Spin-orbit coupling in vortex light: can it be revealed in fundamental electronic transitions?

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ABSTRACT

Recent theoretical work on circular dichroic effects, for absorption processes in chiral materials, has reopened questions over the possibility that the interactions of vortex beams may display a sensitivity to material handedness. The interest in such a phenomenon arises from the fact that any engagement of optical phase gradients, in quadrupole-allowed electronic transitions, will represent a distinctive form of engagement with chiral matter. This is an issue that numerous careful experiments have so far failed to fully resolve, with some of them giving a clear null result, yet others giving positive indications. A definitive outcome from any such investigation would represent a touchstone for a broader, yet more challenging question: is there any mechanism by means of which twisted light, which conveys both orbital and spin angular momentum, can exhibit coupling between the two? It emerges that such a possibility can be identified, but the constraints upon its manifestation are severe. This presentation sets out the principles and the conclusions to which they lead, informing the pathway for ongoing experimentation.

Keywords: Chirality, twisted light, optical vortex, spin-orbit coupling, liquid crystal, photon spin, structured light, optical angular momentum

1. INTRODUCTION

The coupling of optical spin (SAM) and orbital angular momentum (OAM) through a spin-orbit interaction (SOI) has acquired a new realm of application, meaning and significance, as a result of several recent studies on optical vortices, or 'twisted light' – i.e. light with a helically twisted wavefronts.[1-3] The context for most of these studies has been a renewed focus upon the possibility of such 'vortex beams' being able to exhibit a chiroptical sensitivity (through the sign of their topological charge ℓ) in light-matter interactions, in an analogous fashion to the role of circularly polarized light in circular dichroism. Although this kind of interaction has been sought for nearly two decades, definitive and generalized conclusions have proved tantalizingly difficult to achieve. Recent theoretical studies have elucidated one mechanism which details how the engagement of electric quadrupole transition moments (E2) in anisotropic chiral and achiral media, through the absorption of photons possessing both SAM and OAM, leads to the manifestation of such a chiroptical interaction. Moreover, there are certain reasons to suppose that such effects might come into play through an SOI of light.[4-6] The clear identification of such an interaction represents a touchstone for a broader, challenging question: is there any mechanism by means of which can light that conveys both OAM and SAM can unequivocally exhibit coupling between the two, in an electronic transition in atomic or molecular systems? As will be shown, such a possibility is not entirely precluded, but there are severe constraints upon its observable manifestation. To set the scene, it is helpful to first examine the whole notion of spin-orbit coupling, to establish where special features arise in the case of twisted light.

2. ORIGINS OF SPIN-ORBIT COUPLING

The nature and correct representation of coupling between different quantities of angular momentum is a topic of wide relevance in physics. In the most familiar cases, these angular momenta relate to material bodies displaced from an axis about which they execute orbital motions. The term 'spin' is used to identify rotational motions that more specifically take place about an axis passing within the physical confines of the rotating component. This, at least, is the mechanical description that applies to macroscopic bodies, such as planets spinning and rotating about a star within a solar system. Thus, in an astronomical context, 'spin-orbit coupling' signifies the addition of angular momenta, the sum being a conserved quantity. In atoms, a broadly similar principle applies to the dynamics of electrons moving around the nucleus, but the nature of the spin is in this case not directly attributable to conventional mechanical motion. For structureless elementary particles such as electrons, the intrinsic spin is a subtler quantity whose correct representation demands the application of relativistic quantum mechanics. As is well known, the nature of spin-orbit coupling is then responsible for the fine structure level-splitting in atomic spectra. In simple terms this relates to an energy term that is quadratic in a vector angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, the coupling thereby emerging in a cross-term dependent on the scalar product $\mathbf{L}.\mathbf{S}$. (In passing, it may be observed that the term 'spin-orbit coupling' is not used, without distorting its meaning, to describe the interaction of optical spin with orbital electronic motion – the origin of the Laporte rule for single-photon absorption – or, for that matter, optical orbital angular momentum with material spin.)

In optics, the concept of 'spin-orbit coupling' has arisen much more recently, and in an entirely different sphere of application – namely structured light. As with the astronomical and atomic systems, the term is applicable to the interaction of spin and orbital angular momentum in their attribution to the same physical entity, which in this case is the photon. However, in this context, both of the angular momentum aspects have physically distinctive connotations. A primary distinction is the association with the photon of a propagating character: unlike material bodies of any scale, this elementary particle is never found at rest, or even in a state closely approximating to it. (In studies of 'sub-luminal' propagation, the character of the photon is essentially lost.) For the photon, the familiar spin angular momentum is once again an intrinsic quantity connected with the nature of an elementary particle – in this case a mass-less one. In fact, it is only for circular polarizations that the spin has a well-defined value, corresponding to a 'sharp value' in the language of quantum mechanics.[7] Then, the associated angular momentum acquires a magnitude equal to one unit of the Dirac constant, its unit vector aligned in either the positive or negative direction with respect to the propagation direction, for left- and right-handed polarizations respectively.

The counterpart 'orbital' angular momentum, a hallmark of many forms of structured light,[3] has a physical significance that itself relates specifically to the axis of propagation. In principle, the photon can represent one quantum of excitation in any optical mode – which can be defined in terms of five degrees of freedom: in addition to two for the polarization, such as may be represented by coordinates on a Bloch or Poincaré sphere, there are three further degrees of spatial freedom. In conventional optics, the latter degrees of freedom are generally spent in defining the orientation and magnitude of the wave-vector in some arbitrary frame of reference, essentially expressible in terms of the wave-vector components in each of the Cartesian axes (or any other set of three-dimensional spatial coordinates). For plane wave representations of light, this wave-vector is a free vector – the wave-vectors of photons with the same wavelength, travelling in parallel, are all equivalent. However, for most kinds of structured light, one of the degrees of spatial freedom is taken up in defining the wavelength and direction of propagation, with the other two serving to designate the beam structure. And here, another significant issue of distinction arises.

While the propagation vector of the beam is itself a bound vector, in a sense anchored to an axis whose position is defined by the optical elements producing the beam structure, the same cannot be said of individual photons within the beam, within the paraxial approximation. The measurable properties of each photon are identical, as befits their collective status as bosons defining the quanta of excitation of a common optical mode; accordingly it is not possible to discern individual photon wave-vectors. This principle exactly tallies with the ultimately insoluble problems that beset attempts to define wavefunctions for individual photons. Each photon in principle conveys information on the beam structure, as has been definitively shown by Galvez et al.[8]; this is indeed the reason for the huge interest in data transmission using structured light.[9] The relevance for orbital angular momentum is therefore this: it is a measure that references the bound propagation

vector, yet there need be neither particles of matter nor light to serve as local anchor; the orbital motion of each photon refers to an axis intrinsic in the defined mode to which it belongs. As Galvez's work shows, the orbital angular momentum does not have reference to other photons within the beam. Again, any such conjecture is countered by the fact that photons do not directly interact between themselves, as Dirac first explained.[10]

It follows that, while the total angular momentum is a well-defined quantity – whose density is given, as one should expect, by the cross-product of the position and Poynting vectors – any form of its partitioning into spin and orbital parts cannot be unique. In fact neither the components of the spin operator $\mathbf{S}$, nor its orbital counterpart $\mathbf{L}$, satisfy the commutation relations necessary to be acceptable as a true quantum mechanical operator.[11] The term 'spin-orbit coupling' is therefore open to more than one interpretation (and also more than one quantitative measure) in the case of structured light. For any optical process whose observable delivers a contribution dependent on $\mathbf{L}.\mathbf{S}$, the term is appropriate: in particular, it need not be limited to non-paraxial beams, as has occasionally been asserted. However, taking $\mathbf{L}$ and $\mathbf{S}$ as collinear, or at least approximately so, then the coupling $\mathbf{L}.\mathbf{S}$ can more simply be expressed as $l\sigma$, where $l\hbar$ is the magnitude of the orbital angular momentum (i.e. the topological charge) and $\sigma = \pm 1$ for left- and right-handed circular polarizations, respectively. (Here is the only remote similarity to the mechanical application of the term in planetary astronomy: the directions of spin and orbital motion are usually parallel: the Earth is a notable exception.) To focus more explicitly on symmetry aspects in the following exposition, it will also prove expedient to represent the sign of l as η, i.e. $l = \eta|l|$, such that obvious manifestations of spin-orbit effects are those for which there are measurables carrying the signature $\eta\sigma$. The manner in which this facet plays into material chirality will become apparent later, where an example of its explicit manifestation will be identified.

3. SPIN-ORBIT ANGULAR MOMENTUM CONVERSION

Before proceeding further, it is worth recording a variety of studies that have shown how, through interaction with suitable optical elements, it is possible to effect a degree of exchange between spin and orbital angular momentum. Such forms of conversion, which are most often associated with focusing, propagation within anisotropic media or through fibers, are essentially macroscopic (beam-scale, rather than photon-level) interactions that do not specifically engage real electronic transitions: they are briefly mentioned here primarily as a reminder that they may also occur alongside phenomena that do engage transitions or scattering, if local conditions allow. The results of experimental studies may also be complicated by light scattering, in which connection it is well known that the singularity of a vortex beam can be broken into a constellation of singly charged vortices.[12]

The processes that lead to the conversion of spin angular momentum into orbital form were considered in a very significant experimental analysis by Marrucci et al. over a decade ago. Their work demonstrated how, in media that are optically inhomogeneous and anisotropic, the spin angular momentum that is conveyed by a circularly polarized light beam may be converted into orbital angular momentum with a helicity determined by the input polarization.[13] Subsequently, it was also shown that spin-to-orbital angular momentum conversion occurs for zero-order as well as high order circularly polarized Bessel beams propagating along the optical axes of uniaxial and biaxial crystals.[14] In further developments it has been shown that hybrid modes comprising a superposition of circularly polarized vortices can deliver a well-defined total angular momentum – a principle that has been applied in an ultra-thin spin-to-orbital angular momentum converter based on auspiciously oriented plasmonic nano-antennas.[15] Similar ideas had indeed been previously explored in connection with oriented molecular or other nanoscale components.[16,17] A noteworthy addition to the catalog of work in this field is a report showing that, on propagation through chiral media, Bessel-Gaussian beams may split into two beams of oppositely handed circular polarization, with different propagation trajectories.[18] However, none of these effects engages the helical properties of structured light in explicitly measurable electronic transitions: it is these that are the focus in the following analysis.

4. SPIN-ORBIT COUPLING AND CHIROPTICAL INTERACTIONS

As discussed above, the connections of angular momentum with photons are invariably associated with propagation. In mechanical systems, any combination of rotation with translational motion parallel to the rotational axis generates a helical locus. Whilst the concept of helicity is certainly present with light, it is not to be simply conceived as a structure in three-dimensional space. For example, although circularly polarized light is commonly depicted in terms of a rotating and translating electric field vector sweeping out a helical trace, there is no realistic sense of physical motion around the axis. Physically more important is the fact that light with any such helical character has a specific parity with regard to the 3D spatial parity operator $\mathcal{P}$. Since we can learn nothing about light without providing for its interaction with matter, it becomes of interest to consider the prospect for differential forms of interaction with chiral as opposed to achiral materials – the former representing enantiomeric inversion (a change of handedness) under $\mathcal{P}$. To be clear, in the study of spin-orbit optical interactions, it is not a requisite that the matter should be chiral – but if it is, there is scope to additionally consider symmetry constraints, especially if excitation or decay involved electronic excited states are involved. The reason is that excited state wavefunctions commonly lack invariance under the full set of operations corresponding to the symmetry point group for the equilibrium nuclear coordinates. For example, in centrosymmetric molecules, whose ground state equilibrium nuclear displacements from a suitable point of origin represent a set that is even under parity $\mathcal{P}$, all excited states will have a sharp value for the parity signature – some excited states will be even, others odd. For chiral media, parity is not a good quantum number, but since the operation $\mathcal{P}$ is mathematically equivalent to a combination of rotation by π radians and mirror reflection in a plane perpendicular to the axis of rotation,[19] two forms of opposite handedness may arise and these mirror image counterparts known as enantiomers. For these, it is therefore possible to assign a material quantity with positive or negative sign, $\xi = \pm 1$, to represent the distinction. [For organic chemicals, the designations R and S are commonly used to differentiate the pair; an earlier sign convention was usually deployed to indicate a propensity to rotate the plane of linearly polarized light in a clockwise or anticlockwise sense.] In view of the earlier remarks, it is clear that when twisted beams of circular polarization impinge upon chiral material, the totality of the system will have parity aspects that may depend on the signature product spin-orbit effects carry the product signature $\eta\sigma\xi$, or the product of any subset of these parameters.[6]

The issue of whether the OAM of so-called twisted or vortex light beams can play a role in chiroptical interactions, in an analogous fashion to the long-established role of circularly polarized light in processes such as circular dichroism and differential scattering,[20,21] has been debated for nearly two decades. The first studies[22] looked at single-photon absorption processes restricted to the dipole approximation, and correctly concluded such a phenomena was not possible for atoms and molecules; this was soon backed up with experimental evidence.[23,24] However, further studies specifically entailing SOI were able to induce chiroptical effects with OAM by utilizing the helicity-dependent intensity distributions that occur due in focused non-paraxial vortex beams with circular polarization, in what has been given the misleading designation 'circular dichroism'.[25] A similar study revealed 'circular dichroism' in achiral atomic matter,[4] and another conjectured the use of so-called 'spin-orbit beams' to characteristic material chirality.[26] Further studies have looked at using plasmonic coupling in light-matter interactions to fabricate similar chiroptical effects,[27-30] with a similar dichroic effect manifesting itself with vortex electron beams.[31] There has even been experimental work seeking so-called 'magneto-orbital' dichroism, an OAM analogue of magnetic circular dichroism – although without success.[32]

To date, most studies describing the spin-orbit interactions of light have involved looking at non-paraxial optical fields (as in focused or scattered light), SOI effects in inhomogenous media and at interfaces, as well as metasurfaces and evanescent near-fields.[33] These SOI interactions lead to *spin-to-orbit AM conversion* of light – as detailed in the previous section – as well as the *spin Hall* and *orbital Hall effect* of light.[34] Relatively few studies appear to have concerned SOI in freely propagating or paraxial light.[35] Such studies have produced somewhat conflicting statements about SOI.[36] Moreover, most investigations of SOI between light and matter, in both the classical and quantum regime, have been restricted to the dipole approximation. The recent studies to be discussed in the following are distinctly different in that, in the theoretical derivation of optical rates, the photons are assumed to be freely propagating in a paraxial fashion, within the Rayleigh range. None of the SOI addressed above are applicable to this situation: the effects that are now being identified relate to

the direct interaction of the light with individual particles of matter, without the beam being subjected to any scattering or focusing, for example.

Removing the constraints of a dipole approximation allows the possible role of higher-order interactions – the leading contender being electric quadrupole transitions – to be engaged in absorption processes. It has emerged that by allowing for such coupling, chiroptical interactions can indeed be sensitive to the topological charge of a vortex beam, and thus the handedness it possesses. The most recent studies have highlighted that this effect appears to be a manifestation of a SOI interaction. We now aim to consider in more depth the apparent SOI that is occurring in chiroptical effects with chiral and achiral matter interacting with paraxial circularly polarized vortex beams.

To highlight the origins of this SOI we begin with the light-matter interaction Hamiltonian cast in its multipolar form.[37] In the present connection it is expedient to focus on the electric terms alone, since as stated above, previous studies have shown that the magnetic terms can, neither alone nor through interference with electric dipole coupling, produce chiroptical effects that depend on the OAM of a vortex beam.[22] The multipolar Hamiltonian is thus:

$$H_{\text{int}} = \sum_{\xi} \left[-\boldsymbol{\mu}(\xi) \cdot \boldsymbol{e}^{\perp}\left(\boldsymbol{R}_{\xi}\right) - Q_{ij}(\xi) \nabla_{j} e_{i}^{\perp}\left(\boldsymbol{R}_{\xi}\right) ... + h.o.t. \right],$$ (1)

where the Einstein summation notation has been assumed for the component indices, and $\boldsymbol{e}^{\perp}\left(\boldsymbol{R}_{\xi}\right)$ is the mode expansion for the electric field in the paraxial approximation. The first term in (1), involving the transition electric dipole operator, may be referred to as E1 coupling, the second term that involves the transition electric quadrupole operator as E2. At this stage it is obvious that any E1 coupling depends directly upon the intrinsically oscillatory electric field, whereas the presence of the ∇ (gradient) operator in the E2 coupling highlights its dependence upon the gradient of the dynamic electric field. This simple difference cannot be emphasised enough: it is due to this electric field gradient dependence that it is possible for optical rates to have a linear dependence on the sign of the topological charge, and thus the handedness of a vortex beam. To highlight this ℓ-dependence, we isolate the gradient operation on the field from (1) and used the standard quantised mode expansion for the electric field of a Laguerre-Gaussian (LG) beam;[38]

$$\nabla_{j} e_{i}^{\perp}\left(\boldsymbol{R}_{\xi}\right) \approx \nabla u_{\ell,p}\left(r,\phi,z\right) \approx \nabla_{j} f_{\ell,p}\left(r\right) e^{ikz}\, e^{-i\ell\phi},$$ (2)

where $u_{\ell,p}\left(r,\phi,z\right)$ is the z-independent transverse field amplitude in cylindrical co-ordinates; $f_{\ell,p}\left(r\right)$ is a radial distribution function; the azimuthal phase factor $e^{-i\ell\phi}$, which depends upon the angular coordinate, is the factor responsible for the vortex structure and OAM of LG modes. Carrying out the gradient operation gives the following result;

$$\nabla_{j} f_{\ell,p}\left(r\right) e^{(ikz+i\ell\phi)} = \hat{r}_{j} \frac{\partial f_{\ell,p}\left(r\right)}{\partial r} e^{(ikz+i\ell\phi)} + f_{\ell,p}\left(r\right) \frac{1}{r} \left(i\ell\hat{\phi}_{j} - \hat{r}_{j}\right) e^{(ikz+i\ell\phi)} + f_{\ell,p}\left(r\right) ik\hat{z}_{j}\, e^{(ikz+i\ell\phi)},$$ (3)

where the second term involving the quantity $\ell\hat{\phi}_{j}$ clearly highlights the origin of the dependence on the sign of the OAM in light-matter interactions. At this stage, however, it doesn't explicitly highlight a form of spin-orbit coupling; this is only revealed once optical rates are calculated for specific phenomena. It is worth observing that although typically small compared to the generally dominant electric dipole interaction, relatively enhanced interactions can take place between quadrupole transition moments and twisted light beams, precisely because of their intricately structured phase fields.[39-42]

Of importance to us here is the role of angular momentum transfer that takes place in electronic transitions when photons are absorbed by atoms and molecules; this is the theoretically and experimentally simplest form of interaction with a capacity to indicate the sought SOI effects. Just as the intrinsic SAM of a photon is known to be transferred to the orbital angular momentum of an electron, i.e. the internal degrees of freedom of an atom/molecule, the question has naturally been posed as to whether the OAM of a twisted light beam might also be transferred to internal electronic motion. Different theoretical studies provided conflicting conclusions:[43-46] however, it became widely agreed that in dipole transitions, any OAM is transferred to external degrees of freedom – i.e. those associated with movement of the atom or molecule as a whole. However, early theoretical predictions that optical OAM might indeed be transferred to the internal degrees of

freedom through electric *quadrupole* transitions have been vindicated by recent experimental evidence.[43,47] In any such E2 transition, the intrinsic single unit of SAM of a photon is transferred to the electronic motion, along with a single unit of OAM from the beam, with the remaining $(\ell \pm 1)\hbar$ OAM transferred to the centre of mass motion. To be clear: linearly polarized photons can induce an electronic quadrupole transition, and so can circularly polarized photon: it cannot generally be assumed that there is a one-to-one correlation between a transition multipole involved in absorption, and the angular momentum content of the incident field.[48]

In the issues to be addressed here, it is important to note that the QED theory is developed specifically for application to circularly polarized photons: to identify chiroptical effects with an additional OAM dependence, we must represent photons that also possess SAM. Any such spin-orbit interaction clearly ceases to exist when the photons possess no SAM, as is the case with a linearly polarized beam. The circularly polarized photons possessing the SAM can be seen as 'unlocking the door' for optical OAM to be transferred in an E2 transition, manifesting itself through a SOI, which subsequently provides a route for chiroptical effects that are sensitive to the handedness of a vortex twist. Clearly then, the engagement of E2 moments which are dependent upon the gradient of an oscillating electric field is a requisite if we hope to observe spin-orbit coupling.

Using the result (3) above, the rate of single-photon absorption by LG beams, termed circular-vortex dichroism (CVD), has been calculated for chiral molecules, and its leading contribution is manifest though an E1E2 coupling. The result first given in ref.6 can more concisely be expressed as follows:

$$\Gamma_{\text{Chiral}}^{(\text{L/R})}(\ell) = \sigma\ell \frac{I(\omega)}{2c\hbar^2 \varepsilon_o} \frac{1}{r} f_{\ell,p}^{2}(r) \varepsilon_{ikm} \hat{k}_m \hat{\phi}_j \mu_k^{f0} Q_{ij}^{f0}, \tag{4}$$

where $I(\omega)$ is the irradiance per unit frequency interval, ε_{ikm} is the antisymmetric isotropic third-rank Levi-Civita pseudotensor, and $\hat{k}$ is the unit vector for the wave vector $\boldsymbol{k}$. Equation (4) signifies a rate per molecule, just as the total rate is formulated: the *fractional* degree of dichroism that is generally measured and reported is therefore representative of the whole system within the same local volume of the irradiated sample. Near the axis of a beam with non-zero ℓ, the phase singularity gives a zero result, as is consistent with the involvement of dipolar coupling: although other kinds of response, due to quadrupolar interactions with the phase gradient, can occur along this axis,[49,50] the key feature for chiral response is the interference between different forms of coupling, and in this case the conditions for both E1 and E2 couplings have to be locally satisfied.

Evidently, the CVD interaction is a spin-orbit coupling effect, identifiable by the presence of the $\sigma\ell$ at the front of the right hand side of (4). Indeed, since the sign of the E1E2 product itself depends on that of the enantiomeric label ξ, the above expression varies with the product signature $\eta\sigma\xi$ identified earlier. It is obvious from (4) that the rate is dependent upon the position and orientation of the molecule within the beam profile. Standard rotational averaging techniques[51] show that for a system of randomly oriented molecules, the total rate (4) is zero (analogously to the circular dichroism result); moreover, even for molecules with a fixed orientation – as for example in the domains of a liquid crystal – a beam average (across the transverse plane) also leads to a null result. As such, the chiroptical effect (4) is a local effect: the best strategy for its observation would involve measuring the extent of absorption at different locations within the beam profile. This reinforces the fact that the intrinsic nature of the OAM of paraxial beams can in fact be registered on a local scale, in contrast to dipole interactions which register the locally-extrinsic nature of the OAM.[52]

Chiroptical effects that are manifest through light interacting with chiral matter, usually in a solution or other isotropic phase, represent the archetypal system for exhibiting such discriminatory behavior. However, a sensitivity to the handedness of circular polarization can also be manifest in achiral media if the centers of optical response – usually molecules – have a uniform degree of orientational correlation and an appropriate disposition with respect to the throughput radiation.[53] In passing we observe that the SOI associated with LG beams coupling to E2 moments also permits a dichroic

effect with achiral molecules: as noted earlier, an analysis along similar lines has also highlighted a similar phenomenon with atomic matter.[4] Using the same QED techniques that were used to derive (4), the rate contribution for the single-photon absorption process by achiral molecules is now found to be:[5]

$$\Gamma'^{(\text{L/R})}_{\text{Achiral}}(\ell) = \sigma\ell \frac{I(\omega)}{2c\hbar^2\varepsilon_o} \frac{1}{r} f_{\ell,p}^{\ 2}(r)\, \varepsilon_{ikm}\hat{k}_m Q_{ij}^{f0} Q_{kl}^{f0}\left(\hat{\varphi}_j\hat{r}_l - \hat{\varphi}_l\hat{r}_j\right)\left[\frac{\partial \ln f_{\ell,p}(r)}{\partial r} - \frac{1}{r}\right] \tag{5}$$

Once again we may perform a molecular orientational average on this result. Such a fourth-rank tensor average requires tensor contraction of the radiation-specific factors in the expression on the right-hand side of (5) with the following second-rank isotropic Kronecker delta combinations: $\delta_{ij}\delta_{kl}$, $\delta_{ik}\delta_{jl}$ and $\delta_{il}\delta_{kj}$. It is then relatively straightforward to recognize how the involvement of components from different beam-specific unit vectors, in this case $\hat{\varphi}$ and $\hat{r}$, leads to the fourth-rank tensor average becoming zero, just as in the chiral case examined above. In both cases, integration across the beam cross-section leads to a null result.

5. CONCLUSION

This analysis has highlighted how a form of SOI that occurs between paraxially propagating vortex beams and matter allows local chiroptical effects to occur that are dependent on the sign of the topological charge, and hence the sign of the OAM. In single-photon absorption events, whether they involve chiral or achiral molecules, the effect only manifests itself through the engagement of electric quadrupole transitions moments. This is due to the fact that in such E2 transitions, both SAM and OAM are transferred to the electronic internal degrees of freedom of the molecule, rather than the latter being conveyed to the centre of mass motion as happens in dipole transitions. As such, the intrinsic nature of the OAM of paraxial beams can in fact be registered on a local scale. The SOI that provide a basis for these chiroptical effects in molecules are therefore distinctively different from those occurring in non-paraxial beams of light that have been focussed or scattered, or those occurring in plasmonic-enhanced vortex light-matter interactions. Both the SAM and OAM of light must participate in transitions that are simultaneously electric-dipole and electric quadrupole-allowed, in order to observe these local chiroptical effects in chiral molecules. Alongside this requirement is the rule that the molecular systems must be anisotropically distributed, with a degree of orientational order. In any regular fluid, molecular rotational averaging leads to the effects disappearing, so that manifestations of these effects necessitate samples with partial ordering – such as liquid crystals – or a larger meta-structure such as may arise in membranes, for example.

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