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Optical angular momentum: Multipole transitions and photonics

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The premise that multipolar decay should produce photons uniquely imprinted with a measurably corresponding angular momentum is shown in general to be untrue. To assume a one-to-one correlation between the transition multipoles involved in source decay and detector excitation is to impose a generally unsupportable one-to-one correlation between the multipolar form of emission transition and a multipolar character for the detected field. It is specifically proven impossible to determine without ambiguity, by use of any conventional detector, and for any photon emitted through the nondipolar decay of an atomic excited state, a unique multipolar character for the transition associated with its generation. Consistent with the angular quantum uncertainty principle, removal of a detector from the immediate vicinity of the source produces a decreasing angular uncertainty in photon propagation direction, reflected in an increasing range of integer values for the measured angular momentum. In such a context it follows that when the decay of an electronic excited state occurs by an electric quadrupolar transition, for example, any assumption that the radiation so produced is conveyed in the form of "quadrupole photons" is experimentally unverifiable. The results of the general proof based on irreducible tensor analysis invite experimental verification, and they signify certain limitations on quantum optical data transmission.

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I. INTRODUCTION

It is surprising to discover that the deep fundamental link between photon angular momentum and multipolar forms of charge distribution is not as comprehensively well understood as one might suppose. In the field of atomic spectroscopy the rules governing multipole transitions and angular momentum are noncontroversial [1], yet it transpires that unguarded applications of these same rules to the history of any individual photon, emitted by relaxation from an atomic excited state, can raise unresolved questions. Specifically, to resolve the multipolar character of the electronic transitions associated with atomic excited state decay and subsequent detection of the ensuing fluorescence can create apparent paradoxes. Whereas the familiar selection rules for atomic transitions are widely and rightly asserted as arising from a connection between transition dipoles and the unit spin of the photon, incautious extrapolations of this principle to higher-order multipoles may not be as sound. Further complexities arise in the case of molecular systems. Addressing such issues invites a detailed analysis—which resolves not only these, but a host of related questions.

Consider, for example, a very simple system in which a single atom, initially in an excited state, decays through electric-dipole forbidden, electric-quadrupole allowed photon emission. To judge by certain sections of the literature it is often assumed, if not explicitly stated, that electric quadrupole decay transitions produce photons of a distinct character. However, usually little or no theoretical basis is given for such a supposition—neither can one find a robust theory addressing the quantum measurements that would be necessary for its experimental verification. Although radiative emission of a given multipolar origin is in principle identifiable from the characteristic form of its spatial distribution, it does not directly follow that multipolar origination of any specific form should necessarily or measurably translate into a distinction in nature of the individually emitted photons.

One can reasonably pose the question: is there a clear physical meaning, in the sense of a possibility for unambiguous measurement, in using the term *quadrupole photon*? Focusing on the issue of measurability: is it possible to determine, by direct detection of an emitted photon, the multipolar character of the transition associated with its creation? Again, under what circumstances, if any, should it be possible for any such photon to be absorbed by a dipolar detector? And does the answer to any of these questions change if the emitter is anisotropic—if so, is it possible to discern whether an observed emission arises from an atomic, as distinct from a molecular or crystalline source? Previous attempts to tackle these questions are surprisingly sparse; the answers are not generally known.

It is the aim of the analysis that follows to tackle and resolve the issues, and to provide answers, to the above and related questions, through a detailed irreducible tensor analysis. The necessary equations are developed using quantum electrodynamics (QED). It will be shown that when an atomic transition involves an electric multipole of order ΔL, associated with an internal change in electronic orbital angular momentum by this same amount (ignoring spin-orbit coupling), the photon thereby released cannot meaningfully be asserted to convey this same quantity of angular momentum ΔL to a remote photodetector. In the context of quantum optical communication, this is a result that represents a potentially significant and widely overlooked constraint.

II. FOUNDATION THEORY

The classical methodology of atomic emission spectroscopy [2] does not address the mechanism and selection rules for the *detection* of atomic fluorescence, a process whose relationship to the original emission will prove to be a central issue in the following analysis. With the development of a robust theory rigorously based on quantum electrodynamics [3], it has become possible to encompass a complete photon history as an embodiment of the causal linkage between source decay and detector excitation events [4]. In the QED representation, the propagation of light from an emissive source to an absorptive detector is the long-range limit of a general mechanism that, when it operates over subwavelength distances, is usually designated *resonance energy transfer* [5].

To begin, consider a simple system with a source A and detector B, each comprising an electronically distinct, neutral atom. Developing the theory in terms of multipolar coupling in the Coulomb gauge ensures that the associated fields are duly retarded and satisfy causality [6]. In this dynamical system, the process to be addressed in its entirety begins with the excited state decay of A and ends in the resulting electronic excitation of B. Quantum mechanically, this is an evolution from an initial system state in which A is electronically excited and B is in its ground state to a final state with A in a lower energy state and B electronically excited. Reflecting standard experimental conditions, it can be assumed that there is a rapid decay channel for the excited state of B by any means that can produce a measurable signal of the fluorescence detection—so the system as a whole does not support a state of delocalized excitation.

To formulate theory with due regard to the multipolar character of the atomic transitions, it is appropriate to adopt a system Hamiltonian cast in multipolar form, which may be represented as follows;

$$H = H_{\text{rad}} + \sum_{\xi=A,B} H_{\text{at}}(\xi) + \sum_{\xi=A,B} H_{\text{int}}(\xi). \tag{1}$$

Here H_{rad} is the Hamiltonian for the radiation field *in vacuo*, $H_{\text{at}}(\xi)$ is the field-free Hamiltonian for atom ξ, and $H_{\text{int}}(\xi)$ represents an atomic interaction with the radiation field. The tripartite simplicity of Eq. (1) results from an adoption of the multipolar form of light-matter interaction. While it can indeed be argued that the multipolar concept is intrinsically applicable only in a quantum electrodynamical formulation [7], it is a method that delivers results precisely equivalent to those arising in a minimal-coupling formulation [8]. For present purposes, with a focus on electric multipole transitions, the interaction terms in (1) can be determined from the following;

$$H_{\text{int}}(\boldsymbol{\xi}) = -\boldsymbol{\varepsilon}_0^{-1} \int \boldsymbol{p}^{\perp}(\boldsymbol{\xi}, \boldsymbol{r}) \cdot \boldsymbol{d}^{\perp}(\boldsymbol{r}) d^3\boldsymbol{r}. \tag{2}$$

Here, $\boldsymbol{d}^{\perp}(\boldsymbol{r})$ is the transverse electric displacement field operator and $\boldsymbol{p}^{\perp}(\xi, \boldsymbol{r})$ is the transverse electric polarization. The latter operator is succinctly expressible in a form whose expansion in powers of λ delivers the entire multipolar series [9];

$$\boldsymbol{p}^{\perp}(\xi, \boldsymbol{r}) = \sum_{\alpha(\xi)} e_{\alpha}(\boldsymbol{q}_{\alpha} - \boldsymbol{R}_{\xi}) \int_0^1 \delta^{\perp}[\boldsymbol{r} - \boldsymbol{R}_{\xi} - \lambda(\boldsymbol{q}_{\alpha} - \boldsymbol{R}_{\xi})] d\lambda, \tag{3}$$

where the summation is over constituents of the atom ξ located at $\boldsymbol{R}_{\xi}$, i.e., charges e_{α} located at positions $\boldsymbol{q}_{\alpha}$. Here it is necessary to consider only the lowest orders of electric multipole that can support the given source and detector transitions. Moreover, a traceless form can be adopted for the quadrupole, consistent with the transverse character of the electric displacement field [10].

Adopting the shorthand En to denote an electric multipolar interaction of order n ($E2$ denoting the electric quadrupole, for example), we now focus on the electrodynamic coupling between two transition electric multipoles Em and En, the former signifying the source decay and the latter, the detector excitation. Magnetic transitions are to be considered later. For example, in the specific case that prompted this study and which best exemplifies the issues, $m = 2$ and $n = 1$ signify electric quadruple emission registered with an electric dipole detector. In this or any other such case, QED calculation will deliver a quantum amplitude M_{fi} for the entire system, connecting the initial state i (excitation located at the source, detector in its ground state) with the final state f (deactivated source, detector in its excited state). The general result can be cast as follows [11,12];

$$M_{fi}^{Em-En} = E^{(m)}_{A;a_1\ldots a_m} V_{a_1\ldots a_m b_1\ldots b_n}(k, \boldsymbol{R}) E^{(n)}_{B;b_1\ldots b_n}, \tag{4}$$

using the convention of implied summation over repeated Cartesian (lowercase subscript) indices. In Eq. (4), $\boldsymbol{E}_{\xi}^{(m)}$ is the transition multipole tensor of order m for atom ξ, and the following defines the coupling tensor that engages E_m source emission at A with E_n detection at B:

$$\begin{aligned} V_{a_1\ldots a_m b_1\ldots b_n}(k, \boldsymbol{R}) = {} & \frac{(-1)^{m+n-1}}{4\pi\varepsilon_0} \nabla_{a_2} \cdots \nabla_{a_m} \nabla_{b_2} \cdots \nabla_{b_n} \\ & \times \left(-\nabla^2 \delta_{a_1 b_1} + \nabla_{a_1} \nabla_{b_1}\right) \frac{e^{\pm ikR}}{R}. \end{aligned} \tag{5}$$

Here $k = \Delta E/\hbar c$, where ΔE is the energy released in source decay, correspondingly acquired by the detector, and $\boldsymbol{R}$ is the displacement vector defined by $\boldsymbol{R}_B - \boldsymbol{R}_A$.

III. DIPOLE-DIPOLE COUPLING

In the most familiar case $m = 1$, $n = 1$, the result (5) delivers the well-known solution for dipole-dipole coupling [13], $M_{fi}^{E1-E1} = \mu_{A;a_1} V_{a_1 b_1}(k, \boldsymbol{R}) \mu_{B;b_1}$, where;

$$\begin{aligned} V_{a_1 b_1}(k, \boldsymbol{R}) = {} & \frac{e^{ikR}}{4\pi\varepsilon_0 R^3} \{(1 - ikR)(\delta_{a_1 b_1} - 3\hat{R}_{a_1} \hat{R}_{b_1}) \\ & - (kR)^2 (\delta_{a_1 b_1} - \hat{R}_{a_1} \hat{R}_{b_1})\}. \end{aligned} \tag{6}$$

As is also the case for higher-order couplings, the retarded result applies over all distances, accommodating readily identifiable short-range (near-field, $kR \ll 1$) and long-range (wave-zone, $kR \gg 1$) asymptotes. While the former behavior is commonly identified with Förster resonance energy transfer, i.e., virtual photon transfer, and the latter with radiative transfer involving a real photon, the two descriptions merge seamlessly [14–17]. Thus, as the detector is moved outwards from the source, away beyond the subwavelength near-field, a progressively propagating character to the energy transfer emerges.

In performing the calculation that leads to the $E1$-$E1$ result, there is neither any assertion nor an assumption that the photon conveying the excitation to the detector has in any sense a dipole character. Although it might be surmised that the coupling photon conveys a single unit of angular momentum (irrespective of the detector displacement from the source)—consistent with the character of the source and detector transitions—this is a conjecture whose extension to higher multipole transitions has significant pitfalls, as the following analysis shows.

IV. QUADRUPOLE-DIPOLE COUPLING

A specific example that both illustrates the physics and focuses attention on the key issues is the case of electric quadrupole emission. It is evidently not yet widely recognized that quadrupole decay releases radiation that is detectable not only by a quadrupole detector but also by a dipole detector—in fact a clearly nonzero result [12,18] emerges for the latter case of $E2$-$E1$ coupling. Specifically, from (4) and (5) we find the following;

$$M_{fi}^{E2-E1} = Q_{A;a_1a_2} V_{a_1a_2b_1}(k,\boldsymbol{R}) \mu_{B;b_1}, \tag{7}$$

$$\begin{aligned} V_{a_1a_2b_1}(k,\boldsymbol{R}) = \frac{-e^{\mathrm{i}kR}}{4\pi\varepsilon_0 R^4} \big[&(3 - 3\mathrm{i}kR - k^2R^2)\big(\delta_{a_1a_2}\hat{R}_{b_1} \\ &+ \delta_{a_2b_1}\hat{R}_{a_1} + \delta_{a_1b_1}\hat{R}_{a_2} - 5\hat{R}_{a_1}\hat{R}_{a_2}\hat{R}_{b_1}\big) \\ &- (k^2R^2 - \mathrm{i}k^3R^3)\big(\delta_{a_1a_2} - \hat{R}_{a_1}\hat{R}_{a_2}\big)\hat{R}_{b_1}\big]. \end{aligned} \tag{8}$$

Interchanging A and B, the same form of result applies to the detection of electric dipole radiation with a quadrupolar detector. The nonvanishing result (7) is consistent with experimental measurements of atomic quadrupole emission. There are, indeed, many well-studied atomic spectral lines uniquely attributable to electric quadrupole transitions, a well-studied example being the ${}^1S_0 \leftarrow {}^1D_2$ transition in O^{2+} [19]. There has not been, it seems, any suggestion that the detection of such radiation requires anything other than a conventional dipolar detector. There are indeed no constraints on the nature of the detector, other than those of an energy gap to match the photon energy and a suitable disposition with respect to the photon polarization.

On recognition that this and other such processes ($E2$-$E2$ and so on) are both fully allowed and addressed by the general QED theory, and assuming that the source and detector transitions are allowed by no other multipole orders, questions of angular-momentum conservation inevitably arise. In the following section, it is shown that the excitation of the photodetector operates by the same mechanism that is deployed in detecting any other form of light. In describing the detection of quadrupolar emission, for example, it proves unnecessary, even potentially misleading, to introduce the concept of a "quadrupole photon" [20]. With regard to conventional detector measurements, such a designation has a fundamentally unverifiable status. The rigor of the mathematics underlying the QED description needs to be reflected by a commensurate care in semantic distinction; the act of radiation may legitimately be termed *quadrupolar* with regard to the electronic states that the decay transition connects, but that descriptor cannot be applied to single photon measurements on the radiation thereby emitted.

V. IRREDUCIBLE TENSOR ANALYSIS

To make further progress, an irreducible tensor construction is introduced. Although spherical tensors are commonly engaged for the analysis of atomic multipole transitions [21], an irreducible Cartesian tensor formulation [22] significantly facilitates a more immediate connection with the development given above, and it conveys the same physical information. The connection between the two representations is well established [23].

The first step is a decomposition of the three tensor forms in Eq. (4) into a sum of irreducible parts. In general, the transformation properties of these irreducible terms, under the symmetry operations of the relevant material system, conform to irreducible representations that correlate with those of integer angular momentum in a space of spherical symmetry. A Cartesian tensor of rank n thus comprises irreducible constituents of integer weights j in the interval $(0 \leqslant j \leqslant n)$, each j signifying the associated angular momentum; see Fig. 1. The decomposition is trivial in the case of the electric dipole and quadrupole moments since each is properly and uniquely expressible as a *natural tensor*, i.e., one whose angular momentum equals its rank, $j = n$, and which has only $(2j + 1)$ independent, nonvanishing components. As applied to atomic multipole transitions, this property is a direct reflection of the local isotropy. It is not, however, a feature of any of the coupling tensors $V(k,\boldsymbol{R})$ delivered by Eq. (5); the entirety of the source-detector system which those tensors engage is clearly of lower, nonspherical symmetry. For example the familiar result (6) for $E1$-$E1$ coupling comprises irreducible constituents of weights 0 and 2; a prescription for their determination is readily available [24].

An insight into the attributes of the various tensor weights in each coupling tensor $V(k, R)$ is afforded by recognizing in the latter the structure of a power series in R. Exploiting this feature, and using the results of detailed calculations [11,12], it is possible to cast the coupling in the form of a series of

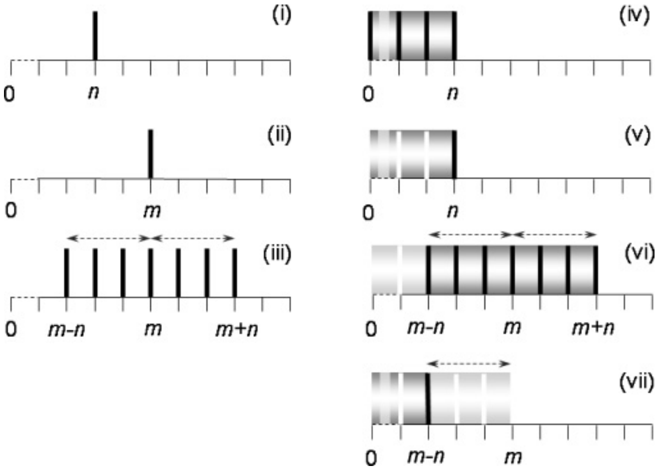

FIG. 1. General representations of angular-momentum (a.m.) coupling, tensors, and weights: (i) $j_1 = n$ units of a.m.; (ii) $j_2 = m$ units; (iii) vector coupling generates integer values in the range $m - n \leqslant j_1 + j_2 \leqslant m + n$; (iv) general tensor T of rank n accommodating weights $0 \leqslant j_{(T)} \leqslant n$; (v) natural tensor of rank n, comprising weight $j_{(T)} = n$ alone; (vi) outer product of natural tensors of ranks m and n, the result of rank $m + n$ spanning weights in the interval $(m - n, m + n)$; (vii) inner product of rank m and n natural tensors, the resulting rank $m - n$ tensor carrying weight $m - n$ alone; any contributions from weights exceeding the rank vanish.

terms in inverse integer powers of kR, expressible as

$$V_{a_1\ldots a_m b_1\ldots b_n}(k,\boldsymbol{R}) = (4\pi\varepsilon_0)^{-1}k^{m+n+1}e^{ikR} \times \sum_{p=1}^{m+n+1}(kR)^{-p}W^{(p)}_{a_1\ldots a_m b_1\ldots b_n}(\hat{\boldsymbol{R}}). \quad (9)$$

Here, the entire tensor and angular-momentum character of the left-hand side is distributed between individual $\boldsymbol{W}^{(p)}(\hat{\boldsymbol{R}})$ tensors (these being dimensionless in terms of physical quantity), in each of which the superscript label serves to identify the associated inverse power of kR. Again focusing on the $E2$-$E1$ case, for example, where $m = 2$, $n = 1$ and the explicit coupling is given by equation (8), the index p on the above summation runs from 1 to $2 + 1 + 1$, signifying that the coupling has terms running from R^{-1} through to R^{-4}.

Resolving each $\boldsymbol{W}^{(p)}(\hat{\boldsymbol{R}})$ into irreducible parts, it emerges that the only nonvanishing terms are those whose weights $j_{(p)}$ are delimited within the range ($p - 1 \leqslant j_{(p)} \leqslant m + n$) [11]. For each value of $j_{(p)}$ of opposite parity to the tensor rank, i.e., where the sum $m + n + j_{(p)}$ is odd, each $\boldsymbol{W}^{(p)}(\hat{\boldsymbol{R}})$ entails an index antisymmetry and hence vanishes. Two examples will serve to illustrate the decomposition.

(i) $E1$-$E1$: In the common case where $m = 1$ and $n = 1$, the parity rule decrees that each term with $j_{(p)} = 1$ term is forbidden, and the coupling has only the following nonzero terms in $p = 1$, 2, and 3;

$$p = 1,\ (R^{-1}) : j_{(1)} = 0, 2;$$
$$p = 2,\ (R^{-2}) : j_{(2)} = 2;$$
$$p = 3,\ (R^{-3}) : j_{(3)} = 2.$$

In each case the allowed values of $j_{(p)}$ are determined by twin conditions, the range limitation ($p - 1 \leqslant j_{(p)} \leqslant m + n$) and the parity rule. The $p = 3$ contribution carries the highest inverse power of R and therefore dominates near-field behavior; the corresponding value $j_{(3)} = 2$ signifies that in this distance regime, precisely two units of angular momentum are involved (essentially one that is coupled with the source transition and another with the detector transition). The same conclusion, concerning the angular momentum, is indeed evident on inspection of Eq. (6); any weight 0 component would involve contraction with $\delta_{a_1b_1}$ which, with the angular factor ($\delta_{a_1b_1} - 3\hat{R}_{a_1}\hat{R}_{b_1}$) in the R^{-3} and R^{-2} terms—see Eq. (6)—yields a vanishing result. Hence only weight 2 components contribute in the short-range.

(ii) $E2$-$E1$: With $m = 2$ and $n = 1$, the coupling has nonzero terms in $p = 1$–4:

$$p = 1,\ (R^{-1}) : j_{(1)} = 1, 3;$$
$$p = 2,\ (R^{-2}) : j_{(2)} = 1, 3;$$
$$p = 3,\ (R^{-3}) : j_{(3)} = 3.$$
$$p = 4,\ (R^{-4}) : j_{(4)} = 3;$$

Here, the short-range contribution ($p = 4$) with $j_{(4)} = 3$ is consistent with a coupling that can accommodate an exchange of three units of angular momentum—two engaging the source, and one the detector. At longer distances, where lower inverse powers of R become prominent, the coupling permits values of both $j_{(p)} = 1$ and $j_{(p)} = 3$ for the angular momentum.

Returning to the general case, and reappraising the tensor contractions in Eq. (4) with regard to their irreducible components, the first of several general conclusions can be drawn. Consider the result of the following tensor contraction:

$$F_{b_1\ldots b_n}(k,\boldsymbol{R}) \equiv E^{(m)}_{A;a_1\ldots a_m}V_{a_1\ldots a_m b_1\ldots b_n}(k,\boldsymbol{R}). \quad (10)$$

In the $E1$-$E1$ case, $F_{b_1}(k,\boldsymbol{R})$ physically signifies the retarded electric (vector) field generated by dipolar decay in the source, in accordance with the classical result [25,26]. More generally, $F_{b_1\ldots b_n}(k,\boldsymbol{R})$ denotes a generated tensor field of rank n, and the weights $j_{(F)}$ that it comprises are determined from its $E^{(m)}$ and $V(k,\boldsymbol{R})$ constituents by the usual rules of angular-momentum addition [2]. The connection between the familiar rules for the coupling of electronic angular momenta and the general principles operating here are exhibited in Fig. 1. Taking into account all possible values of p, it transpires that the reducible tensor $F_{b_1\ldots b_n}(k,\boldsymbol{R})$ may convey any angular momentum in the range $0 \leqslant j_{(F)} \leqslant n$. However, with reference to Eq. (9) there is, in addition, a clearly significant and characteristic distance-dependence associated with the manifestations of each such angular momentum.

(i) In the near-zone ($kR \ll 1$) it emerges that the term in R^{m+n+1}, the one with the *highest* inverse power of R and which dominates $V_{a_1\ldots a_m b_1\ldots b_n}(k,\boldsymbol{R})$, entails weight $m + n$ alone [since this relates to the highest value of p; the result also follows from Eq. (5), $k \to 0$ corresponding to the short-range result; see the appendix]. In this case, Eq. (10) gives $F_{b_1\ldots b_n}(k,\boldsymbol{R})$ as a product of natural tensors, producing a natural tensor that delivers exactly n units of angular momentum. The detector thus acquires the angular momentum necessary to effect its multipolar electronic excitation by the source field, *irrespective* of the multipolar character of the transition involved in the detection;

(ii) In the wave zone ($kR \gg 1$) the term with the *lowest* inverse power of R (always R^{-1}) dominates $V_{a_1\ldots a_m b_1\ldots b_n}(k,\boldsymbol{R})$, and the resulting $F_{b_1\ldots b_n}(k,\boldsymbol{R})$ entails a spectrum of integer weights in the range $[0 \leqslant j_{(F)} \leqslant n]$. Given the exclusion of alternate weights on index symmetry grounds, each allowed weight in the generated field can deliver a corresponding quantity of angular momentum. The multipolar electronic excitation of the detector necessarily engages only the irreducible component of the field that confers the requisite angular momentum.

In either case, of course, angular momentum is locally conserved in both the source emission and detector excitation quantum transitions; this reflects the spatial isotropy of each atomic center, consistent with *Noether's theorem*—see Ref. [27]. As noted above, however, local isotropy is not a feature that extends to the *combined* source-detector system.

Now consider the matrix element (4) represented as $F_{b_1\ldots b_n}(k,\boldsymbol{R})E^{(n)}_{B;b_1\ldots b_n}$, the scalar product of the source field and the detector transition multipole—two tensors of equal rank and known irreducible decompositions. In every distance regime, $F_{b_1\ldots b_n}(k,\boldsymbol{R})$ accommodates at least one weight $j_{(F)} = n$ component—which, on vector addition to the weight n component of the detector multipole, the natural tensor $E^{(n)}_{B;b_1\ldots b_n}$, produces a range of contributions, including $|j_{(F)}–n| = 0$. This is the term necessary to deliver a finite scalar, i.e., a nonzero result for Eq. (4), signifying the quantum amplitude for a complete photon transit.

VI. PHYSICAL INTERPRETATION

The difference between near-zone and wave-zone behavior exhibits the fact that the results of measurement on the quantity of angular momentum conveyed by the tensor field are modified on propagation beyond the near-zone. This feature parallels other, better-known retardation effects, such as the progression from a short-range to a long-range asymptote in the form of distance dependence [12,13] and a correspondingly diminishing longitudinal character of the electric field [16]. It is also consistent with the angular quantum uncertainty principle [28,29]: as a detector recedes, the decreasing angular uncertainty in photon propagation direction is reflected in an increasing range of values for the angular-momentum content. A central conclusion and a range of corollaries now emerge.

(i) There is no restriction on the order of multipole involved in the detection of atomic decay fluorescence: specifically, *there is no constraint effecting a one-to-one correlation between the transition multipoles involved in source decay and detector excitation.*

This result amplifies an earlier remark to the effect that, whereas a process of atomic decay may legitimately be termed *multipolar* with regard to selection rules for the electronic transition, the same term cannot be applied to the emitted radiation. Specifically, to assert that a quadrupole decay transition $|q\rangle \leftarrow |p\rangle$ produces a photon of uniquely identifiably "quadrupolar" character is demonstrably unverifiable. Furthermore, there are significant corollaries.

(ii) It is impossible to uniquely imprint any multipole character in a decay transition on a single photon or with complete fidelity to communicate the angular-momentum change associated with radiative decay of this kind to a remote detector.

(iii) Whereas the character of multipolar emission shapes the angular distribution of the radiation, and hence the location dependence of any detector signal, such features are not measurable by detection of any individual photon of the emergent radiation.

To reinforce the second and third of the above assertions, it is instructive to consider the application of time-reversal symmetry to a simple example. The above assertions resolve an apparent paradox that can arise when multipolar connectivity is too loosely assumed. As has been shown, a photon released by electric quadrupole emission at A can, on its annihilation, produce dipolar excitation at B. If the photon so employed were to be deemed a "quadrupole" photon, then the time-reversed process—dipolar decay at B leading to the excitation of A—would afford the equally logical *but incompatible* inference that the quadrupolar excitation $|p\rangle \leftarrow |q\rangle$ is effected by a "dipole" photon. The self-contradictory nature of the description is evident; the photon responsible would be ascribed a different multipolar character in each case. In fact, apart from their opposing directions of propagation, the two photons are not measurably different; each is a single quantum of the same radiation field. The thought-experiment powerfully demonstrates that, at the level of fundamental quantum measurement, any "multipole photon" terminology is fundamentally inconsistent with the principles of time-reversal symmetry.

VII. THE DETECTION OF MULTIPOLAR RADIATION

It is illuminating to introduce another perspective on the main conclusions from the last section. The results certainly exhibit the fact that, as the detector recedes, there are identifiable physical consequences of a decreasing angular uncertainty about the source-detector axis; however, there are also consequences for mixed-origin angular momentum. For any "point" source, such as an atom undergoing a decay transition, it is well known that one can develop the radiating electromagnetic field in the form of a multipolar expansion cast in spherically symmetric radiation modes [30–33]. These are definite parity eigenfunctions of the operators for the total angular momentum of the field and its azimuthal component. However, removal of a detector from the immediate vicinity of the source generates increasing departures in form between spherical radiation modes centered on each location as origin. In particular, eigenstates of the operator for the azimuthal component of angular momentum are no longer eigenstates of the correspondingly displaced operator—as has recently been pointed out in connection with schemes for the management of optical angular momentum [34]. Viewed in this context, it is not surprising to find that a pure state produced at the source as origin engenders a mixture of states that can be registered as a spectrum of different angular-momentum values, exactly consistent with the results of Sec. IV.

The corollary that emerges from this perspective is that, even if one could in principle design a remote detector whose excitation could be achieved only by electromagnetic fields of a given multipolar type, the registration of an individual photon by such a detector could not generally be interpreted as unequivocal evidence of a corresponding multipolar origination in the prior process of photon emission. The exception would be a multipolar detector either colocated with the source, or else cleverly formed as a spherical shell, centered on the source. Notwithstanding the fundamental viability of the latter concept, the technical demands associated with producing such a device appear daunting.

Since, therefore, one cannot demand a unique, one-to-one correlation between multipolar characters in the decay emission and detector absorption in conventionally engineered systems, there is a compelling case for discarding the terminology of "multipolar photons" as a useful descriptor of the associated electromagnetic quanta. Moreover the specific instance that has illustrated these principles, concerning the detection of electric quadrupole emission by a regular dipolar detector, is not only of fundamental importance – it is in principle testable. Here is a pivotal question; ignoring relative intensities, could the radiation emitted in such a decay be experimentally differentiated from the dipole emission of another source (at the same wavelength), using the same detector? From the analysis presented here the answer is that it would be possible only with a tantalizingly complex detector. In any other case, the information to afford such discrimination is not remotely communicable. This conclusion establishes a previously unrecognized fundamental limitation on the propagation of multipolar character, representing a constraint on achievable information delivery in quantum communication.

VIII. MOLECULAR SYSTEMS

The isotropy of atomic systems, which engages irreducible representations (irreps) of the full rotation group $O(3)$, affords a simple and direct one-to-one connectivity between angular momentum and multipolar form. In the case of molecular systems, necessarily of lower symmetry than atoms, such a correspondence is no less rigorous – but the decay and excitation transition moments typically have components that span *more than one* irreducible representation of the molecular point group. The general rule for an allowed transition is that the product of the irreps for the initial and final states (here the ground and excited states, or vice-versa) spans one or more irreps under which components of the transition moment transform, under symmetry operations determined by the molecular structure [35].

For example in one important type of antenna molecule, a carotenoid of C_{2h} symmetry, components of the $E1$ electric dipole operator transform as $A_u + 2B_u$. This signifies that transitions to or from the A_u and B_u excited states are electric dipole allowed (assuming a totally symmetric A_g ground state). Equally, transitions to or from A_g and B_g states are $E2$, electric quadrupole allowed. However, in planar dendrimers of D_{3h} symmetry, $E1$ components transform as $A_2'' + E'$, and $E2$ components as $A_2' + E' + E''$, with the result that ground-state transitions to or from states of E' symmetry are equally $E1$ and $E2$ allowed. Consequently the decay of an E' electronic excited state cannot conceivably be said to deliver a photon of either dipole or quadrupole character; there are no grounds for adopting such a terminology, and even the atom-focused arguments advanced in earlier sections become redundant. In molecules of C_{2v} symmetry, moreover, symmetry-preserving transitions are simultaneously allowed by *all* orders of electric multipole [36].

The other issue that becomes important in molecular systems is the possibility of transitions allowed by Mn magnetic coupling. Whereas in atoms the magnetic multipoles have opposite parity to their electric counterparts, and therefore transform under different irreducible representations, the situation is more complicated in systems that lack a center of symmetry. In the case of *chiral* molecules (those lacking any rotation-inversion axis), the irreps under which electric and magnetic multipole operators transform become identical. Any electric dipole-allowed transition in such a molecule is also necessarily magnetic dipole allowed, for example—and the effect is manifest in phenomena such as circular dichroism that exhibit the chirality [37,38]. There are further intricacies with achiral molecules such as the D_{3h} case considered above, where the decay of an E' state proves to be both electric *quadrupole* and magnetic *dipole* allowed. Clearly, there is no sensible multipolar designation for the photons emitted in such a process.

One further corollary has another experimental consequence. If there were indeed to be a means of determining quadrupole character in photons released by electric quadrupolar decay, then it might be considered that with judiciously chosen samples it should be possible to discriminate between atomic and molecular or crystalline sources delivering fluorescence of the same wavelength. The present analysis leads to the inexorable conclusion that any such discrimination, on the basis of a different character in the emitted photons, is manifestly impossible. One cannot anticipate achieving the requisite fidelity of information transfer by detection of an emitted photon.

IX. CONCLUSION

The designation of any multipolar character to photons, on any assumption of a direct mapping from the character of the responsible decay transition, is of very limited application and is in general misleading. There are indeed numerous cases where a decay transition is allowed by more than one form of multipole—such as the $M1$-$E2$ interference observable in Pb [39]. Moreover the received usage cultivates a misconception; that there exists the possibility of long-range communication of multipolar character, from an atom or molecule in which an emissive or absorptive multipolar transition occurs. To be clear, this does not undermine usage of the term *quadrupole radiation*: the latter designates an angular distribution in emission that does indeed reflect the nature of the decay transition in atomic systems. However, at the quantum level such spatial distributions are to be regarded as serving only to identify the relative probabilities of emitted photons propagating in different directions.

With the sole exception of dipole emission, each emitted photon as it travels from its source conveys an angular momentum that acquires a progressively broader spectrum of values, signified by weights in the tensor field $F_{b_1 \ldots b_n}(k, \boldsymbol{R})$. The detection of any individual photon at a specific point in space serves to demolish the directional uncertainty in its emission, and the price is a loss of angular-momentum information [40]. In this connection it is worth recalling that, whereas in the multipole formulation the electric fields associated with photons are orthogonally disposed to their directions of propagation, this transversality does not hold with respect to the displacement, $\boldsymbol{R}$, between the source and detector. With regard to the $\boldsymbol{R}$ the retarded source field, which in the near-zone has a longitudinal character, acquires a progressively transverse character as it propagates [16]. This again reflects the diminishing uncertainty in identifying the direction of photon propagation with $\boldsymbol{R}$. Here, there is plenty of scope for future work to address in more detail the correlation between these behaviors.

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APPENDIX

Proof that $\lim_{k\to 0} V_{i_1\ldots i_m j_1\ldots j_n}(k,\boldsymbol{R})$ *is a natural tensor*. From Eq. (5),

$$\lim_{k\to 0} V_{i_1\ldots i_m j_1\ldots j_n}(k,\boldsymbol{R}) = \frac{(-1)^m}{4\pi\varepsilon_0}\nabla_{i_2}\cdots\nabla_{i_m}\nabla_{j_2}\cdots\nabla_{j_n} \times\left(-\nabla^2\delta_{i_1 j_1} + \nabla_{i_1}\nabla_{j_1}\right)\frac{1}{R}. \quad \text{(A1)}$$

The rank $m+n$ tensor may comprise weights in the range $(0, m+n)$; to identify the result for each weight $j_{(p)} < m+n$ involves contraction with at least one Kronecker delta or one Levi-Civita tensor.

In the case of contracting (A1) with a Kronecker delta, the result is clearly zero if both its indices are in the set containing $i_2\cdots i_m$ and $j_2\cdots j_n$, since this will generate a Laplacian, and $\nabla^2(\frac{1}{R}) = -4\pi\delta(\boldsymbol{R})$; the result is therefore zero for any finite source-detector separation. In the case where the one index of the delta is in the set $i_2\cdots i_m, j_2\cdots j_n$—call it i_t—and the other is i_1, the del operator carrying the index i_t, on contraction with the bracketed term in (A1), gives $\nabla_{i_t}(-\nabla^2\delta_{i_t j_1} + \nabla_{i_t}\nabla_{j_1}) = -\nabla_{j_1}\nabla^2 + \nabla^2\nabla_{j_1} = 0$; the same conclusion of a zero result is drawn if one index of the delta is from the set $i_2\ldots i_m, j_2\ldots j_n$ and the other is j_1. Last, when the two indices of the Kronecker delta are $i_1 j_1$, the bracketed term in (A1) produces $(-3\nabla^2 + \nabla^2)\frac{1}{R} = 8\pi\delta(\boldsymbol{R})$, again leading to a vanishing result.

The other case that arises is that of a contraction of (A1) with a Levi-Civita antisymmetric tensor. Concerning the latter, at least two of its indices must be in the full set $i_1\ldots i_m, j_1\ldots j_n$. Effecting the contraction, the result will clearly be zero if two or three of the Levi-Civita tensor indices are in the set $i_2\ldots i_m, j_2\ldots j_n$, or indeed if they include $i_1 j_1$; no other possibilities arise.

Consequently, since it is proven that the tensor defined by (A1), i.e., the short-range limit of $V_{i_1\ldots i_m j_1\ldots j_n}(k,\boldsymbol{R})$, comprises no contributions of weights less than $m+n$; it is a natural tensor, of weight $m+n$ alone. Q.E.D.

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[1] R. N. Zare, *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics* (Wiley, New York, 1988), p. 184.

[2] M. Weissbluth, *Atoms and Molecules* (Academic, New York, 1978), p. 26.

[3] D. L. Andrews, D. P. Craig, and T. Thirunamachandran, Int. Rev. Phys. Chem. **8**, 339 (1989).

[4] D. L. Andrews, Chem. Phys. **135**, 195 (1989).

[5] D. L. Andrews, Can. J. Chem. **86**, 855 (2008).

[6] E. A. Power and T. Thirunamachandran, Phys. Rev. A **56**, 3395 (1997).

[7] R. G. Woolley, Adv. Quantum Chem. **32**, 167 (1999).

[8] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Dover, New York, 1998), chap. 10.

[9] M. Babiker, E. A. Power, and T. Thirunamachandran, Proc. R. Soc. London A: Math. Phys. Eng. Sci. **338**, 235 (1974).

[10] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (University Press, Oxford, 1984), p. 51.

[11] G. D. Scholes and D. L. Andrews, J. Chem. Phys. **107**, 5374 (1997).

[12] A. Salam, J. Chem. Phys. **122**, 044112 (2005).

[13] G. Juzeliūnas and D. L. Andrews, Adv. Chem. Phys. **112**, 357 (2000).

[14] D. L. Andrews and B. S. Sherborne, J. Chem. Phys. **86**, 4011 (1987).

[15] G. J. Daniels, R. D. Jenkins, D. S. Bradshaw, and D. L. Andrews, J. Chem. Phys. **119**, 2264 (2003).

[16] D. L. Andrews and D. S. Bradshaw, Eur. J. Phys. **25**, 845 (2004).

[17] R. D. Jenkins, G. J. Daniels, and D. L. Andrews, J. Chem. Phys. **120**, 11442 (2004).

[18] D. S. Bradshaw, Ph.D. thesis, University of East Anglia (2005).

[19] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), p. 451.

[20] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Quantum Electrodynamics*, 2nd ed. (Butterworth, Oxford, UK, 1982), p. 18.

[21] R. Grinter, J. Phys. B: At. Mol. Opt. Phys. **41**, 095001 (2008).

[22] J. A. R. Coope, R. F. Snider, and F. R. McCourt, J. Chem. Phys. **43**, 2269 (1965).

[23] J. Jerphagnon, D. Chemla, and R. Bonneville, Adv. Phys. **27**, 609 (1978).

[24] D. L. Andrews and P. Allcock, *Optical Harmonics in Molecular Systems* (Wiley-VCH, Weinheim, 2002), Appendix 4.

[25] J. D. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, New York, 1999), p. 411.

[26] L. Novotny and B. Hecht, *Principles of Nano-Optics* (University Press, Cambridge, UK, 2006), p. 262.

[27] J. Hanc, S. Tuleja, and M. Hancova, Am. J. Phys. **72**, 428 (2004).

[28] S. M. Barnett and D. T. Pegg, Phys. Rev. A **41**, 3427 (1990).

[29] S. Franke-Arnold, S. M. Barnett, E. Yao, J. Leach, J. Courtial, and M. Padgett, New J. Phys. **6**, 103 (2004).

[30] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms: Introduction to Quantum Electrodynamics* (Wiley Interscience, New York, 1989), p. 45.

[31] B. W. Shore, *The Theory of Coherent Atomic Excitation: Multilevel Atoms and Incoherence* (Wiley Interscience, New York, 1990), Vol. 2, p. 1219.

[32] M. E. Rose, *Elementary Theory of Angular Momentum* (Dover, Mineola NY, 1995), p. 127.

[33] G. Nienhuis, in *Structured Light and Its Applications*, edited D. L. Andrews (Academic, Burlington, MA, 2008) chap. 2, p. 27.

[34] G. Molina-Terriza, J. P. Torres, and L. Torner, Phys. Rev. Lett. **88**, 013601 (2002).

[35] D. L. Andrews, Spectrochim. Acta A **46**, 871 (1990).

[36] D. C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy* (Dover, New York, 1990), Appendix A.

[37] E. A. Power and T. Thirunamachandran, Int. Rev. Phys. Chem. **5**, 273 (1986).

[38] T. D. Crawford, Theor. Chem. Acc. **115**, 227 (2006).

[39] S. Werbowy and J. Kwela, J. Phys. B: At. Mol. Opt. Phys. **42**, 065002 (2009).

[40] S. Franke and S. M. Barnett, J. Phys. B: At. Mol. Opt. Phys. **29**, 2141 (1996).