberstein (RS) formulation in their account of duality symmetry in transformation optics [39], for the transformation Equation (3) can then be cast as follows:

$$\boldsymbol{f}(\boldsymbol{r}) \rightarrow \exp(\pm i\theta)\boldsymbol{f}(\boldsymbol{r}) \tag{8}$$

In a detailed analysis of the parity and general symmetry properties of dual symmetry, duality transformations, and helicity density associated with electromagnetic waves in widely-ranging dispersive media, it has recently been noted that the generator of the dual transformation has eigenmodes that are fields of well-defined $(\pm)$ helicity [40]. In earlier work, Bialynicki-Birula proposed that the RS field vector fulfils the function of a photon wavefunction. [41] However, there are obstacles to such an interpretation. Consider any specific radiation mode $(\mathbf{k},\eta)$, for wave-vector $\boldsymbol{k}$ and polarization $\eta$; there is no way to represent the wavefunction for the two-photon state, $|2(\mathbf{k},\eta)\rangle$, as any kind of combination or product of one-photon $|1(\mathbf{k},\eta)\rangle$ state functions (just as it is not possible to represent the wavefunction for a 2*s* electron in hydrogen in simple terms of 1*s* wavefunctions). The notion of a photon wavefunction can serve as a workable pragmatism when single photons are involved, and the distinction from a state vector poses less of a problem, but for states with two or more identical photons, there is no conventional sense in which any one photon can be considered to have its own wavefunction [42].

A range of conservation principles also relates to the symmetry properties of electromagnetic radiation. However, the engagement of light with matter undermines the applicability in most cases. For example, although energy is conserved between matter and radiation as an overall quantity in any optical interaction, for any measurement that is made beyond a near-field region of quantum uncertainty, the same cannot necessarily be asserted for all other quantities conserved in freely propagating radiation. A key illustration, to be examined below, is afforded by an optical chirality measure known after its originator as the *Lipkin zilch*. Associated with conservation of polarization [43–46], this is just one of a group of properties that is conserved in free electromagnetic fields, representative of a group whose invariance under the space–time Poincaré group is associated with an eight-dimensional Lie algebra of non-geometric symmetry transformations.

Work by Bliokh and Nori has uncovered close connections between the optical chirality density and such measures as polarization helicity and energy density [47], and the results have been shown to have a direct dependence on a difference in the photon number operators for left- and right- handed modes [48]. For example, the helicity operator for the free field, defined by the volume integral of $\boldsymbol{a}.\boldsymbol{b}$ emerges as follows:

$$\kappa \equiv \int \boldsymbol{a}.\boldsymbol{b}\ d^3\boldsymbol{r} = \frac{\hbar}{c\varepsilon_0}\sum_{\boldsymbol{k}}\left[n^{(\mathrm{L})}(\boldsymbol{k}) - n^{(\mathrm{R})}(\boldsymbol{k})\right] \tag{9}$$

where the brackets on the right contain a difference of the number operators for left- and right-handed circularly polarized photons. Locally, the appropriate operators for measures of radiation helicity are a chirality flux $\boldsymbol{\varphi}(\mathbf{r},t)$ and chirality density $\chi(\mathbf{r},t)$, which together satisfy a continuity (helicity conservation) equation [48];

$$\frac{\partial\chi}{\partial t} + \nabla.\boldsymbol{\varphi} = 0 \tag{10}$$

with the defining equations

$$\chi = \frac{\varepsilon_0}{2}\left[\boldsymbol{e}.(\nabla\times\boldsymbol{e}) + c^2\boldsymbol{b}.(\nabla\times\boldsymbol{b})\right] \tag{11}$$

$$\boldsymbol{\varphi} = \frac{c^2\varepsilon_0}{2}[\boldsymbol{e}\times(\nabla\times\boldsymbol{b}) - \boldsymbol{b}\times(\nabla\times\boldsymbol{e})] \tag{12}$$

in terms of fundamental symmetries, the matrix elements of $\chi$ are pseudoscalar fields, odd with respect to the operator for space inversion (or parity), $\mathcal{P}$, but even under time reversal, $\mathcal{T}$; $\boldsymbol{\varphi}$ is a polar vector field, even under $\mathcal{P}$ and odd under $\mathcal{T}$. Together, the operators defined by Equations (11) and (12) represent components of a four-vector $(c\chi,\boldsymbol{\varphi})$ in Minkowski space [49], signifying the conserved Lipkin 'zilch' [43].

The issues of electromagnetic helicity become considerably more intricate for radiation passively propagating within complex media; the subject is thoroughly explored in a recent paper by Alpeggiani et al. [50]. However, the pursuit of conservation laws in connection with *active* processes, where real electronic transitions occur and energy is exchanged between radiation and matter, is a fundamentally different proposition [51]. In this respect, helicity-related aspects of optical radiation behave quite differently from energy, linear momentum, and angular momentum, to which global conservation laws apply. For example, when any molecule absorbs a circularly polarized photon, it does not thereby gain in helicity, nor does circularly polarized emission deplete any measurable chiral character in the emitter. Fundamentally, there is no quantum operator for helicity/chirality in a material system—nor can there be. The spectroscopic study of circular dichroism (CD), that is, circularly differential single-photon absorption, manifests the implausibility of any such measure, for quantitative measurements exhibit a dependence on optical wavelength that is far from absolute; generally, the CD rate differential is a sensitive and intricate function of the electronic wavefunctions, excited state energies, and transition dipoles for each material.

## 4. Symmetry Principles for Photon–Molecule Interactions

Having outlined the symmetry principles that apply for free radiation, we can now undertake a review of the principles that apply to photon–molecule interactions, with a particular view to electronic transitions. Accordingly, this section begins with a concise summary of key equations that will underpin any conventional deployment of QED, in deriving expressions for the observables in optical transitions. The generic framework described in previous work [9,52], which provides a basis for describing both processes and electrodynamic properties based on the Power–Zienau–Woolley (PZW) Hamiltonian [1,53–55], is here consolidated for specific application to electronic transitions—facilitating simplification by excluding features that would only feature in the theory of optically parametric processes, or in the representation of static quantities such as permanent dipoles or susceptibilities.

The approach to be taken allows provision for the full symmetry of the free electromagnetic field to engage with the full symmetry of the molecular system. In this respect, it substantially differs in its approach from complementary forms of analysis considering direct reductions of electromagnetic field symmetry through propagation within gyrotropic media, for example [56].

Although the principles to be enunciated are in principle applicable to 'photonic molecules'—a term that was introduced to highlight a similarity between the optical modes in simple cavity photonics and those of diatomic molecules [57]—the former constructs generally lack the rich diversity of symmetry elements afforded by real molecular systems, and in this respect, a more general use of the term is perhaps misleading. Equally, the fabrication of structures to impose excitation symmetry in surface plasmonics has no real connection with the intrinsic selection rules for electronic transitions [58]. However, applications of the symmetry framework to be developed in the following analysis do invite extension to nanofabricated dielectric structures, where transition processes such as circular dichroism occur, even as specifically quantum aspects of the radiation become less prominent. An example of recent work in this area is a fine combination of theory and experimental work on dichroism in chiral sculptured thin films [59].

The key observable for optical transitions is a signal proportional to the rate $\Gamma$—which may directly represent a rate of transition, or equally a rate of change in the energy, linear or angular momentum content of the radiation fields that are responsible. Unless saturation occurs, the rate is usually cast in terms of Fermi's Golden Rule:

$$\Gamma = \frac{2\pi\rho}{\hbar}|M_{FI}|^2 \tag{13}$$

if either saturation or oscillatory behaviour occurs, the detailed dynamics is still essentially determined by the matrix element for the process The density of states $\rho$ exhibited in this equation is in principle a convolution of functions representing the number of states per unit energy interval for each of the light-matter system components; in practice, one component usually dominates, and for the many applications (including almost all multiphoton processes) that involve narrow linewidth lasers, it is usually the molecular excited state whose linewidth effectively determines the value. The core of Equation (13) is $M_{FI}$, the *matrix element* of an operator $M$ that couples an initial state $|I\rangle$ to a final state $|F\rangle$ in a composite *system* (i.e., molecule plus radiation). In the present connection, with a focus on processes in which energy is exchanged between the radiation and matter, the final state is presumed to be measurably different from, though necessarily isoenergetic with, the initial state of energy $E_I$. The operator $M$ may itself be cast in the following resolvent operator form [22]:

$$M = \sum_{p=0}^{\infty} H_{\text{int}}(G_0 H_{\text{int}})^p \tag{14}$$

where the propagator is given by

$$G_0 \simeq (E_I - H_0)^{-1} \tag{15}$$

$$H_0 = H_{\text{mol}} + H_{\text{rad}} \tag{16}$$

Here, $H_0$ is the basis Hamiltonian, comprising the unperturbed molecular and radiation operators. Implementing the completeness relation delivers the system matrix element $(M_{FI})_{\text{sys}}$ in the form of a familiar expansion in the light-matter interaction operator $H_{\text{int}}$, representing a time-dependent perturbation:

$$(M_{FI})_{\text{sys}} = \langle F|H_{\text{int}}|I\rangle + \sum_R \frac{\langle F|H_{\text{int}}|R\rangle\langle R|H_{\text{int}}|I\rangle}{(E_I - E_R)} + \sum_{R,S} \frac{\langle F|H_{\text{int}}|S\rangle\langle S|H_{\text{int}}|R\rangle\langle R|H_{\text{int}}|I\rangle}{(E_I - E_R)(E_I - E_S)} + \ldots \tag{17}$$

the intermediate states $|R\rangle$, $|S\rangle$ associated with energies $E_R$, $E_S$, and so on, are also cast in the system basis. Each Dirac bracket featured in the numerators of terms in Equation (17), and thus entails both matter and radiation components—and to identify symmetry aspects, both must be brought into explicit consideration.

It is the structure of the operator $M$, given by Equation (14), that proves a key to unlocking the symmetry aspects of light-matter interactions examined in the following section. As the system basis comprises products of molecular and radiation states, the symmetry of the propagator $G_0$ is separable in each component. Clearly, all energies are scalar quantities, and $H_{\mathrm{mol}}$ is invariant under the same full set of symmetry operations as the molecule, whose symmetry class is always identified with the ground state (or higher, in the case of chiral species [60]—where the ground state wavefunction lacks a two-fold permutational symmetry that is present in the molecular Hamiltonian).

As noted above, it is most expedient to deploy the PZW form of interaction Hamiltonian, cast as multipolar coupling in terms of a transverse electric field operator $\boldsymbol{e}^{\perp}$ and a counterpart magnetic induction operator $\boldsymbol{b}$. This affords major calculational advantages and insights; expressing the couplings between the optical fields and charges directly in terms of experimentally meaningful electric and magnetic fields also highlights their involvement with corresponding multipole moments and optical response tensors in Cartesian form, thus elucidating their connection to molecular symmetry. Strictly, when casting theory in terms of a PZW Hamiltonian formulation, all orders of the electric multipole coupling should be cast in terms of a transverse electric displacement $\boldsymbol{d}^{\perp}$, rather than the electric field $\boldsymbol{e}^{\perp}$ [4,61]. However, in isotropic media such as gases, and all conventional liquids and solutions, the two quantities are related by a scalar, so precisely the same symmetry arguments apply. The equations here are written in terms of the electric field for simplicity, and consistency with previous work. The leading terms of $H_{\mathrm{int}}$ are thus expressible as follows:

$$H_{\mathrm{int}} = -\mu_i e_i^{\perp} - Q_{ij} \nabla_j e_i^{\perp} - \ldots - m_i b_i - \ldots \tag{18}$$

where $\boldsymbol{\mu}$ is the electric dipole operator, $Q$ is the (second rank tensor) electric quadrupole operator, and $\boldsymbol{m}$ is the magnetic dipole operator. The first and third of these are vectors; the quadrupole operator is a second rank tensor; and the indices $i, j$ represent coordinates in any consistent frame of spatial reference with orthonormal axes—usually Cartesian, but not necessarily so (see Section 11). Every index that is repeated signifies an implied summation over the 3D basis set.

For concise reference in the text, the three consecutive terms in the above Equation (18) will be referred to as E1, E2, and M1, respectively, and as a rule, the first of these represents a coupling that is significantly stronger than the other two—where selection rules permit them all to occur (see later). It is important to recognize that the E2 and M1 forms of coupling may in principle constitute equally significant contributions to the light-matter coupling, together representing a leading correction to the E1 term. The proof of this connection is straightforward; both terms emerge from the same level of approximation in transforming between minimal coupling and multipolar Hamiltonian forms [62].

In addition to the terms explicitly exhibited in Equation (18), there are further terms of higher order—which generally indicates that they will be responsible for much weaker effects. These include a diamagnetisation contribution that has recently attracted fresh interest. As this term is quadratic in the optical magnetic field, it is of even parity with respect to both space and time, and may therefore in principle be considered pervasive (in this respect it is like the conventional polarizability, which is non-zero for every material). However, the same property also renders this form of coupling less potentially useful as a tool of symmetry analysis. Thus, although it is now recognized that in some connections, diamagnetisation coupling may prove quantitatively more significant than warrants its usual disregard [63–65], it is not a concern in a primary focus on symmetry features.

For most optical applications—the majority, which do not specifically concern the confined geometries of a fabricated microcavity, or an exotic beam structure as such may be imparted by optical elements—electromagnetic fields are most expediently commonly cast in terms of plane waves; these represent propagation modes whose wave-fronts are perpendicular to a single director in all cases. Moreover, in order to accommodate multimode radiation fields, the field operators are best expressed as mode expansions in the form of Fourier representations. Promoting the two fields to operator status leads to the following standard expansions [4]:

$$\boldsymbol{e}^{\perp}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\eta}\left\{ i\left(\frac{\hbar ck}{2\varepsilon_0 V}\right)^{\frac{1}{2}} \boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k}) a^{(\eta)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) + h.c. \right\} \tag{19}$$

$$\boldsymbol{b}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\eta}\left\{ i\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{\frac{1}{2}} \left(\hat{\boldsymbol{k}} \times \boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k})\right) a^{(\eta)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) + h.c. \right\} \tag{20}$$

where $h.c.$ denotes Hermitian conjugate. The above equations express the fields at position $\boldsymbol{r}$, within an arbitrary quantization volume $V$, in terms of sums over wave-vector $\boldsymbol{k}$ and polarization state $\eta$. The latter sum may in principle be taken on a basis comprising any two states that are represented by opposing points on the Poincaré sphere; [66] commonly, those chosen are either left and right circular polarizations, or *horizontal* and *vertical* plane polarizations. The circularly polarized basis can in fact be expressed in terms of the following unit vectors:

$$\boldsymbol{\varepsilon}^{(\mathrm{L})}(\boldsymbol{k}) = \frac{1}{\sqrt{2}}(\hat{\boldsymbol{i}} + i\hat{\boldsymbol{j}});\ \boldsymbol{\varepsilon}^{(\mathrm{R})}(\boldsymbol{k}) = \frac{1}{\sqrt{2}}(\hat{\boldsymbol{i}} - i\hat{\boldsymbol{j}}) \tag{21}$$

where $\hat{\boldsymbol{i}}$ and $\hat{\boldsymbol{j}}$ are Cartesian unit vectors such that $\left(\hat{\boldsymbol{i}},\ \hat{\boldsymbol{j}},\ \hat{\boldsymbol{k}}\right)$ comprise a right-handed orthogonal group. The quantum optical features of Equations (19) and (20) reside in the photon annihilation operators $a^{(\eta)}(\boldsymbol{k})$ for each mode $(\boldsymbol{k},\eta)$, and in their counterpart creation operators $a^{\dagger(\eta)}(\boldsymbol{k})$ implicit in the Hermitian conjugate part of each expression. In passing, it is interesting to observe that the RS field vectors, constructed from (19) and (20) using the defining Equation (7), have the particular property that $\boldsymbol{f}$ annihilates a left-handed photon and creates a right-handed photon, whereas its Hermitian conjugate $\boldsymbol{f}^{\dagger}$ does the opposite [37]. An important corollary follows; noting the linearity of the electromagnetic fields in $H_{\mathrm{int}}$ (a feature that also carries through to the RS expression of coupling, see below), it becomes evident from the above sequence of expressions that the $n^{\mathrm{th}}$ term in the matrix element $M_{FI}$, Equation (17), delivers the leading contribution for any process involving $n$ photons.

We can now introduce symmetry principles—but first, a caveat. A difference in the symmetry behaviour of electric and magnetic transition moments is sometimes expressed in terms of their being orthogonal to each other—presumably an inference derived from that feature of the relationship between the vector characters of the electric and magnetic fields, exhibited by the cross-product in Equation (20). Others write of the difference as signifying the two kinds of moments are out of phase, as indeed the counterpart fields are out of phase in circularly polarised radiation. In certain applications to atoms, such essentially classical arguments may appear superficially credible, but in general, such inferences are very misleading—not least, because *transition* moments are very different from *induced* moments. Moreover, quadrupole and higher moments cease to be amenable to such straightforward unidirectional interpretations. In molecules, more significantly, both static and transition moments are quantities whose vector or tensor components relate specifically to directions with a fixed and specific relation to the internal molecular geometry.

To establish the ensuing analysis on a firm footing, we first recall that the electric field of the radiation is formally odd with respect to parity $\mathcal{P}$, and even with respect to $\mathcal{T}$; the magnetic field has the opposite character in both respects. Individual modes of the radiation field need not conform to either parity, but in the sum over all modes, this is the definitive character [17]. Clearly, since $H_{\mathrm{int}}$ is an energy operator, and therefore even in both space and time, the electric dipole operator $\boldsymbol{\mu}$ is necessarily also odd with respect to parity $\mathcal{P}$, and even with respect to $\mathcal{T}$, its magnetic counterpart $\boldsymbol{m}$ is even in $\mathcal{P}$ and odd in $\mathcal{T}$. Accounting for the gradient operator featured in the second term of (18), the electric quadrupole operator $\boldsymbol{Q}$ has to be even in both forms of parity. To illustrate the significance of a difference in spatial parity, it emerges that the difference between electric and magnetic transition moments is the key to most common forms of chirality-sensitive response. As the former are polar vectors (odd in $\mathcal{P}$), and the latter are axial vectors (even in $\mathcal{P}$), it takes a molecule with no center of symmetry—that is, one that is *not* invariant under $\mathcal{P}$, such as a chiral molecule—to support an electronic transition involving both electric and magnetic transition moments. It is indeed an interference of these two kinds of coupling that proves to supply the main mechanism for chiroptical differentiation—see the literature for an example [67].

Before proceeding further, it is worth returning to the Riemann–Silberstein formulation introduced in Section 3, to observing a superficial appeal in connecting creation and annihilation operations with photons of a specific handedness. To this end, for processes of potentially chiroptical significance, the interaction Hamiltonian is, in some accounts, written as follows:

$$H_{int} \simeq -\frac{1}{2}\left[\boldsymbol{d}^{\dagger}.\boldsymbol{f} + \boldsymbol{d}.\boldsymbol{f}^{\dagger}\right] \tag{22}$$

where

$$\boldsymbol{d} = \boldsymbol{\mu} + ic^{-1}\boldsymbol{m} \tag{23}$$

this cast of the interaction operator is readily shown to precisely replicate the E1 and M1 terms in Equation (18). Although electric quadrupole interactions are thereby excluded from consideration, it transpires for phenomena such as circular dichroism and optical rotation that the absent E2 term in fact plays no role in randomly oriented media; in conjunction with E1 coupling, it generates only terms that vanish on orientational averaging (see Section 10).

The combination of electric and magnetic dipole operators in (23) is real (the former involves only charge positions, and the latter only the corresponding angular momenta operators) and it is of even temporal parity, but it is not an eigenfunction of $\mathcal{P}$; spatial parity is not a good quantum number. The same, of course, is true for $\boldsymbol{f}$. So although, for chiral molecules, transition dipoles based on Equation (23) may comprise non-vanishing contributions from both its electric and magnetic components, the difference in selection rules that applies for most other materials means that $\boldsymbol{d}$ itself cannot be regarded as a secure gauge of chiral propensity. Moreover, for many chiroptical processes, E2 contributions do not indeed disappear on orientational averaging; Raman optical activity is a familiar example [68,69]. Any advantage of deploying the RS formulation for light-matter coupling is therefore circumscribed; the representation is not generally applicable.

## 5. The Coupling of Radiation and Molecular Tensors

When we consider any multiphoton process involving $n \geq 2$ photons, the detailed structure of the relevant term in Equation (17) generates tensorial forms of interaction, coupling the material response to elements of the optical fields. Because the denominators of each term in (18) are scalars, symmetry aspects of the result are entirely associated with the products of Dirac brackets in numerator expressions. The rule for each Dirac bracket is that the product of the irreducible representations (*irreps*) of the states of the molecule at each end of the bracket must be spanned by one or more components of the appropriate multipole operator. With regard to the initial and final states for the overall process, the same rule applies with respect to the operator $M$, introduced in Equation (14). From earlier observations on the symmetry of the associated propagator $G_0$, it follows that the irrep $\chi(M)$ for $M$ is a product of the individual irreps for each of the multipoles involved in the whole process. Attending to the leading multipole terms given in Equation (18), we can write the following:

$$\chi(M) = \prod_{i=1}^{e}\prod_{j=1}^{m}\prod_{k=1}^{q}\chi_i(e)\chi_j(m)\chi_k(q) \tag{24}$$

where labels $e$, $m$, and $q$ represent the number of E1, M1, and E2 interactions, respectively, whose sum $n = (e + m + q)$ is the total number of photon interactions. For most absorption or scattering processes—and also emission to the ground state—the irreducible representation of the transition specifies the extent of symmetry difference between the relevant molecular excited state and the stable, ground state.

Commonly, excited state wavefunctions lack invariance under the full set of operations corresponding to symmetry elements of the ground state function. For example, in centrosymmetric molecules, whose equilibrium nuclear coordinates from a suitable point of origin represent a set that is even under parity $\mathcal{P}$, some excited states will also be even; others will display odd parity. Often, under C$_n$ rotations to which a ground state is invariant, excited states acquire an integer power of the phase factor exp($2\pi i/n$). Consider, for example, each term of the matrix element for a two-interaction process (noting that more than one term will usually arise, because all sequences of interaction are accommodated in the theory). Each term may entail one Dirac bracket of E1 form and the other of M1 form; all combinations of multipoles are possible in principle, though not all will necessarily be symmetry-allowed. Nonetheless, a first step is to consider what constraints are imposed on each individual interaction, as a result of the group theoretical rules imposed by molecular symmetry [70].

The matrix element $M_{FI}$ for any specific $n$-photon interaction now emerges in the form of a linear combination of terms, each of which entails vector and tensor interactions between molecule-based and radiation-based properties. The molecular system is cast in terms of products of transition moments, and the corresponding radiation constructs comprise products of components of the field vectors. The general form can be expressed as follows:

$$M_{FI} \sim \sum_{e=0}^{n}\sum_{q=0}^{n}\sum_{m=n-e-q}^{n} \boldsymbol{S}^{(e+m+2q)}_{e;m;n-e-m} \odot^{(e+m+2q)} \boldsymbol{T}^{(e+m+2q)}_{e;m;n-e-m} \tag{25}$$

which is Equation (25) in the literature [9], without the phase factor that becomes redundant for transition processes—where it disappears in the Fermi rate equation. Here, the result comprises the inner product, signified by $\odot$, of a radiation tensor $\boldsymbol{S}$ and a molecular response tensor $\boldsymbol{T}$. Specifically, $\boldsymbol{S}^{(r)} \equiv S_{i_1 i_2 \ldots i_r}$ comprises an outer product of components of the electric field and the magnetic field (and in addition, where quadrupoles are involved, the field wave-vector); the corresponding molecular tensor $\boldsymbol{T}^{(r)} = T_{i_1 i_2 \ldots i_r}$ entails products of $n$ Dirac brackets, and its spatial symmetry properties are determined by Equation (24). Each tensor has a rank $r$ given by $r = (e + m + 2q)$ so that the inner product contrasts this number of indices; the molecular tensor $\boldsymbol{T}^{(r)}$ specifically incorporates $(e + m + q)$ products of transition multipole moments.

Because their product $M_{FI}$ has the physical dimensions of energy, the $\boldsymbol{S}^{(r)}$ and $\boldsymbol{T}^{(r)}$ tensors must have identical signatures of parity for each separate parity operation, $\mathcal{P}$ and $\mathcal{T}$. The respective eigenvalues are $(-1)^e$ and $(-1)^m$, as determined by the space-odd, time-even character of the electric field, and the space-even, time-odd character of the magnetic field. Any electric quadrupole, having even parity under both $\mathcal{P}$ and $\mathcal{T}$, plays no part in this determination. If, for example, the $\boldsymbol{S}^{(r)}$ and $\boldsymbol{T}^{(r)}$ tensors are odd with respect to both parity operations, their product will remain the same if both radiation and matter are inverted in space, physically representing opposite parity enantiomers, and also opposite helicity radiation.

In this connection, it is worth briefly noting certain aspects of the physics relating to molecular orientation, with an important bearing on chirality principles. The angular disposition of molecules with respect to any propagating stimulus can play a role in the exhibition of chiral differentiation; the commonly long lifetime for quantum tunneling between oppositely handed enantiomeric forms (which are usually high orders of magnitude greater than optical interaction times) may also be a significant factor. Consider, as a counterexample, a molecule of hydrogen peroxide, $H_2O_2$; in its ground electronic state, it has only C$_2$ rotational symmetry and is therefore chiral in principle, but it is not normally regarded as such—because at common ambient temperatures, where the substance is a liquid, thermal energy is sufficient to provide equilibration between the two oppositely handed forms. Relatively low potential energy barriers must be surmounted for interconversion to occur [71]; in this case, evidence is readily afforded by the significant energy splitting between even and odd parity combinations of the two enantiomeric state functions [72].

Conversely, consider a molecule such as boric acid, $B(OH)_3$, which possesses, in addition to a pure rotational (C$_3$) axis, a plane of symmetry (it belongs to the C$_{3h}$ point group); it is not intrinsically chiral, but if the molecule is held at a fixed angle with respect to any transversely propagating signal beam of light, it has the capacity to differentiate between circular polarizations. This type of effect—essentially 2D chirality—is more commonly encountered (and more easily registered) in the surface features of suitably fabricated metamaterials—gammadion structures are a well-studied example—where even in the absence of an external stimulus, there is a clear disparity across the planar interface between physically dissimilar regions. In this way, effects more commonly associated with optical activity may be exhibited by an intrinsically achiral material or metamaterial [73]. Nonetheless, consideration of the complete light-matter system reveals that chiroptical differentiation will only be manifest in optical fields with a helical character—either through circular polarizations, in chirally configured beams, or within optical nanofibres [74]. When circularly polarized light impinges upon a suitably nanostructured surface, propagation by reflection or transmission may exhibit differences according to direction of travel, as opposite directions are not equivalent under the operations of spatial parity $\mathcal{P}$ [75].

## 6. Structure and Permutation Symmetry in Material and Radiation Tensors

It is easy to recognise, in the general tensor form of light-matter coupling for nonlinear optical interactions, a potential for the theory to deliver expressions of great complexity, rapidly increasing with the number of photons involved. It will emerge that three-photon absorption, for example, in its most general formulation, leads to a rate equation with 225 independent terms; for four-photon absorption, the figure is 8281 (the explanation of these figures will emerge in Section 10). Such complicated results are of little practical value, and only narrow academic interest. However, a raft of symmetry considerations dramatically redeems the situation. The features discussed below will often reduce the number of independent parameters to a mere handful. The implementation of symmetry principles thus not only lends important physical insights, it also leads to equations that are realistic for experimental application and data interpretation.

There are three distinct structure and geometry-related symmetry properties that can produce major simplifications; in each case, considerations of symmetry lead to a reduction in the number of independent variables. One aspect concerns the inherent photonic character of the nonlinear process itself, reflected in a permutational symmetry between equivalent photon interactions. Another is the possibility of polarization-configured symmetry, which is directly under experimental control. Finally, there are symmetry features determined by the intrinsic symmetry of the molecular component, dependent upon the geometry of its nuclear framework and the spatial symmetry of the transition taking place. We are now in a position to address the first two of these, and in the following section, each feature is illustrated by a specific, typical case: the hyper-Raman effect. Issues associated with molecular structural symmetry are deferred to Sections 8 and 9, pending the further development of the tensor formulation that next ensues.

First, we consider the photonic symmetry that may be intrinsic in the nature of any optical process. The hyper-Raman effect [76] is an inelastic scattering effect in which an intense input beam of optical frequency $\omega$ produces scattering, Stokes-shifted (slightly lowered in frequency) from the second harmonic $2\omega$ by a vibrational frequency $\omega_{\text{vib}}$ for one of the normal modes of the molecule. Thus, it is a three-photon process, detectable in the optical output of a frequency $\omega' = 2\omega - \omega_{\text{vib}}$. Recognising that the leading form of coupling is associated with E1 transitions alone, Equation (25) casts the matrix element as $\boldsymbol{S}^{(3)}_{3;0;0} \odot^{3} T^{(3)}_{3;0;0}$. The detailed structure of the molecular tensor $\boldsymbol{T}^{(3)}_{3;0;0}$—a form of transition hyperpolarizability—is usually determined through the construction of time-ordered diagrams [77], which represent every topologically distinct sequence of the individual photon interactions—three in this case; see Figure 1. The same information is in fact conveyed by a single state-sequence diagram, Figure 2 [78,79]. Each path in a state-sequence diagram is in a *topological* sense a dual transform of one of the time-ordered diagrams, interchanging vertices with line segments. The complications that arise in this case, when other multipoles are entertained, will be considered subsequently. The explicit expression for the E1$^{3}$ molecular tensor, written as a sum of three corresponding terms, accounting for overall energy conservation in each case, is as follows:

$$\beta^{nm}_{\lambda\mu\nu} = \sum_{r,s}\left[\frac{\mu^{ns}_{\lambda}\mu^{sr}_{\mu}\mu^{rm}_{\nu}}{(E_{sm}-2\hbar\omega)(E_{rm}-\hbar\omega)} + \frac{\mu^{ns}_{\mu}\mu^{sr}_{\lambda}\mu^{rm}_{\nu}}{(E_{sn}+\hbar\omega)(E_{rm}-\hbar\omega)} + \frac{\mu^{ns}_{\mu}\mu^{sr}_{\nu}\mu^{rm}_{\lambda}}{(E_{sn}+\hbar\omega)(E_{rn}+2\hbar\omega)}\right] \tag{26}$$

where $\hbar$ is the reduced Planck's constant $h/2\pi$, subscript Greek indices denote Cartesian indices referring to a molecule-fixed reference frame, vector components of the form $\mu^{ab}_{\lambda}$ and so on refer to electric dipole transition moments for transition $a \leftarrow b$, and $E_{ab}$ denotes an energy difference $E_a - E_b$. Three terms arise because this is the order of index permutations given by the symmetric group product $S_3 \times S_2$.

It will be evident on inspection that Equation (26) does not exhibit the permutational symmetry between the indices $\mu$ and $\nu$ connected with the two physically indistinguishable input photons (vertices coloured red in Figure 1). However, the radiation tensor with which it forms an inner product, does so as follows:

$$S_{\lambda\mu\nu} = \bar{\varepsilon}'_{\lambda}\varepsilon_{\mu}\varepsilon_{\nu} \tag{27}$$

where an overbar (on the polarization vector for the emitted photon) denotes complex conjugation. This same permutational symmetry can therefore be accommodated in a symmetrized tensor, expediently identified by bracketing the relevant index pair:

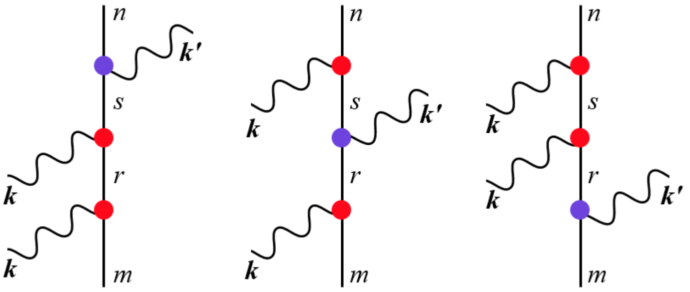

**Figure 1.** Three topologically distinct time-ordered diagrams (time progressing upwards) for hyper-Raman scattering from an input mode $\boldsymbol{k}$ into an output mode $k'$: the molecule undergoes a transition $n \leftarrow m$ via two virtual intermediate states $r$ and $s$.

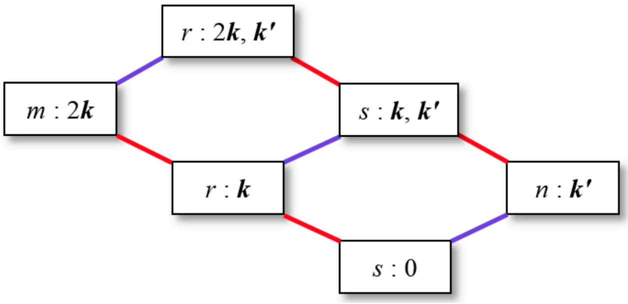

**Figure 2.** State-sequence diagram (time progressing to the right) for hyper-Raman scattering, subsuming all three pathways exhibited in Figure 1. Here, the interactions denoted by line sequences are colour-coded to highlight the input and output modes.

$$\beta^{nm}_{\lambda(\mu\nu)} \equiv \frac{1}{2}\left(\beta^{nm}_{\lambda\mu\nu} + \beta^{nm}_{\lambda\nu\mu}\right) \tag{28}$$

it is readily shown that this serves to deliver the same completely correct result when it is implemented as $\boldsymbol{T}^{(3)}_{3;0;0}$ in Equation (25).

In general, for any multiphoton process in which two or more of the photons derive from the same monochromatic beam, a corresponding permutational symmetry will be latent in the radiation tensor. This symmetry is ensured if the corresponding photon interactions engage the same level if multipole interaction—usually E1; it is potentially compromised by admitting mixtures of different multipoles. For example, in any form of frequency-doubling conversion—including second harmonic generation (SHG) and elastic second harmonic (hyper-Rayleigh) scattering, as well as the hyper-Raman effect—the substitution of one E1 interaction by M1 or E2 gives the leading correction terms of the form E1$^2$M1 and E1$^2$E2. The associated '$\boldsymbol{J}$' and '$\boldsymbol{K}$' tensors molecular tensors retain index permutational symmetry if the M1 or E2 interaction is involved in the output emission, but not if it is linked with one of the two input photon annihilation events [80,81].

The second form of index symmetry is now easily identified. Again, consider the hyper-Raman case, exhibited in (27). There need not be any correlation between the polarizations of the two input and single output photons—but in an experiment, it may prove useful to make a measurement (using polarizing optics) in which the polarizations are identical. One example for the commonly studied case of right-angle scattering is if all polarizations are linear and perpendicular to the scattering plane; another is if a forward-scattering geometry is used and the input and output photons are circularly polarized with opposite helicity, as follows from the form of Equation (21). In either case, the $\boldsymbol{S}$ tensor acquires full permutational symmetry amongst all three of its indices—and by similar arguments to those presented above, the same index symmetry is effectively conferred upon the molecular tensor.

To address The third symmetry feature, associated with molecular symmetry and the nature of transitions, will become more accessible on the introduction of an irreducible form of tensor analysis in Section 8. As will emerge, there are further considerations that can serve to very substantially ameliorate the complexity of analysis in the case of more complex forms of optical interaction; to secure their application, there are additional symmetry principles that first need to be developed.

## 7. Observables

At this stage, it becomes important to return to the generalized matrix elements $M_{FI}$ to distinguish expectation values (signifying identical initial and final system states) from the off-diagonal matrix elements that feature as modulus squares in process observables. The distinction, recently re-emphasized by Stokes [82], becomes especially important when physically identifiable effects arise from the interference between terms involving different kinds of multipolar coupling—chiral and mechanical effects in particular, as shown in other recent work [83–85] To secure an expression for the rate of an observable transition process, we now work from Equation (13) to arrive at the following:

$$\Gamma \sim \sum_{e=0}^{n} \sum_{q=0}^{n} \sum_{m=n-e-q}^{n} \sum_{e'=0}^{n} \sum_{q'=0}^{n} \sum_{m'=n-e'-q'}^{n} \boldsymbol{\Sigma}^{(e+m+2q+e'+m'+2q')} \odot^{(e+m+2q+e'+m'+2q')} \boldsymbol{\Pi}^{(e+m+2q+e'+m'+2q')} \tag{29}$$

where

$$\boldsymbol{\Pi}^{(e+m+2q+e'+m'+2q')} \equiv \left( \boldsymbol{T}^{(e+m+2q)}_{e;m;n-e-m} \otimes^{t} \overline{\boldsymbol{T}}^{(e'+m'+2q')}_{e';m';n-e'-m'} \right) \tag{30}$$

$$\boldsymbol{\Sigma}^{(e+m+2q+e'+m'+2q')} = \left( \boldsymbol{S}^{(e+m+2q)}_{e;m;n-e-m} \otimes^{t} \overline{\boldsymbol{S}}^{(e'+m'+2q')}_{e';m';n-e'-m'} \right) \tag{31}$$

Here, the superscript $t$ denotes 'total'—signifying that in the outer product, $\otimes^{t}$ effects no index contractions and therefore generates a tensor product whose rank is the sum of ranks for its tensor multiplicands. In Equation (30), the shorter representation of the outer product $\boldsymbol{T}^{(r)}\overline{\boldsymbol{T}}^{(r')}$ may be regarded as a material tensor $\boldsymbol{\Pi}^{(r+r')}$; the $\boldsymbol{S}^{(r)}\overline{\boldsymbol{S}}^{(r')}$ construct in (31) may equally be regarded as a radiation tensor $\boldsymbol{\Sigma}^{(r+r')}$. It is evident that for the terms with $r = r'$, each $\boldsymbol{\Sigma}^{(r+r')}$ and counterpart $\boldsymbol{\Pi}^{(r+r')}$ tensor product in (29) will have even parity with respect to both $\mathcal{P}$ and $\mathcal{T}$. However, in the quantum interference terms, $r \neq r'$, some products may have odd parity.

The alarming complexity of the above equations primarily reflects the generality of form in which they are cast; major simplifications arise in almost every specific application. Consider, for example, a single-photon transition $\alpha \leftarrow 0$. In the leading E1$^2$ contribution to the rate equation, $\Gamma = \left| M_{FI}^{(\mathrm{E1})} \right|^2$, is expressible in terms of the product $\boldsymbol{S}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{S}}^{(1)}_{1;0;0} \odot^{2} \boldsymbol{T}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{T}}^{(1)}_{1;0;0}$. Here, the material and radiation tensor constructs, as defined above, take the form of a transition electric dipole product $\mu_\lambda^{\alpha 0}\overline{\mu}_\mu^{\alpha 0}$, and a polarization component product $e_\lambda \overline{e}_\mu$ (where these subscript indices imply components in principle referred to the molecule-fixed Cartesian frame—with implications to be addressed in the following sections). This rate contribution, which even for chiral molecules retains its sign irrespective of the enantiomeric form or the circular handedness of the input radiation, is almost invariably the term that generates the largest contribution to the absorption rate. However, attending to the terms beyond E1 in the coupling delivers a corrected rate equation of the form

$$\Gamma = \left| M_{FI}^{(\mathrm{E1})} \right|^2 + M_{FI}^{(\mathrm{E1})} \overline{M}_{FI}^{(\mathrm{M1})} + \overline{M}_{FI}^{(\mathrm{E1})} M_{FI}^{(\mathrm{M1})} + \ldots \tag{32}$$

in which the E1M1 correction terms—which may be non-zero for transitions in chiral media—deliver odd-parity $\boldsymbol{\Sigma}^{(r+r')} \equiv \boldsymbol{S}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{S}}^{(1)}_{1;0;0} \odot^2 \boldsymbol{T}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{T}}^{(1)}_{0;1;0}$, and its conjugate, both of which clearly change sign either on substituting enantiomers (necessarily changing the sign of $\boldsymbol{T}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{T}}^{(1)}_{0;1;0}$)—or, alternatively, by inverting the circularity of the input (producing the same effect on $\boldsymbol{S}^{(1)}_{1;0;0} \otimes \overline{\boldsymbol{S}}^{(1)}_{0;1;0}$)). In either case, the absolute value of the sum (32) changes, resulting in circular dichroic absorption. [84] In the less familiar case, of the hyper-Raman effect, Equation (29) delivers the product $\boldsymbol{S}^{(3)}_{1;0;0} \otimes \overline{\boldsymbol{S}}^{(3)}_{1;0;0} \odot^6 \boldsymbol{T}^{(3)}_{1;0;0} \otimes \overline{\boldsymbol{T}}^{(3)}_{1;0;0}$.

## 8. Irreducible Cartesian Tensor Framework for Multiphoton Interactions

Molecules, necessarily of less than spherical symmetry, may possess no other symmetry elements than those that can together constitute a subset of the orthogonal group O(3) [86]. Mapping the irreducible representations of this group onto any lower symmetry is *surjective*, and the physical consequence is to permit transitions to occur between states of more than one symmetry class. The irreducible representations of any molecular point group are therefore related through chain decomposition to irreps of O(3) associated with odd or even parity representations of quantum angular momentum states S, P, D, and so on [87]. Functional expressions of the latter are, of course, the vector spherical harmonics, which thereby constitute a natural choice for describing atomic transitions [88,89]. However, with the lower symmetry of molecules, at least one direction within the structure is commonly distinct—usually an axis with the highest level rotational symmetry. The nature of most commonly arising symmetry elements then generally favors a representation of molecular vector or tensor properties in terms of a Cartesian basis. In fact, the advantage often carries over to the representation of the radiation field too.

In principle, the derivation and expression of selection rules for molecular transition moments and other properties can therefore benefit from expression in either a spherical tensor or a Cartesian basis. The deployment of spherical tensors [90] most clearly exhibits angular momentum aspects; it can, for example, elicit important physical insights with regard to angular momentum transfer and multipolar forms of interaction in single-photon processes [91,92]. However, developing an equivalent *irreducible* Cartesian basis can also establish connections with aspects of beam geometry and molecular shape; it is much more directly suited to analyzing multiphoton processes with regard to optical selection rules, because molecular symmetry properties are also usually registered in Cartesian form [70,93–97]. This is especially important because, in the nonlinear optical spectroscopy of molecules, different lines or bands in the spectrum will commonly be associated with transitions of disparate symmetry, and it is possible, by judicious experimentation based on multiple polarization studies, to elicit their individual character. It is also notable that optical beam configurations are most readily specified in an $(x, y, z)$ form. For example, in a conventional geometry optical table set up for scattering or fluorescence measurements, a Cartesian basis is the standard for describing the orientations of beam propagation and polarization vectors. It has furthermore been shown how the applicability of Cartesian bases extends to beams of complex Gaussian-weighted structure [98].

The two distinct formalisms, spherical and Cartesian—which are, of course, rigorously equivalent—both have an intricacy that rapidly escalates with the tensor rank. However, while conversion between the two forms is not simple [90,93,94,96,99], it is rarely necessary, and the power of analysis that they afford proves its value in processes of more complex photonic interactions. Because the detailed forms of results for arbitrary tensors of up to fourth rank have been calculated, the necessary formulae can be directly deployed [95,97,100,101]. Most of the original QED work on multiphoton electronic processes in molecules was conducted using such an irreducible Cartesian framework [102–106], as well as subsequent studies based on a semiclassical formulation [107]; it is this Cartesian cast of theory that most readily establishes connections between the angular momentum properties of electromagnetic radiation and the multipoles or nonlinear response tensors of molecules, with which the light engages in any particular form of interaction.

The starting point for constructing an irreducible Cartesian calculus is to identify a *natural tensor* basis. Natural tensors are tensors that are fully symmetric under interchange of any (Cartesian) index pair, and are also fully traceless with respect to each such pair. Any such tensor of rank $n$ can be expressed in terms of exactly $(2n + 1)$ linearly independent, non-zero components. In the more general case, a *reducible* Cartesian tensor of a given rank $n$ comprises a sum of irreducible constituent tensors of the same rank $n$, individually distinguished by *weights* $j = 0 \ldots n$. Each irreducible tensor of weight $j$ and rank $n$ thus represents a natural tensor of rank $j$ embedded in a space of rank $n$. [70] The advantages of connection to an angular momentum basis are retained in the Cartesian basis, as the coupling between irreducible tensors follows the usual rules of angular momentum coupling. For tensors or rank greater than two, individual weights may have a degenerate representation; in general, the multiplicity of weights $j$ for a tensor of rank $n$ is given by the following [108,109];

$$Q_n^{(j)} = \sum_{k=0}^{\lfloor (n-j)/3 \rfloor} (-1)^k \frac{n(n-1)(2n-3k-j-2)!}{k!(n-3k-j)!(n-k)!} \tag{33}$$

in which the upper limit on the summation is cast in terms of the floor function (signifying the highest integer no greater than the argument). The above result necessarily satisfies the following formula for the total number of independent components:

$$\sum_{j=0}^{n} (2j+1)\, Q_n^{(j)} = 3^n \tag{34}$$

the factor of $(2j+1)$ accounts for the fact that, for even parity tensors, any $j = 0$ term transforms under the symmetry operations of the molecular point group as a scalar, any $j = 1$ term as a vector (three independent components), $j = 2$ as a *deviator* (a traceless symmetric second rank tensor with five independent components), and so on. For odd parity tensors, $j = 0$ represents a *pseudoscalar* (odd under $\mathcal{P}$) and so on. However, when any degree of index symmetry is present in the tensor, the number of independent components is obviously decreased, and accordingly the multiplicities in representation of each weight are also subject to reductions.

Table 1 lists the structure of decomposition into weights relevant for the most extensively studied kinds of optical interaction; the most prevalent forms of index symmetry are accommodated in tensors up to rank $n = 6$ (which, though less familiar, arise, for example, for six-wave mixing). [110–114] In this table, the tilde on $\widetilde{Q}_n^{(j)}$ indicates that index symmetry is taken into account. Other cases of index permutational symmetry are possible, and most can be identified from the distinct partitions of $n$; although additional possibilities such as $T_{((\lambda\mu)(\nu\pi))}$ are possible in principle, no experimental implementations of such cases are evident in the optics literature as yet. The parameters $t_n$ and $\overset{\frown}{t}_n$ listed in the right-hand pair of columns will be introduced in Section 10.

**Table 1.** Maximum number of independent components for the tensors $\boldsymbol{T}^{(n)}$ that most commonly arise in *n*-photon molecular interactions, brackets embracing indices with permutational symmetry. Illustrative examples: Abs—single photon absorption; *n*PA—*n*-photon absorption (single-beam); RRE—resonance Raman effect; HR—hyper-Raman effect; HS—second harmonic scattering; SFG—sum-frequency generation; SFS—sum-frequency scattering; 4WM—four-wave mixing; OKE—optical Kerr effect; THS—third harmonic scattering; SWM—six-wave mixing.

| $\boldsymbol{T}^{(n)}$ | *Effect* | *N* | $\tilde{Q}_n^{(0)}$ | $\tilde{Q}_n^{(1)}$ | $\tilde{Q}_n^{(2)}$ | $\tilde{Q}_n^{(3)}$ | $\tilde{Q}_n^{(4)}$ | $\tilde{Q}_n^{(5)}$ | $\tilde{Q}_n^{(6)}$ | $t_n$ | $\overset{\frown}{t}_n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $n = 1$ | | | | | | | | | | | |
| $T_{\lambda}$ | Abs | 3 | 0 | 1 | | | | | | 1 | 1 |
| $n = 2$ | | | | | | | | | | | |
| $T_{\lambda\mu}$ | RRE | 9 | 1 | 1 | 1 | | | | | 3 | 3 |
| $T_{(\lambda\mu)}$ | 2PA | 6 | 1 | 0 | 1 | | | | | 2 | 2 |
| $n = 3$ | | | | | | | | | | | |
| $T_{\lambda\mu\nu}$ | SFG/SFS | 27 | 1 | 3 | 2 | 1 | | | | 15 | 11 |
| $T_{\lambda(\mu\nu)}$ | HR/SHS | 18 | 0 | 2 | 1 | 1 | | | | 6 | 5 |
| $T_{(\lambda\mu\nu)}$ | 3PA | 10 | 0 | 1 | 0 | 1 | | | | 2 | 2 |
| $n = 4$ | | | | | | | | | | | |
| $T_{\lambda\mu(\nu\pi)}$ | 4WM | 54 | 2 | 3 | 4 | 2 | 1 | | | 34 | 23 |
| $T_{(\lambda\mu)(\nu\pi)}$ | OKE | 36 | 2 | 1 | 3 | 1 | 1 | | | 16 | 12 |
| $T_{\lambda(\mu\nu\pi)}$ | THS | 30 | 1 | 1 | 2 | 1 | 1 | | | 8 | 7 |
| $T_{(\lambda\mu\nu\pi)}$ | 4PA | 15 | 1 | 0 | 1 | 0 | 1 | | | 3 | 3 |
| $n = 5$ | | | | | | | | | | | |
| $T_{(\lambda\mu\nu\pi\rho)}$ | 5PA | 21 | 0 | 1 | 0 | 1 | 0 | 1 | | 3 | 3 |
| $n = 6$ | | | | | | | | | | | |
| $T_{(\lambda\mu\nu\pi)(\rho\sigma)}$ | SWM | 90 | 2 | 1 | 4 | 2 | 3 | 1 | 1 | 36 | 25 |
| $T_{(\lambda\mu\nu\pi\rho\sigma)}$ | 6PA | 28 | 1 | 0 | 1 | 0 | 1 | 0 | 1 | 4 | 4 |

Returning once again to the hyper-Raman effect to provide an example, it is immediately evident from the above that considerable simplification ensues in the response tensor on taking account of the pair index symmetry in $\beta^{nm}_{\lambda(\mu\nu)}$, observed in Section 6. The number of independent tensor elements is reduced from 27 to 18; just as significantly, weight 0 contributions fall away entirely; weights 1, 2, and 3 are sustained. So the conclusion is that transitions are only allowed when the product of irreducible representations for the initial and final state—which in the hyper-Raman case, equates to the symmetry of the molecular vibration excited in its course—must span one or more of the irreps for weights 1, 2, and/or 3 in the relevant molecular point group. The odd parity of the $\mathrm{E1}^3$ coupling also applies.

It is relatively straightforward to derive the transformation properties for successive weights of either even or odd parity, and an extensive tabulation of the results is available in the literature. [17,70] Earlier work identified specific components rather than weights, [115] but these prove unnecessary for effective conclusions to be drawn on the simple basis of considering symmetry. Consider, for example, the case of the octahedral molecule sulfur hexafluoride, $\mathrm{SF_6}$; the Schoenflies point group is $\mathrm{O_h}$ and the odd-parity representations of weights 1, 2, and 3 are $\mathrm{T_{1u}}$, $(\mathrm{E_u}+\mathrm{T_{2u}})$, $(\mathrm{A_{2u}}+\mathrm{T_{1u}}+\mathrm{T_{2u}})$, respectively. This signifies that only vibrations of $\mathrm{A_{2u}}$, $\mathrm{E_u}$, $\mathrm{T_{1u}}$, or $\mathrm{T_{2u}}$ symmetry can produce a hyper-Raman signal. For vibrations of all other symmetries, the process is forbidden. It is to be emphasized that the symmetry properties of the *transition* are key here—not the permanent properties of the molecule itself. Again, taking the instance of $\mathrm{SF_6}$; because it is octahedral, it has no *permanent* hyperpolarizability—and as such, it cannot exhibit the *elastic* frequency doubling process of second harmonic generation (SHG). Nonetheless, the molecule can produce a hyper-Raman spectrum.

In other connections, decomposition into irreducible terms still has considerable value and power when it is applied to static tensor properties—in which case the rule for a non-vanishing response is simply that one or more of the irreps for non-vanishing weights must transform under the totally symmetric representation of the relevant molecular point group. In a classic paper, Zyss showed in clear and elaborate detail how such principles provide a basis for the molecular engineering of nonlinear optical materials [116]. (In that and subsequent work, the term with weight *j* is referred to as a $2^j$-pole, e.g., a deviator is identified as quadrupolar. In its own specific context, where it is implicit that every photon interaction in fact has E1 form, there is no likelihood of confusion, but the potential ambiguity is noted.)

At this juncture, however, it needs to be pointed out that erroneous deductions can be (and some studies have been) made if complete tensor index symmetry is assumed. Such an approach, which became widespread owing to its appealing simplicity, is largely credited to Kleinman [117], whose expressly limited intention was indeed to make the interpretation of early experiments in nonlinear optics more tractable. The slender argument, not to be pursued in detail here, is based on a case that in expressions such as Equation (26), photon energy terms such as $\hbar\omega$ and $2\hbar\omega$ are small compared with the electronic energy differences that arise in the sum over states. Appeals to such arguments led to a supposition that the hyper-Raman and analogous tensors could effectively be treated as fully index-symmetric. As Table 1 shows, in its entry for $T_{(\lambda\mu\nu)}$, one hidden implication was that weight 2 contributions could not arise. In the $SF_6$ case examined above, this would wrongly suggest that $E_u$ vibrations are also forbidden. The essential flaws and general inapplicability of Kleinman symmetry were in fact quickly pointed out by Wagnière [118]. Recent work on third harmonic scattering has again shown that emphatic differences arise, according to whether or not full index symmetry is assumed [119]. As a corollary to all such cases, however, it is of interest that in a specific case where all the photons involved in the interaction have identical polarization, then, for the same reasons discussed in Section 6, the results will indeed be consistent with Kleinman symmetry.

## 9. Transition Classes and Information Content

The various combinations of weight that are possible for each order $n$ have been used to designate *classes* of transition symmetry, which are individually discernible with suitably configured polarization measurements in principle. For $n \geq 2$, the permissible classes are essentially the partitions of $n$, subject to the exclusion rules: $2 \Rightarrow 4$, and the combination $p1 \Rightarrow p+1$ for any integer $p$. For example, the pairing 01, equivalent to 10, implies the additional presence of weight 2. Then, allowing weight 2 serve to introduce the pair 21, which in turn implies weight 3 (rank allowing), and so forth. While not excluded by these rules, in rank 4, there are no known occurrences of 41 or 30. Classes up to $n$ = 4, with known implementations among the commonly listed molecular point groups, are shown in Table 2.

**Table 2.** Combinations of weight that arise in processes involving up to four photons, in all common molecular point groups (those with up to six-fold rotational symmetry, and also the linear groups).

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_{\lambda\mu}$ | 210 | 21 | 20 | 2 | 1 | 0 | | | | | | | | |
| $T_{(\lambda\mu)}$ | | | 20 | 2 | | 0 | | | | | | | | |
| $T_{\lambda\mu\nu}$ | 3210 | 321 | 320 | 32 | 31 | 30 | 20 | 3 | 2 | 1 | 0 | | | |
| $T_{\lambda(\mu\nu)}$ | | 321 | | 32 | | | | 3 | 2 | 1 | | | | |
| $T_{(\lambda\mu\nu)}$ | | | | | 31 | | | 3 | | 1 | | | | |
| $T_{\lambda(\mu\nu\pi)}$ | 43210 | 4321 | 4320 | 432 | 431 | 430 | 420 | 43 | 42 | 40 | 4 | 3 | 1 | 0 |
| $T_{(\lambda\mu\nu\pi)}$ | | | | | | | 420 | | 42 | | 4 | | | 0 |

Every one of the classes exhibited in Table 2 is represented in different point group/irrep combinations. More strikingly, any transition, in a molecule of any known symmetry, must conform to one of them; extensive listings are given elsewhere [70]. There are no known materials in which *every* class arises, however. In the octahedral group $O_h$, for example, the following classes arise for any even-parity, fourth rank tensor lacking full index symmetry: (432)—$T_{2g}$; (431)—$T_{1g}$; (42)—$E_g$; (40)—$A_{1g}$; and (3)—$A_{2g}$. As shown in the Table, the number of classes is generally diminished by any admission of tensor index symmetry. Specific processes for which classification schemes based on these principles have been introduced are hyper-Raman scattering, [84] multiphoton absorption [85–88], and third harmonic scattering [96].

It is interesting to observe the growth in order of the number of classes, which can be considered physical (i.e., excited state) implementations of symmetry properties conferred through multiphoton excitation. Given the associated experimental difficulty, it is evident that there is only a marginal advantage to be gained in progressing from $n = 3$ to 4. The number of distinctly identifiable classes in either instance might nonetheless appear to present a potential prospect for high-dimensional data, with a capacity to exceed the second order of a simple binary basis per photon. However, a single $n$-photon experiment cannot provide an unequivocal basis for class assignment. To achieve that end, in general, requires a *complete polarization study*—a term and concept enunciated by McClain [120,121]. As will become evident in the next section, the number of such experiments required always exceeds the number of distinct classes.

Before moving on to consider fluid media, it is noteworthy that casting electrodynamic theory in terms of irreducible Cartesian tensors proves its value in a variety of other connections. One clever example is afforded by Bancewicz's work on two-centre (collisional) corrections to molecular hyperpolarizabilities, [122] and there are several applications connected with multipole coupling in intermolecular energy transfer [123–125]. The same formalism also facilitates the derivation of analytically tractable formulations for the properties of optically ordered anisotropic nanoparticles [126].

## 10. Isotropic and Axial Invariants and Ensemble Averages

The majority of optical phenomena in molecules are registered in liquid or solution, where individual molecular constituents are orientationally unconstrained over the timespan for most experimental measurements. The molecules' effective symmetry can then accurately be identified with the properties of their intrinsic nuclear framework in the ground state equilibrium. To secure the appropriate forms of results for experiments on such systems, it therefore becomes necessary to account for an optical response whose time-average, for any individual molecule, will equate to the ensemble average, based on the ergodic theorem. Moreover, the distribution of orientations within the ensemble is usually isotropic (unless orienting fields are present; a case to be considered shortly). The analysis that follows, pursuing the irreducible tensor formulation, represents an alternative perspective to the one given in detail in Section 9 of Ruggenthaler [9].

To begin, a general result can be noted. In general, the product of two irreducible tensors $\boldsymbol{A}_{j_1}^{(n_1)}$ and $\boldsymbol{B}_{j_2}^{(n_2)}$ may entail a fully outer product, in which case it generates a result of the highest possible rank, or at the other extreme, a fully inner product (if the two have the same rank), thus generating a tensor of rank 0—that is, a scalar. In the most general case comprising $p$ inner products (tensor index contractions, $p \leq \min(n_1, n_2)$), the result may be expressed as follows:

$$\boldsymbol{A}_{j_1}^{(n_1)} \begin{matrix} \otimes^{n_1+n_2-2p} \\ \odot^{p} \end{matrix} \boldsymbol{B}_{j_2}^{(n_2)} = \sum_{r=0}^{r_{\max}} \mathbf{C}_{|j_1-j_2|+r}^{(n_1+n_2-2p)} \tag{35}$$

where $r_{\max} = \min[2j_1,\ 2j_2,\ (n_1 + n_2 - 2p - |j_1 - j_2|)]$. The principles involved in this coupling are illustrated in Figure 3. Relation (35) proves to be extremely important for the simplifications that it can effect as we consider isotropic fluids. To this end, consider the constructs for the product tensors $\boldsymbol{\Pi}$ as given by Equation (30). To most simply illustrate the implementation of an orientational average, let us restrict consideration to dipole (allowing for both E1 and M1) coupling—that is, the representation of E2 couplings, $q = 0$. The product tensor thus has rank $e + m + e' + m'$, which equates to $2n$. Again, one example from hyper-Raman scattering is the sixth rank term $\beta_{\lambda(\mu\nu)}^{nm} \overline{\beta}_{\pi(\pi\rho)}^{nm}$.

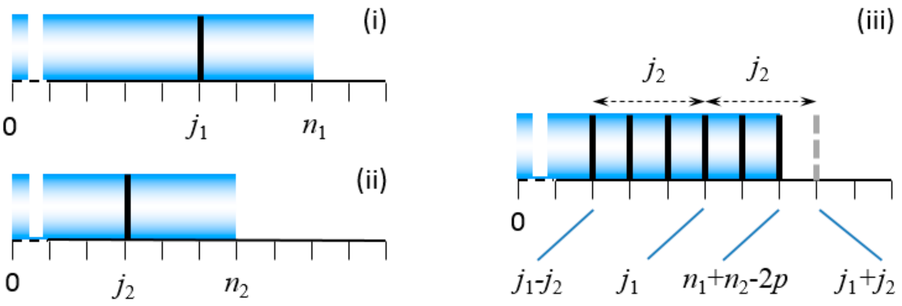

**Figure 3.** Illustration of coupling weights $j_1$ and $j_2$, in a partially inner, partially outer products of two tensors, of respective ranks $n_1$ and $n_2$, as given by Equation (35). Assuming $j_1 > j_2$, the span of weights in the product may range from $j_1 - j_2$ to $j_1 + j_2$, capped by an upper limit $n_1 + n_2 - 2p$ that is the rank of the product tensor.

Now, as follows from a theorem by Jeffreys [127], orientation-averaged parameters (in the present application both molecular and radiation forms) must have the transformation properties of scalars under the full rotation group SO(3). As such, they can only be cast as scalar multiples of isotropic tensors $\boldsymbol{g}$ with the same, even rank ($r + r' = 2n$), which comprise products of Kronecker deltas. Averaging can proceed on this basis using Equation (32) in the literature [9]—which also provides for more complicated cases—but by utilising irreducible forms, we now take a different tack. The inner product of the $\boldsymbol{\Pi}$ and $\boldsymbol{g}$ tensors generates results of the following form, utilizing Equation (35) from the present section and the defining Equation (30) for the explicit form of $\boldsymbol{\Pi}$ (while the $\boldsymbol{\Sigma}$ tensors are treated in the same way):

$$\boldsymbol{\Pi}^{(2n)} \odot^{2n} \boldsymbol{g}^{(2n)} = \sum_{j_1=0}^{n}\sum_{j_2=0}^{n} T_{j_1}^{(n)}\overline{T}_{j_2}^{(n)} \odot^{2n} \boldsymbol{g}^{(2n)} = \sum_{j=0}^{n} T_{j}^{(n)}\overline{T}_{j}^{(n)} \odot^{2n} \boldsymbol{g}^{(2n)} \tag{36}$$

the simplification in the second step, which enforces $j_1 = j_2$, is a consequence of the range for the coupled weights being subject to an upper limit of 0—as the isotropic tensors are weight 0 alone, and the whole expression (which results in a scalar, i.e., a tensor of rank zero) must itself result in weight 0.

Averaging can now proceed on the basis of the above Equation (36), as shown by Andrews and Blake [128]. It then follows that the emerging rate equation will be cast in terms of molecular invariants generated by this equation. These comprise a set of $t_n$ linearly independent set of parameters whose number follows from the multiplicity $\widetilde{Q}_n^j$ of each weight, as listed in Table 1; each weight only couples with itself, and hence we have the following:

$$t = \sum_{j=0}^{n} \left(\widetilde{Q}_n^j\right)^2 \tag{37}$$

this is the result for the general case (complex $\boldsymbol{T}$); if the molecular tensor can be treated as real (which generally applies for E1 coupling in regions far from optical resonance), then it follows that the number of invariants reduces to the following:

$$\overset{\frown}{t} = \frac{1}{2}\sum_{j=0}^{n}\left[\left(\widetilde{Q}_n^j\right)^2 + \widetilde{Q}_n^j\right] \tag{38}$$

therefore, for example, the orientationally averaged rate equation for a three-photon process entailing the index non-symmetric tensor $T_{\lambda\mu\nu}$ is cast in terms of $t_n = 15$ molecular invariants. Because, in general, the radiation tensor is subject to the same development, the rate (29) in principle accommodates $t_3^2 = 15^2 = 225$ terms (for four-photon processes lacking permutational symmetry, the corresponding number is $t_4^2 = 8281$). However, if the molecular tensor is real, $\overset{\frown}{t}_3 = 11$ and the number of terms in the rate is almost halved.

In practice, because the set of molecular invariants in any case constitutes a complete, linearly independent set, it is equally possible to express results in terms of any other set obtained by injective linear transform—and these are the invariants that emerge from the direct averaging process [127,129]. McClain's approach to securing the maximum information from multiphoton studies of fluids is fundamentally based on the premise of conducting a number $\overset{\frown}{t}_n$ of experiments with polarization conditions ensuring linearly independent radiation terms. In general, it is not possible to configure the radiation tensor constructs $\boldsymbol{\Sigma}$, using electromagnetic fields of conventional, plane wave form to only comprise any chosen, arbitrary combination of weights. By exploiting the orbital angular momentum of structured beams, Molina-Terriza et al. have shown that it is in fact possible to prepare photons in multidimensional vector states of angular momentum [130]—but orbital angular momentum is known not to engage with the leading E1 form of coupling for electronic transitions [131]. In consequence, as observed earlier, to secure the fullest information from separate experiments with different polarization conditions, the required number of studies always exceeds the number of distinct symmetry classes. Whichever method of tensor representation is deployed (reducible or irreducible), it is noteworthy that it is unnecessary to derive expressions for individual tensor components; they are not required, nor are they measurable in fluid media.

The same kinds of approaches as those considered above can be applied to molecular systems with partial orientational order—one familiar example being cholesteric liquid crystals under the influence of a static electric field acting as a *director* vector. In the most general case, the distribution of molecular orientations is no longer isotropic, but residual degrees of freedom provide for an axially weighted distribution. In the dipole approximation, the associated orientational averaging procedure then requires contracting the radiation and material constructs $\boldsymbol{\Pi}$ and $\boldsymbol{\Sigma}$ with isotropic tensors of rank $(2n + 1)$, as shown in Andrews [9] and detailed in reference Wagnière [132].

Although the focus through much of this account is on processes involving up to four photons, it is interesting to note that some theory has been developed for absorption processes of higher order—notably by Wagnière [133] and Friese [134], the latter recently providing remarkable results for five-, six-, and seven-photon excitations. Those calculations make explicit use of index symmetry from the outset, so the results are not claimed to have general applicability for multiphoton interactions. It does not appear that group theoretical methods have as yet been applied to such cases—but the degree of experimental challenge in resolving the associated spectra suggests that such a symmetry analysis would not serve any immediately practicable purpose.

## 11. Intricate Aspects of Dichroism

To illustrate the principles, and to highlight the powerful significance of orientational averaging, it proves salutary to consider some potentially circular dichroic aspects of single photon absorption—where, despite the simplicity, some recent developments invite such a perspective. At its simplest, there is only a single interaction to consider, as given by Equation (18); the interference terms between forms of coupling with different parity signatures can only be elicited in chiral materials, and using radiation with a degree of helicity—which, as we observed earlier, generally indicates the use of circular polarizations. The original case of circular dichroism (CD), introduced at the end of Section 7, has been addressed in numerous works—see, for example, the treatment given in Craig and Thirunamachandran [4].

One of the features of conventional CD is that in leading order, it entails E1–M1, but not E1–E2, interference terms. The reason for the exclusion of the latter, which also satisfies the spatial symmetry criterion for eliciting chiral response, is that in a fluid, the associated orientational average entails isotopic tensors of rank 3—which are scalar multiples of a Levi–Civita antisymmetric tensor. The inner product of this tensor with the E1–E2 molecular tensor product vanishes, because of the index symmetry in the quadrupole transition moment. However, the fact that this situation changes when orientational order is present, has invited study of the possible engagement of E2 terms in chirality associated with vortex beams (whose photons convey the orbital angular momentum introduced in Section 3). A recent analysis has shown that this is indeed the case, leading to a distinctive circular vortex dichroism (CVD) provided orientational order is present [135]. It nonetheless emerges, by applying the orientational average in a cylindrical coordinate basis (in which the local orthonormality of the basis unit vectors still applies), that the effect once more disappears in isotropic media.

Now, returning to the case of conventional radiation, let us consider that a static magnetic field is introduced. As discussed by Andrews [9], the presence of a static magnetic field is often described as 'symmetry breaking'. When it engages with any optical interaction linearly (or indeed in any odd power), its time-odd character imparts a propensity to undermine Helmholtz reciprocity (i.e., forward-backward equivalence), as, for example, in the familiar Faraday effect. However, due inclusion of the field as a full component of the light-matter system confirms that its involvement is entirely consistent with $\mathcal{PT}$ symmetry. In principle, a static magnetic field might engage with electron spin, in molecules or radicals with one (or more) unpaired electron. In such cases, strong magnetic fields can lift the degeneracy of spin states to a photophysically significant degree, and the result is to permit circularly polarized photons of opposite handedness to excite each component of any resulting spin doublet. However, there are other more interesting, and more general mechanisms that may come into play where magnetic fields are involved, where the significance of both molecular symmetry and rotational averaging become especially evident. In the following section, we assume 'closed-shell' states of time-even parity, for simplicity excluding states with unpaired electron spin. By far the majority of stable molecules and larger assemblies are known to be of this kind.

To suitably develop the theory, we now extend the single-interaction Equation (18) by writing the following:

$$M_{FI} = \sum_{\Omega} M_{FI}^{(\Omega)} \quad (\Omega \equiv \text{E1, E2, M1, E1M01, E2M01, M1M01}, \ldots) \tag{39}$$

where the first three terms can be identified in explicit form with those given in Equation (18), and the second three are double-interaction terms engaging each multipolar form of photon interaction, along with a static magnetic field dipole interaction denoted M01. Figure 4 shows the salient forms of time-ordered diagram, for the influence of the magnetic field on single-photon absorption, with the static (i.e., non-propagating) field depicted by a horizontal line; Figure 5 is the corresponding state-sequence diagram, accommodating all time-orderings to this level of interaction.

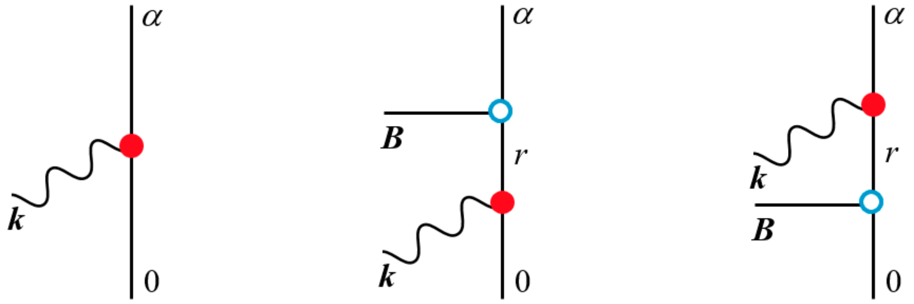

**Figure 4.** Key time-ordered diagrams for engaging a static magnetic field ***B*** in the absorption of a single photon of wave-vector ***k***. The diagram on the left represents the leading term, where the red circles denote E1, E2, or M1 coupling. Additional coupling with the static field (empty blue circle) engages two distinct time-orderings.

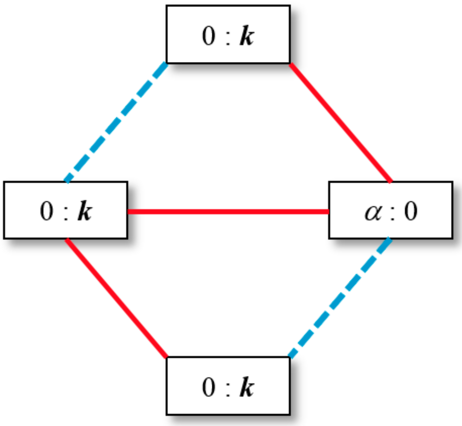

**Figure 5.** State-sequence diagram for magnetic field engagement in single-photon absorption, connectors coloured to match the time-ordered representations of Figure 4.

Before proceeding further, it is worth noting that the present method of dealing with the engagement in an optical process of any static field, whether magnetic or electric, is a pragmatic shortcut to correct results. Formally, although static fields are absent in the PZW Hamitonian, their effect on a system of interest can be introduced either by applying time-independent perturbation theory to establish static field-modified basis states for a standard time-dependent perturbation theoretic treatment of the optical process [136], or equally by including, as a source, a static dipole whose influence on the system is mediated by E1–E1 or M1–M1 virtual photon coupling; the former has been demonstrated in several connections—see the literature for an example [137].

Now, applying Equation (13) to secure an observable, the rate of absorption, Equation (39) yields a series of terms; details have been reported elsewhere [138]. The leading term is quadratic in E1 (assuming the transition is conventionally allowed); then follow cross-terms such as E1–E1M01, and so on. Suppose we look for terms that will exhibit involvement with the magnetic field, but which are allowed only by non-centrosymmetric molecules. As E1 is of odd parity under $\mathcal{P}$, but E2, M1, and M01 are even, the leading terms of interest are E1–E2M01 and E1–M1M01. The significance of these was first considered by Wagnière and Meier [139], whose depiction of the former cross-term deploys another diagrammatic form shown in Figure 6.

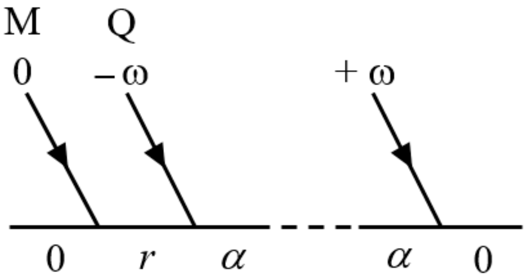

**Figure 6.** Cross-term for magnetic field engagement in single-photon absorption (Wagnière and Meier depiction). Such diagrams signify partial rate contributions, as compared with the individual matrix element depictions in Figures 4 and 5.

Consider first the E1–E2M01 term. This generates fourth rank $\boldsymbol{\Pi}$ and $\boldsymbol{\Sigma}$ tensors constructed according to Equations (30) and (31), each to be contracted with an isotropic tensor of the same rank that is, a product of two Kronecker deltas. In particular, the field tensor $\boldsymbol{\Sigma}$ comprises products of components of $\boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k})$, $\overline{\boldsymbol{\varepsilon}}^{(\eta)}(\boldsymbol{k})$, $\boldsymbol{k}$, and $\boldsymbol{B}$ (one component of the polarization vector, one of its complex conjugate, one of the wave-vector, and one of the magnetic field). Therefore, the result of contraction with two deltas, which produces two scalar products, may appear to be non-zero and acquire its maximum value if the static field is aligned with the direction of beam input; because $\boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k}) \cdot \overline{\boldsymbol{\varepsilon}}^{(\eta)}(\boldsymbol{k}) = 1$ for any polarization, the result is ostensibly non-zero. An interesting aspect for chiral molecules is that the two opposite enantiomeric forms would appear to produce opposite E1–E2M01 contributions of opposite signs, even when linearly polarized light is deployed. However, the molecular part $\boldsymbol{\Pi}$ of this result involves two terms, each one entailing a transition magnetic dipole moment—one with the transition dipole $\boldsymbol{m}^{\alpha r}$ and the other $\boldsymbol{m}^{r0}$, corresponding to the interaction vertices denoted by empty blue circles in the middle and right-hand diagrams in Figure 4. With real wavefunctions, the values of these moments are imaginary, because the angular momentum operator implicit in a magnetic moment operator is itself imaginary; hence, the associated rate contribution in fact vanishes (the rate equation entails twice the real part of this imaginary cross-term contribution).

A similar logic, but with a different outcome, applies to the E1–M1M01 term. Here, the $\boldsymbol{\Pi}$ and $\boldsymbol{\Sigma}$ tensors that arise are third rank, and accordingly, each demands contraction with the isotropic tensor of rank 3, that is, the Levi–Civita tensor. For $\boldsymbol{\Sigma}$, comprising a product of components of $\boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k})$, $\hat{\boldsymbol{k}} \times \overline{\boldsymbol{\varepsilon}}^{(\eta)}(\boldsymbol{k})$, and $\boldsymbol{B}$, this generates a vector triple product that can again be non-zero if $\boldsymbol{B}$ is aligned with $\boldsymbol{k}$. In this case, the molecular part $\boldsymbol{\Pi}$ of the result again entails two terms, from the middle and right-hand diagrams in Figure 4, but now each one comprises *two* magnetic moments, so that the molecular part of the rate contribution is real. The result persists for both linearly and circularly polarized light; the vector triple product entails the cross-product of $\boldsymbol{\varepsilon}^{(\eta)}(\boldsymbol{k})$ with $\hat{\boldsymbol{k}} \times \overline{\boldsymbol{\varepsilon}}^{(\eta)}(\boldsymbol{k})$, which equals $\hat{\boldsymbol{k}}$ for any polarization state—which, therefore, also includes the case of unpolarized light. This distinct difference in physical significance, compared with E1–E2M01, appears not to have been noted before.

It can, therefore, be directly concluded that the presence of a static magnetic field, with any non-zero component along the propagation axis of incident light, enables chiral molecules to exhibit a differential response according to the handedness of the enantiomer. The involement of this phenomenon, which has been categorised as one aspect of a magnetochiral anisotropy [140], has been suggested as being responsible for magneto-chiral enantioselective photochemistry [141]. It is now conjectured that it may also play a role in recent reports of enantioselective adsorption onto a magnetic substrate [142], interpreted using CD measurements.

## 12. Discussion

This account has aimed to exemplify symmetry principles that can profitably be applied to secure information of various kinds, in the context of molecular photonics. Over and above its well-known relevance to material properties, symmetry considerations most obviously provide a basis for determining whether any specific form of optical effect is allowed or forbidden. This kind of criterion has comprehensive application to optical phenomena of all kinds; furthermore, it extends to individual optical transitions. Using a quantum electrodynamical basis for the physics provides a framework of equations in which the interplay of radiation and material symmetries becomes especially lucid, as the molecules and radiation are treated as twin components of a fully quantized system. QED methods also facilitate the identification of information content relating to transition symmetry classes, and they provide a framework for devising or interpreting the relevant optical experiments. In this connection, an emphasis on observables—generally process rates and signal intensities—has additional impact; it affords advantages over semiclassical equations whose potentiality in representing observables can be obscure. The distinction is especially important in dealing with theory for systems in which the molecules are randomly oriented, as the implementation of orientational averaging can itself have major implications for the viability of the mechanism. The results of averaging provide a means for establishing rigorous conditions under which processes may be detected. The spheres of optical and material chirality provide numerous examples of how all these principles lend insights into the prospects and possibilities for achieving chiroptical differentiation.

**Acknowledgments:** The author is grateful for comments from Kayn Forbes.

**Conflicts of Interest:** The author declares no conflict of interest.

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