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Chapter 8

TWISTED LASER BEAMS AND THEIR OPTICAL INTERACTIONS WITH CHIRAL MATTER

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Abstract

Recently, optical beams with a new and distinctive type of helicity have become the subject of considerable interest. While circularly polarised light is associated with electromagnetic fields whose locus takes a helical form, for these optically engineered phase-bearing or ‘twisted’ laser beams it is the wave-front surface that is helical. Consequently, a new and intriguing manifestation of optical handedness is available for characterising optical interactions with matter. Many of the interactions that have been studied with such beams utilise or exhibit their intrinsic ‘orbital’ angular momentum. To date, however, such studies have mostly focused on interactions with achiral (generally mirror-symmetric) matter. It is timely to assess what new features, if any, can be expected when such beams are used to interrogate a chiral (molecularly right- or left-handed) system. In this review we introduce and analyse the concepts that determine whether optically twisted beams should offer a controllable specificity in their interactions with chiral matter, associated with orbital angular momentum transfer. By explicit analysis of the grounds for chiroptical behaviour, and with a specific focus on circular dichroism, we establish the principle that the helicity of optical vortices cannot directly engage through any parametric or non-parametric optical process with the chirality of a molecular system, up to the level of electric quadrupole interactions. These conclusions have been corroborated by recent experimental results.

1 Introduction

Of the many notable advances marked by its designation as World Year of Physics, 2005 is the hundredth anniversary of the photon concept. As the quantum of electromagnetic

radiation – the gauge boson for electromagnetic coupling – the photon has properties that are generally well known and which can be found listed in any table of elementary particles. Amongst these properties it is usual to include the unit spin angular momentum – whose manifestation in circular polarisations is also very well known and corresponds to projections $\pm\hbar$, according to the circular sense, along the direction of propagation. [1] Circularly polarised light is intrinsically handed, its left- or right-handed helicity associated with the locus of the electromagnetic field vectors. Less well known is the fact that such features are usually interpreted with implicit reference to a well-collimated non-divergent beam with a planar wavefront, reflecting common experimental practice. When other kinds of light beam are engineered, novel features can emerge that have no counterpart in conventional optics. Just over ten years ago, [2] recognition first emerged that light beams with a helical wavefront could display other kinds of angular momentum, now generally called *orbital*. Specifically, if such a *twisted beam* has an integer number l twists within its wavelength, an orbital angular momentum of $l\hbar$ is associated with each photon – quite distinct from any spin angular momentum determined by the polarisation. Such beams are now readily producible in the laboratory. [3-5] This new field is rife with synonyms: the radiation itself is often described as comprising *optical vortices*, and the associated technology has also been termed an *optical spanner* (though this term has also been applied to beams whose wave-front is mechanically rotated). Amongst the many issues that arise in the construction, application and representation of twisted beams is the question of how their handedness may or may not engage with chiral matter. [6]

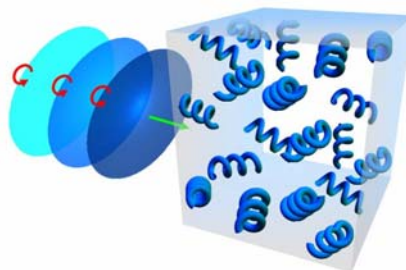
Molecular chirality signifies a structural handedness that changes under spatial inversion or a combination of inversion and rotation, equivalent to the usually stated criterion of a lack of any improper axes of rotation. The optical manifestations of such chirality known as *optical activity* are well attested, [7] ranging from the optical rotation widely used to characterise the enantiomeric (left- and right-handed optical isomeric) forms of sugars, to the circular differential Raman scattering that has emerged as a means of exhibiting the chirality of protein folding. [8] Traditionally, chiral optics engages circularly polarised light – even in the case of optical rotation, the phenomenon is commonly interpreted through a description of the plane polarised state as a superposition of circular polarisations with opposite handedness. It is for this reason that the interactions of circularly polarised light with matter are enantiomerically specific. Whereas twisted beams have until now been studied primarily in their interactions with achiral matter, extensive interest has arisen in the intriguing possibilities represented by their interactions with chiral systems, such as some recent work with liquid crystals. [9] Interested parties range from those researching in the theory of optical angular momentum to others interested in possible applications to molecular motors, nano-manipulation and biotechnology. It is in this broad context that we assess what new features, if any, can be expected if such beams are used to interrogate a system whose optical response is associated with enantiomerically specific molecules.

In the following, we introduce salient quantum electrodynamical principles for subsequent discussion of issues relating to the interplay of quantised spin and orbital angular momentum – the latter with particular reference to twisted beams. The theoretical basis for our discussion is molecular quantum electrodynamics – the only theory in which the photon concept has full legitimacy. [10,11] To avoid unnecessary distraction by lengthy detail, the arguments are pursued with only the most salient equations explicitly presented. Section 2 introduces the principles of molecular chirality at a fundamental level appropriate for

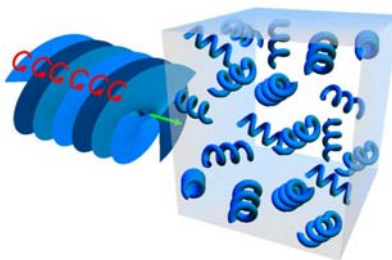
subsequent discussion, in section 3, of issues relating to the interplay of quantised spin and orbital angular momentum – the latter with particular reference to twisted beams. The key results are summarised in section 4.

2 Foundation Principles

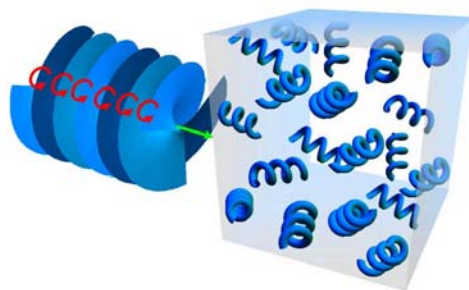
Considerable intricacies of symmetry can arise when a twisted laser beam interacts with chiral matter. Specifically, it is necessary to construct a theory that can accommodate as independent quantities the handedness of the molecules, the circularity of the optical polarisation, and the sense of twist in the laser beam – see Figure 1. In anticipation of the complexity that ensues, we shall therefore first determine a theoretical framework amenable to the issues of interest, to exact in generalised form the criteria for manifestations of chiroptical interactions. From this framework, in which conventional chirality can be understood in terms of molecular symmetry and multipole properties, we can extend the arguments to address light with a twisted wavefront. For simplicity, materials with a unique enantiomeric specificity are assumed – signifying a chirality that is intrinsic and common to all molecular components (or chromophores) involved in the optical response. Results for systems of this kind will also apply to single-molecule studies. Longer-range translation/rotation order can also produce chirality, as in twisted nematic crystals, but such mesoscopic chirality cannot directly engender enantiomerically specific interactions except under particular conditions. The only exception is where optical waves probe two or more electronically distinct, dissymmetrically oriented but intrinsically achiral molecules or chromophores. Then chirality can be manifest as in the two-group model (see below). Here we are concerned with intrinsically chiral centres rather than chiral arrays.



(a)



(b)



(c)

Fig. 1. Interaction of left circularly polarised radiation (represented by red arrows) with left-hand (randomly oriented) chiral molecules: a) plane waves; b) left-handed Laguerre-Gaussian beam, $l = 3$ and c) right-handed Laguerre-Gaussian beam $l = -3$. In all three cases the radiation is represented by surfaces of constant phase.

Chiroptical interactions can be distinguished by their electromagnetic origins. For molecular systems in their usual singlet electronic ground state (where we exclude free electron spin effects), chiroptical interactions are linked at a fundamental level with the spatial variation of the electric and magnetic fields associated with the input of optical radiation. This variation over space can be understood to engage chirality either through its coupling with dissymmetrically placed, neighbouring chromophore groups (Kirkwood's two-group coupled-dipole model, [12] now of limited application) or more generally through the coupling of its associated electric and magnetic fields with individual groups. As chirality signifies a local breaking of parity selection rules, *i.e.* parity is no longer a good quantum number, it thereby permits the interference of electric and magnetic interactions – or, for example, the interference of multipolar electric interactions having different parity. Even in the two-group case, the paired electric dipole interactions of the system equate to electric and magnetic interactions of the single entity which the two groups comprise. Thus, for convenience, the term 'chiral centre' is used in the following to denote either chromophore or molecule. To understand how this works, it will be necessary to unveil the structure of the quantum amplitude, specified as the amplitude for the optical interaction of a single intrinsically chiral species.

2.1 Hamiltonian and Field Expansions

In order to properly represent the quantum features of the radiation we shall develop the theory using the framework of quantum electrodynamics. The Hamiltonian for any chiroptical interaction comprises the unperturbed operators for the radiation and for N chiral centres, here differentiated by a label ξ , and also a light-matter interaction Hamiltonian;

$$H = H_{\text{rad}} + \sum_{\xi}^N H_{\text{centre}}(\xi) + \sum_{\xi}^N H_{\text{int}}(\xi) . \quad (1)$$

As an energy operator, each component of the Hamiltonian is necessarily of even parity with respect to space inversion and also even with respect to time reversal. The first two terms of (1) determine the basis in which the different states of the system can be described, *i.e.* a direct product of eigenstates of the radiation and the matter. The interaction term can be expressed either in minimal coupling form (cast in terms of coupling with the vector potential of the radiation field) or the more familiar multipolar formulation, directly expressed in terms of electric and magnetic fields. [13] These two (and also other less well-known) options lead to identical results for real processes, that is those subject to overall energy conservation; [14, 15] for convenience in the following we develop theory using the multipolar form.

The multipolar interaction Hamiltonian divides into three parts: one is a linear coupling of the molecular polarisation field (accommodating all electric multipoles E_n) with the transverse electric field $\mathbf{e}(\mathbf{r})$ of the radiation; another entails linear coupling of the molecular magnetisation field (all magnetic multipoles M_n) with the magnetic field $\mathbf{b}(\mathbf{r})$ of the radiation. The third is a coupling of the molecular diamagnetisation field, quadratically with the magnetic radiation field:

$$H_{\text{int}} = -\int \mathbf{p}(\mathbf{r}) \cdot \mathbf{e}^\perp(\mathbf{r}) d^3\mathbf{r} - \int \mathbf{m}(\mathbf{r}) \cdot \mathbf{b}(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int O_{ij}(\mathbf{r}, \mathbf{r}') b_i(\mathbf{r}) b_j(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}'. \quad (2)$$

In the Schrödinger representation the time-dependence of these operators is suppressed. The first term in equation (2) depends on the molecular polarisation field $\mathbf{p}(\mathbf{r})$ while the second depends on the magnetisation field $\mathbf{m}(\mathbf{r})$; the last term, which involves the diamagnetisation field $O_{ij}(\mathbf{r}, \mathbf{r}')$, is associated with the variation of current density when the fields are switched on. The latter term is typically an order of magnitude smaller than the first two (by a factor of the order α^2 , with α the fine structure constant) and for present purposes it need concern us no further – indeed there appears to be no suggestion of its engagement in any form of molecular chirality.

The interaction Hamiltonian is considered a perturbation of the system, allowing transition from one eigenstate of the unperturbed Hamiltonian, $H_{\text{rad}} + H_{\text{centres}}$, to another. By expanding the parent polarisation and magnetisation fields as Taylor series about the molecular positions, the terms comprising equation (2) can be expanded in multipolar orders – principal amongst which (retaining terms up to the order of α) are the electric-dipole $\boldsymbol{\mu}(\boldsymbol{\xi})$, electric-quadrupole $q_{ij}(\boldsymbol{\xi})$ and the magnetic-dipole $\mathbf{m}(\boldsymbol{\xi})$. The leading terms of (2) are thus cast as follows;

$$H_{\text{int}} = -\sum_{\boldsymbol{\xi}} \boldsymbol{\mu}(\boldsymbol{\xi}) \cdot \mathbf{e}^\perp(\mathbf{R}_{\boldsymbol{\xi}}) + \sum_{\boldsymbol{\xi}} q_{ij}(\boldsymbol{\xi}) \nabla_i e_j^\perp(\mathbf{R}_{\boldsymbol{\xi}}) + \dots - \sum_{\boldsymbol{\xi}} \mathbf{m}(\boldsymbol{\xi}) \cdot \mathbf{b}(\mathbf{R}_{\boldsymbol{\xi}}) + \dots \quad (3)$$

The parity under time and space symmetry of the electric dipole, electric quadrupole and magnetic dipole are given in Table 1.

Table 1: Space and time parity of electromagnetic quantities

Operator	Time parity	Space parity
Hamiltonian	+1	+1
Electric field	+1	-1
Electric field of LG mode (k, λ, l, p)	+1	$(-1)^{l+1}$
Electric dipole	+1	-1
Magnetic field	-1	+1
Magnetic field of LG mode (k, λ, l, p)	-1	$(-1)^l$
Magnetic dipole	-1	+1
Wave-vector	-1	-1

The electric and magnetic fields that feature in (3) are solutions of Maxwell's equations within the QED framework. In free space, and within the Coulomb gauge, the simplest solutions are given by the plane waves;

$$\mathbf{e}(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} \left\{ i \left(\frac{\hbar c k}{2\epsilon_0 V} \right)^{\frac{1}{2}} \boldsymbol{\epsilon}^{(\lambda)}(\mathbf{k}) a^{(\lambda)}(\mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{r}] + h.c. \right\} \quad (4a)$$

$$\mathbf{b}(\mathbf{r}) = \sum_{\mathbf{k}, \lambda} \left\{ i \left(\frac{\hbar k}{2\epsilon_0 c V} \right)^{\frac{1}{2}} (\hat{\mathbf{k}} \times \boldsymbol{\epsilon}^{(\lambda)}(\mathbf{k})) a^{(\lambda)}(\mathbf{k}) \exp[i\mathbf{k} \cdot \mathbf{r}] + h.c. \right\} \quad (4b)$$

Here V is the quantisation volume, \mathbf{k} is the wave-vector and λ is a polarisation label; the latter two quantities together represent four independent degrees of freedom. In the classical interpretation, the terms represented explicitly in equation (4) signify the positive frequency analytic signals [16]; corresponding negative frequency components are conveyed by the hermitian conjugate terms (in which the phase factor has the opposite sign).

For optically engineered radiation with orbital angular momentum, the electromagnetic fields are commonly cast in terms of Laguerre-Gaussian (LG) modes. From an analytical point of view, these modes constitute another complete set, also arising as paraxial solutions of the source-free Maxwell equations. For example the LG_0^1 mode is a phase quadrature superposition of HG_{10} and HG_{01} Hermite-Gaussian modes. [2] Explicitly, the electric and magnetic field expansions for a beam propagating in the z direction emerge in the following form as functions of cylindrical coordinates (r, z, ϕ) ;

$$\mathbf{e}^\perp(\mathbf{r}) = \sum_{\mathbf{k}, \lambda, l, p} \left\{ i \left(\frac{\hbar c k}{2\epsilon_0 A_p V} \right)^{\frac{1}{2}} \boldsymbol{\epsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) f_{lp}(r) a_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) \exp[i(kz - l\phi)] + h.c. \right\}, \quad (5a)$$

$$\mathbf{b}(\mathbf{r}) = \sum_{\mathbf{k}, \lambda, l, p} \left\{ i \left(\frac{\hbar k}{2\epsilon_0 c A_p V} \right)^{\frac{1}{2}} (\hat{\mathbf{k}} \times \boldsymbol{\epsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}})) f_{lp}(r) a_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) \exp[i(kz - l\phi)] + h.c. \right\}, \quad (5b)$$

where $a_{lp}^{(\lambda)}$ is the photon annihilation operator and $\boldsymbol{\epsilon}_{lp}^{(\lambda)}$ is the wave polarisation vector, which can describe linear, circular or any other basis polarisation. The four degrees of freedom manifest in the summation variables are the magnitude of the wave-vector (its direction assigned to a specified direction z), the polarisation λ and two other labels, l and p , that designate the order of the associated Laguerre polynomial [3,17] – see Appendix 1. Also, l denotes the orbital angular momentum quantum number, for which a positive sign denotes left helicity and a negative sign, right. Here we note that the radial functions $f_{lp}(r)$ are independent on the sign of l ; consequently all information of the handedness of the optical vortex is in the phase factor $\exp[-il\phi]$, a characteristic that is crucial when analysing the interactions of such beams with chiral centres.

Returning to the expression given by equation (3), the electric dipoles $\boldsymbol{\mu}(\mathbf{r})$ (E1) have an odd signature for space parity and even for time; electric quadrupoles \mathbf{q} (E2) are even in both space and time, while the magnetic dipoles $\mathbf{m}(\mathbf{r})$ (M1) are even in space and odd in time. Similarly, independent of which mode expansion is used, the electric field $\mathbf{e}(\mathbf{r})$ of the overall radiation field is space-odd and time-even; conversely the magnetic field $\mathbf{b}(\mathbf{r})$ is of even parity under space inversion and of odd parity under time inversion – the latter temporal features readily apparent in the interaction picture representation.[11] Note, however, that the symmetry assertions for the electric and magnetic fields of the radiation are true *only* for the whole; they do *not* necessarily apply when only one or a finite number of modes is considered (independent of the mode expansion used). These and other fundamental symmetry properties are summarised in Table 1. Cognisance of these features proves extremely significant in developing and identifying non-zero terms in the quantum amplitude for optical processes.

The polarisations of the photon can be described by the vectors $\boldsymbol{\epsilon}^{(\lambda)}(\mathbf{k})$. For circular polarisations the explicit expressions are;

$$\boldsymbol{\epsilon}^{(\pm)}(\mathbf{k}) = \frac{1}{\sqrt{2}} (\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) \quad (6)$$

where the positive (negative) superscript denotes left-(right-) circular polarisation. It can be seen that $\boldsymbol{\epsilon}^{(\pm)}(\mathbf{k}) = \bar{\boldsymbol{\epsilon}}^{(\mp)}(\mathbf{k})$ and $\boldsymbol{\epsilon}^{(\pm)}(-\mathbf{k}) = -\bar{\boldsymbol{\epsilon}}^{(\mp)}(\mathbf{k})$. With the wave-vector \mathbf{k} , $\boldsymbol{\epsilon}^{(+)}(\mathbf{k})$ and $\boldsymbol{\epsilon}^{(-)}(\mathbf{k})$ form a right triad.

2.2 Perturbation Theory and Quantum Amplitudes

The probability of a given chiroptical process is determined by its quantum amplitude. For one molecule ξ we have;

$$M_{fi}^{\xi} \equiv \langle f | U(t, t_0) | i \rangle = \langle f | \left\{ 1 + \sum_{n=1}^{\infty} \left(\frac{1}{i\hbar} \right)^n \int_{t_0}^{t_1} dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_n} dt_n V_I(t_1) V_I(t_2) \dots V_I(t_n) \right\} | i \rangle \quad (7)$$

where the operator $V_I(t)$ is the interaction Hamiltonian H_{int} in the interaction picture. Depending on the number of photons involved in the process the relevant term of the expansion is considered – for example for second harmonic generation, SHG, where two photons are annihilated and one created in each fundamental interaction, the term $n = 3$ is the one that gives the first contribution. Generally, for an n -photon process we have;

$$M_{fi}^{\xi(n)} \equiv \langle f | U(t, t_0) | i \rangle = \langle f | H_{\text{int}} \left(\frac{1}{(H_0 - E_i)} H_{\text{int}} \right)^{n-1} | i \rangle \quad (8)$$

The quantum amplitude M_{fi} for a specific optical interaction in a single chiral centre is constructed from time-dependent perturbation theory and entails a linear combination of scalar terms, each of which is the inner product of two rank r tensors: $\mathbf{S}^{(r)}$, a radiation tensor, and $\mathbf{T}^{(r)}$, a molecular tensor, both detailed below; [18]

$$M_{fi}^{\xi} = \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_{\xi}) \sum_{e,m=0}^n \mathbf{S}_{e;m;n-e-m}^{(r)} \otimes \mathbf{T}_{e;m;n-e-m}^{(r)} \quad (9)$$

Here, $\Delta\mathbf{k}$ is the mismatch between the wave-vector sum of all input and the sum of all output photons (if any) involved in the process at a chiral centre ξ located at \mathbf{R}_{ξ} . To identify the radiation and molecular tensors, $\mathbf{S}^{(r)} \equiv S_{i_1 i_2 \dots i_r}$ and $\mathbf{T}^{(r)} = T_{i_1 i_2 \dots i_r}$ respectively, three labels are used: $(e; m; q)$, corresponding to the number of electric-dipole, magnetic-dipole and electric quadrupole interactions, respectively. The sum of these equals the number of photon interactions involved in the process, $e + m + q = n$.

The rank (r) of the tensors $\mathbf{S}^{(r)}$ and $\mathbf{T}^{(r)}$ is determined by the labels $(e; m; q)$ through the simple relation $r = e + m + 2q$, which signifies that the rank is between n and $2n$. For plane wave photons, the structure of the radiation tensor $\mathbf{S}^{(r)}$ is that of an outer product of the beam polarisation vectors $\boldsymbol{\epsilon}^{(\lambda)}(\mathbf{k})$, taking the complex conjugate for emitted photons – and also wave-vector components, in the case where quadrupole (or higher) multipoles are involved. This tensor also carries factors relating to other beam parameters – which, in the signal derived from $|M_{fi}^{\xi(n)}|^2$ (see below) will manifest the dependence on beam intensities and degrees of coherence. If the LG mode expansion is considered, the radiation tensor $\mathbf{S}^{(r)}$ will also include the complex profile structure of the radiation, given by $f_{lp}(r)$ and its derivatives (see also Appendix 1). The molecular tensor $\mathbf{T}^{(r)}$ can be written in a form that entails a product of one or more molecular transition integrals, as determined by the number of photons involved. In every case the origin of such forms is a single transition integral,

expressible as a Dirac bracket with the appropriate number of electromagnetic interactions coupling the initial state to the final state. The simple case of single-photon absorption serves to illustrate the point. Here one interaction couples the two molecular states, and that interaction embodies the entire family of multipolar contributions. In order for the transition integral not to vanish identically, the triple product of the group theoretic representations for the initial and final state wavefunctions with that of the interaction must contain the totally symmetric representation. It is here that the implications of molecular chirality emerge.

Before considering chiral systems in more detail, it is instructive to reflect on the case of a centrosymmetric molecular system, where parity is a good quantum number and all wavefunctions have definite parity. Here, the only non-zero contributions to the transition integral can be those whose parity equates to the product signature of the initial and final state molecular wavefunctions. For example if electric dipole coupling is to give a non-vanishing contribution (i.e. that coupling is *allowed*) then, for that same transition, electric quadrupole and magnetic dipole contributions would indeed vanish (they would be forbidden) by virtue of their opposite spatial parity. Thus, for centrosymmetric species, all multipolar contributions to any given quantum amplitude will have the same spatial parity. Clearly for chiral systems, where parity is not a good quantum number, no such rule applies and the amplitude may entail contributions of both positive and negative parity signature.

2.3 System Response

Not only molecular symmetry determines the nature and extent of any chiroptical response; macroscopic symmetry is important too. In particular, when the system of interest is a fluid or other microscopically disordered medium, the isotropic symmetry of the bulk comes into play. In general, experimental measurements result from the optical interactions of more than one chiral centre, and the observable results from a quantum amplitude comprising an ensemble sum of contributions from all relevant centres. In calculating the observable associated with a particular optical interaction it is usual to apply the Fermi Rule;

$$\Gamma = \frac{d}{dt} P_{TOTAL} = \frac{2\pi}{\hbar} |M_{fi}|^2 \rho_f . \quad (10)$$

Here the transition matrix represents all the system, *i.e.* all the molecules present in the sample and therefore we have:

$$M_{fi} = \sum_{\xi=1}^N M_{fi}^{\xi} \quad (11)$$

and hence,

$$\Gamma \propto |M_{fi}|^2 = \sum_{\xi, \xi'} M_{fi}^{\xi} \bar{M}_{fi}^{\xi'} \quad (12)$$

a result that emerges from the modulus square of the quantum amplitude. For chiral species this therefore includes, in addition to diagonal terms that are all of even parity in both radiation and molecular parameters, various terms associated with the quantum interference of couplings with opposite parity, correspondingly of odd parity for both the radiation and molecule.

As is apparent from the $\exp(i\Delta\mathbf{k}\cdot\mathbf{R}_\xi)$ factor in (9), each quantum amplitude contribution generally has a different phase associated with spatial variance in the registration of light at the corresponding chiral centre. Most optical processes are incoherent and *non-parametric* (*i.e.* $\Delta\mathbf{k} \neq 0$), such that the interference of quantum amplitudes from different centres gives a null contribution when those centres are isotropically distributed – a principle that holds generally true except in certain nanomaterials.¹[19,20,21] For such processes, no role is played by any orientational order characterising *long-range* chirality. In the following we focus specifically on chiroptical observables associated with non-parametric processes in which the ensemble signal, by virtue of the ergodic theorem, represents the time-averaged response of a single chiral centre. The two reasons for studying such optical processes are; (i) it is processes of this category that are involved in the most common manifestations of chirality (circular dichroism, differential Rayleigh and Raman scattering, circularly polarised luminescence etc.); (ii) where optical vortices are concerned, it is known that parametric processes generally entail conservation of orbital angular momentum by the radiation field, such that chirality is not engaged. [17]

For a non-parametric interaction the transition rate of a single chiral centre is a sum of amplitude contribution products, featuring amongst which are quantum interferences of a particular class, *i.e.* products that are odd in parity for both the matter and radiation – terms that can only arise in the case of chiral systems. Handedness is apparent in two respects. If the space inversion operator (signifying a change to the opposite enantiomeric form) is applied to all properties of the molecule – and in particular its multipole moments – but not the radiation (signifying retention of its circularity), then these interference terms change sign. The same is true if the radiation changes handedness, (on space inversion) but the molecule retains its enantiomeric form; then again, these specific interference terms change sign. Clearly all contributions to the signal are invariant to inversion of the whole system. This is indeed the reason why chiral interactions must involve handed radiation, usually circular (elliptical polarisations are also permissible). Plane polarisations are invariant under space inversion; consequently, applying space inversion to a molecular system interacting with plane polarised light has the same effect as applying it to both the molecule and the radiation; clearly no chiral specificity can emerge. Optical rotation, as noted earlier, is an exception since it is a parametric process.

For the interference terms that support chiral selectivity; it remains to discover any further conditions that need to be satisfied to ensure that they are not identically zero. To this end we focus on the issue of rotational averaging. For any component of a non-parametric signal – and in particular the odd-parity quantum interference terms – rotational averaging effects a disentanglement of the radiation and molecular fields, $\mathbf{S}^{(n)}$ and $\mathbf{T}^{(n)}$ respectively. When rotational averaging is implemented the result is a product of scalars (or, for tensors of

¹ Amplitudes of different centres effectively add within a range $(\Delta\mathbf{k})^{-1}$, eliciting coherent response in mesoscopically disordered systems comprising structured nanoparticles.

rank four or more, a linear combination of such scalars), one scalar for the radiation and one for the molecule (see Appendix 2). Each scalar is derived by contracting the tensor, $\mathbf{S}^{(n)}$ or $\mathbf{T}^{(n)}$, with an isotropic tensor of the same rank – in the language of spherical tensors this signifies the angular momentum $J = 0$ contribution. For example in the E1-M1 interference term for photon absorption by a chiral molecule the molecular tensor $\mathbf{T}^{(2)} = [\boldsymbol{\mu}][\bar{\mathbf{m}}]$, on contraction with the isotropic tensor of rank 2 (the Kronecker delta), yields the scalar $T = (\boldsymbol{\mu} \cdot \bar{\mathbf{m}})$ – signifying that the electric and magnetic transition moments must not be orthogonal (in transitions between non-degenerate states, $\bar{\mathbf{m}}$ will be antiparallel to \mathbf{m}). Equally $\mathbf{S}^{(2)} = [\mathbf{e}][\bar{\mathbf{b}}]$ yields the scalar $S = (\mathbf{e} \cdot \bar{\mathbf{b}})$; this determines that chiral resolution vanishes when plane polarised light is employed, for then the field polarisations are real and the orthogonality of the electric and magnetic vectors gives $(\mathbf{e} \cdot \bar{\mathbf{b}}) = 0$. But for any circular (or even for elliptical) polarisation, \mathbf{S} is non-zero and, since it also changes sign on reversal of circularity;

$$S = (\mathbf{e} \cdot \bar{\mathbf{b}}) \xrightarrow{\mathcal{J}} ((-\mathbf{e}) \cdot \bar{\mathbf{b}}) = -S \quad (13)$$

chiral specificity is manifest. Since T takes opposite signs for chiral molecules of opposite enantiomeric form,

$$T = (\boldsymbol{\mu} \cdot \bar{\mathbf{m}}) \xrightarrow{\mathcal{J}} ((-\boldsymbol{\mu}) \cdot \bar{\mathbf{m}}) = -T \quad (14)$$

the rate of absorption of left-handed circularly polarised radiation, for example, is different for left- and right-handed enantiomers – though only marginally, because of the relative weakness of the salient interference terms compared to the dominant (usually electric dipole) diagonal contributions to the signal. Equally, each enantiomer exhibits a slightly different rate of absorption for left and for right-handed circular input. This is the origin of circular dichroism. Similar remarks apply to optically more intricate processes involving more than one photon, where the quantum amplitude itself comprises products of multipolar couplings, each associated with a definite resultant spatial parity, and the key interference terms arise from products of these products with opposite inversion symmetry. Again, for a chirally specific signal to emerge, it is necessary that the resultant radiation and molecular scalars do not vanish identically.

3 The Interactions of Twisted Beams

Having elicited the key principles, we can now address the central issue of how, if at all, a twisted laser beam can engage in a chirally differentiable way with matter. Most of the tools for addressing this issue have been introduced in the last section. The helicity of optical vortices is present in their wave-front structure. As we have seen, the chirality of the electric and magnetic fields is manifest through additional phase factors in the positive and negative frequency components. In particular, from equation (5a) the (un-normalised) positive frequency analytic signal for the electric field of a Laguerre-Gaussian (LG) mode propagating in the z -direction with a wave-vector of magnitude k , is expressible as;

$$\mathbf{e}^\perp(\mathbf{r}) = i\boldsymbol{\varepsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) f_{lp}(r) a_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) \exp[i(kz - l\phi)] \quad (15)$$

where $\hat{\mathbf{e}}$ is the polarisation operator. Of the two space-dependent terms in the field phase, the first is the origin of the wave-vector mismatch factor in (9) – here delivered as $z_\xi \Delta \mathbf{k}$ – and the second is an azimuthal phase factor, a characteristic of twisted beams. The first component of the phase in (15) changes sign on space inversion (and equally, on complex conjugation) just as the circular polarisation vectors behave. The second phase factor changes by addition of π on space inversion. The magnetic field for a twisted beam has an exactly similar form. [20]

No difference should be expected between the behaviour of right and left forms of any twisted mode if the photons it comprises are plane polarised and the material they interact with is achiral, in accordance with the dictates of parity. This is equivalent to the case of circularly polarised, planar wave-front (*e.g.* Gaussian) modes, interacting with achiral material. However, there are several differences between LG photons and those associated with planar wave-fronts. In the present context a significant difference is that plane waves have no restriction in the direction of propagation, while the symmetry of LG photons designates propagation in one direction, $\hat{\mathbf{z}}$. This characteristic indicates that mirror inversion along a plane containing the $\hat{\mathbf{z}}$ axis becomes the relevant symmetry element, as opposed to space inversion. Arguing symmetry on these grounds is sufficient to establish that there is no differentiation between LG beams of opposite handedness when achiral material is interrogated, since a left-handed optical vortex transforms to a right-handed one.

Now we come to the crux, the interaction of a twisted beam with chiral matter. Consider first the case of a twisted beam comprising plane polarised photons; superficially this appears exactly analogous to the case of circular polarisations in a plane wave. Mirror inversion of either part of the system (molecule or radiation) gives a system different from the original, and so a change in signal signifying chiral specificity might be anticipated. Representing in brackets the circularity of the radiation and the matter respectively, both cases require identity of (L, L) and (R, R) , and so too (L, R) and (R, L) . However (L, L) and (L, R) differ. More succinctly, denoting either handedness L/R by a circularity c and the reverse by \bar{c} , we have $(c, c) = (\bar{c}, \bar{c})$ – which may or may not be equal to (c, \bar{c}) .

For the twisted beam case it is therefore necessary to ascertain whether there is a mechanism, by means of which signals that are *permissibly* different in these terms may *in fact* differ. In the previous section it was seen that in a fluid, the observable is obtained as the ensemble sum of contributions from all relevant centres. As in the case of plane waves, the factor $\exp(iz_\xi \Delta k)$ continues to play an important role and represents any net (longitudinal) optical phase shift associated with a process mediated by a chiral centre ξ located at $\mathbf{r}_\xi = (r, \phi, z)$. However, another (azimuthal) phase factor of similar form, $\exp(-i\Delta l\phi)$, now appears alongside it² and also enters M_{ji}^ξ through the radiation tensor $\mathbf{S}^{(n)}$. Here $\Delta l \hbar$ represents any mismatch between the orbital angular momentum sum of all input and the sum of all output photons involved in the process at the chiral centre. First, if the optical process is parametric, then $\Delta l = 0$ and all dependence on the sign of the orbital angular momentum of the radiation is lost. The transition rate, proportional to the modulus square of the rotationally

² In separate work we have verified that this form for the azimuthal phase factor is unchanged when higher order multipole couplings are entertained.

averaged quantum amplitude, $\left| \langle M_{fi} \rangle \right|^2$, has no dependence on the sign of the orbital angular momentum l and therefore is not a chiral discriminator. If, on the other hand, we consider a *non-parametric* process where $\Delta l \neq 0$, the incoherent character means that the rate is proportional to the rotational average of the modulus square of the quantum amplitude, $\langle |M_{fi}|^2 \rangle$, in which the azimuthal phase factor cancels each and every centre ξ ; again the observable transition rate does not involve the orbital angular momentum or its sign. Hence the circularity of the beam is immaterial.

In the case of chiral molecules interacting with *twisted* light comprising *circular* photons, and in view of the observations made above, the problem reduces to exactly that which applies to other beams of circular polarisation – but now there is a mechanism for the associated signals actually to differ. Again the helicity of the wave-front is immaterial so far as chiral specificity is concerned. Consider for example Figure 1(b), in which a left-handed twisted beam comprising left-handed circular photons interacts with a system of left-handed molecular enantiomers. Let us entertain the simplest optical process in which chirality can be manifest, namely circular dichroism. Then, the quantum interference terms responsible for chiral discrimination change sign if either the circularity of the photons or the isomeric form of the molecules is changed; the interference terms are invariant to a change of both. No component of the rate changes if, for example, the beam becomes a right-handed vortex but the sense of the photons and molecular handedness is the same as before. Note that this conclusion is contingent upon the azimuthal phase factors for the electric and magnetic fields being identical; however this is a necessary consequence of Maxwell's equations, as has been shown explicitly for quantised Laguerre-Gaussian modes. [17] This lack of exchange of orbital angular momentum between the optical vortex and the chiral matter has been experimentally demonstrated by the research group at The Laboratory of Chemical and Biological Dynamics at Leuven, Belgium. [22]

3.1 Explicit Calculation for Circular Dichroism

To ground the above analysis with a specific application, let us consider the simplest case, *i.e.* photon absorption, where any enantiomeric rate dependence would signify a type of dichroism. In this case the initial and final state of the system is given by;

$$|i\rangle = |A; n(k\hat{z}, \lambda, l, p)\rangle \quad (16a)$$

$$|f\rangle = |B; (n-1)(k\hat{z}, \lambda, l, p)\rangle \quad (16b)$$

The three leading contributions to the transition matrix are in this case expressible as;

$$\begin{aligned} M_{fi} &= \langle f | -\mu_i e_i^\perp - m_i b_i + q_{ij} \nabla_j e_i^\perp | i \rangle \\ &= \underbrace{\langle f | (-\mu_i e_i^\perp) | i \rangle}_{M_{fi}^\mu} + \underbrace{\langle f | (-m_i b_i) | i \rangle}_{M_{fi}^m} + \underbrace{\langle f | (q_{ij} \nabla_j e_i^\perp) | i \rangle}_{M_{fi}^q}, \end{aligned} \quad (17)$$

whose evaluation invokes the result;

$$\nabla_j e_i^\perp(\mathbf{r}) = \sum_{k,\lambda,l,p} \left\{ i \left(\frac{\hbar ck}{2A_{lp} \varepsilon_0 V} \right)^{\frac{1}{2}} e_i^{(\lambda)}(k\hat{\mathbf{z}}) f_{lp}(r) a_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) [\mathbf{G}_{lp}(r, \phi)]_j \exp[i(kz - l\phi)] + h.c. \right\} \quad (18)$$

with

$$\mathbf{G}_{lp}(r, \phi) = \left[\frac{\partial_r f_{lp}}{f_{lp}} \cos \phi + \frac{l}{r} \sin \phi \right] \hat{\mathbf{x}} + \left[\frac{\partial_r f_{lp}}{f_{lp}} \sin \phi - \frac{l}{r} \cos \phi \right] \hat{\mathbf{y}} + [ik] \hat{\mathbf{z}} \quad (19)$$

This is worth considering in detail because it can be seen that, when the quadrupole interaction is involved, not only is the handedness of l present in the azimuthal factor, but it is also present in the profile factor $\mathbf{G}_{lp}(r, \phi)$. Therefore it is at least conceivable that, when electric-quadrupole interactions are taken into account, the selectivity of OAM is similar to that of the photon spin. Using the notation given in equation (9) we have;

$$\begin{aligned} M_{fi}^\xi &= \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_\xi) \sum_{e,m=0}^1 \mathbf{S}_{e;m;1-e-m}^{(r)} \otimes \mathbf{T}_{e;m;1-e-m}^{(r)} \\ &= \exp(i\Delta\mathbf{k} \cdot \mathbf{R}_\xi) \left[\mathbf{S}_{1;0;0}^{(1)} \otimes \mathbf{T}_{1;0;0}^{(1)} + \mathbf{S}_{0;1;0}^{(1)} \otimes \mathbf{T}_{0;1;0}^{(1)} + \mathbf{S}_{0;0;1}^{(1)} \otimes \mathbf{T}_{0;0;1}^{(1)} \right], \end{aligned} \quad (20)$$

which we can succinctly represent as a sum of the three terms $M_{fi}^\mu = \mathbf{S}_{1;0;0}^{(1)} \otimes \mathbf{T}_{1;0;0}^{(1)}$; $M_{fi}^m = \mathbf{S}_{0;1;0}^{(1)} \otimes \mathbf{T}_{0;1;0}^{(1)}$ and $M_{fi}^q = \mathbf{S}_{0;0;1}^{(1)} \otimes \mathbf{T}_{0;0;1}^{(1)}$.

Since single-photon absorption is associated with an inelastic interaction it is non-parametric and the rate observable is proportional to $\langle |M_{fi}|^2 \rangle$. Thus, if the rate is to depend on the sign of l it can only be through the x and y components of the $\mathbf{G}_{lp}(r, \phi)$ tensor. When the term $\langle |M_{fi}|^2 \rangle$ is calculated we obtain;

$$\begin{aligned} \langle \Gamma \rangle^{\text{incoherent}} &= \frac{2\pi}{\hbar} \rho_f N \left\{ \langle M_{fi}^\mu \bar{M}_{fi}^\mu \rangle + \langle M_{fi}^m \bar{M}_{fi}^m \rangle + \langle M_{fi}^q \bar{M}_{fi}^q \rangle \right. \\ &\quad \left. + 2 \text{Re} \left[\langle M_{fi}^\mu \bar{M}_{fi}^m \rangle \right] + 2 \text{Re} \left[\langle M_{fi}^\mu \bar{M}_{fi}^q \rangle \right] + 2 \text{Re} \left[\langle M_{fi}^m \bar{M}_{fi}^q \rangle \right] \right\} \end{aligned} \quad (21)$$

Of the six terms in equation (21) we already know that $\langle M_{fi}^\mu \bar{M}_{fi}^\mu \rangle$, $\langle M_{fi}^m \bar{M}_{fi}^m \rangle$ and $\langle M_{fi}^q \bar{M}_{fi}^q \rangle$ are independent of the handedness of l . The other three terms, those which are connected to the electric-quadrupole interaction, must be analysed individually. We first consider the $\langle M_{fi}^q \bar{M}_{fi}^q \rangle$ case. The explicit expression of this term is;

$$\begin{aligned} \langle M_{fi}^q \bar{M}_{fi}^q \rangle &= - \left(\frac{\hbar ck}{2A_{lp} \varepsilon_0 V} \right) \frac{|f_{lp}|^2}{30} \times \\ &\quad \times e_{i_1}^{(\lambda)}(\mathbf{k}) \bar{e}_{i_3}^{(\lambda)}(\mathbf{k}) [G_{lp}(r, \phi)]_{i_2} [\bar{G}_{lp}(r, \phi)]_{i_4} I_{i_1 i_2 i_3 i_4; \lambda_1 \lambda_2 \lambda_3 \lambda_4}^{(4)} q_{\lambda_1 \lambda_2}^{ba} \bar{q}_{\lambda_3 \lambda_4}^{ba} \end{aligned} \quad (22)$$

where the 4th rank rotational average tensor is; [13]

$$I_{i_1 i_2 i_3 i_4; \lambda_1 \lambda_2 \lambda_3 \lambda_4}^{(4)} = \frac{1}{30} \begin{bmatrix} \delta_{i_1 i_2} & \delta_{i_3 i_4} \\ \delta_{i_1 i_3} & \delta_{i_2 i_4} \\ \delta_{i_1 i_4} & \delta_{i_2 i_3} \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} \delta_{\lambda_1 \lambda_2} & \delta_{\lambda_3 \lambda_4} \\ \delta_{\lambda_1 \lambda_3} & \delta_{\lambda_2 \lambda_4} \\ \delta_{\lambda_1 \lambda_4} & \delta_{\lambda_2 \lambda_3} \end{bmatrix} \quad (23)$$

Therefore $\langle M_{\hat{r}}^q \bar{M}_{\hat{r}}^q \rangle$ takes the form;

$$\langle M_{\hat{r}}^q \bar{M}_{\hat{r}}^q \rangle = - \left(\frac{\hbar c k}{2A_p \epsilon_o V} \right) \frac{|f_{lp}|^2}{30} \times \begin{bmatrix} [\mathbf{e}^{(\lambda)} \cdot \mathbf{G}_{lp}(r, \phi)] [\bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{G}}_{lp}(r, \phi)] \\ [\mathbf{e}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k})] [\mathbf{G}_{lp}(r, \phi) \cdot \bar{\mathbf{G}}_{lp}(r, \phi)] \\ [\mathbf{e}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{G}}_{lp}(r, \phi)] [\bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) \cdot \mathbf{G}_{lp}(r, \phi)] \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} q_{\lambda\lambda}^{ba} \bar{q}_{\nu\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\lambda\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\nu\lambda}^{ba} \end{bmatrix} \quad (24)$$

To proceed further we have to consider the different possible polarisations of the absorbed photon. Let us first consider that the photon is linearly polarised; say $\mathbf{e}^{(\lambda)}(\mathbf{k}) = \hat{y}$. Then;

$$\langle M_{\hat{r}}^q \bar{M}_{\hat{r}}^q \rangle = - \left(\frac{\hbar c k}{2A_p \epsilon_o V} \right) \frac{|f_{lp}|^2}{30} \times \begin{bmatrix} \left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 \sin^2 \phi + \frac{l^2}{r^2} \cos^2 \phi \\ \left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 + \frac{l^2}{r^2} + k^2 \\ \left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 \sin^2 \phi + \frac{l^2}{r^2} \cos^2 \phi \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} q_{\lambda\lambda}^{ba} \bar{q}_{\nu\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\lambda\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\nu\lambda}^{ba} \end{bmatrix} \quad (25)$$

which is independent of the sign of l . If, instead, we consider the photon to be circularly polarised; i.e. $\mathbf{e}^{(\lambda)}(\mathbf{k}) = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{y})$, then;

$$\langle M_{\hat{r}}^q \bar{M}_{\hat{r}}^q \rangle = - \left(\frac{\hbar c k}{2A_p \epsilon_o V} \right) \frac{|f_{lp}|^2}{60} \times \begin{bmatrix} \left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 + \frac{l^2}{r^2} \\ 2 \left(\left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 + \frac{l^2}{r^2} + k^2 \right) \\ \left| \frac{\partial_r f_{lp}}{f_{lp}} \right|^2 + \frac{l^2}{r^2} \end{bmatrix}^T \begin{bmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{bmatrix} \begin{bmatrix} q_{\lambda\lambda}^{ba} \bar{q}_{\nu\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\lambda\nu}^{ba} \\ q_{\lambda\nu}^{ba} \bar{q}_{\nu\lambda}^{ba} \end{bmatrix} \quad (26)$$

which is also independent of the l sign.

The next term we consider is $\langle M_{\hat{r}}^\mu \bar{M}_{\hat{r}}^q \rangle$, which can be written as;

$$\begin{aligned}
\langle M_{fi}^\mu \bar{M}_{fi}^q \rangle &= - \left(\frac{\hbar ck}{2A_{lp} \varepsilon_o V} \right) |f_{lp}|^2 e_{i_1}^{(\lambda)}(\mathbf{k}) \bar{e}_{i_2}^{(\lambda)}(\mathbf{k}) [\bar{G}_{lp}(r, \phi)]_{i_3} I_{i_1 i_2 i_3; \lambda_1 \lambda_2 \lambda_3}^{(3)} \mu_{\lambda_1}^{ba} \bar{q}_{\lambda_2 \lambda_3}^{ba} \\
&= - \left(\frac{\hbar ckn}{2A_{lp} \varepsilon_o V} \right) \frac{|f_{lp}|^2}{6} \left[\mathbf{e}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) \times \bar{\mathbf{G}}_{lp}(r, \phi) \right] \left[\varepsilon_{\lambda_1 \lambda_2 \lambda_3} \mu_{\lambda_1}^{ba} \bar{q}_{\lambda_2 \lambda_3}^{ba} \right]
\end{aligned} \tag{27}$$

where we have used $I_{i_1 i_2 i_3; \lambda_1 \lambda_2 \lambda_3}^{(3)} = \frac{1}{6} \varepsilon_{i_1 i_2 i_3} \varepsilon_{\lambda_1 \lambda_2 \lambda_3}$. In the case of linearly polarised light it can easily be seen that $\left[\mathbf{e}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) \times \bar{\mathbf{G}}_{lp}(r, \phi) \right] \equiv 0$. The other possible case, *i.e.* circularly polarised light, results in $\left[\mathbf{e}^{(\lambda)}(\mathbf{k}) \cdot \bar{\mathbf{e}}^{(\lambda)}(\mathbf{k}) \times \bar{\mathbf{G}}_{lp}(r, \phi) \right] = (-k)$, and therefore $\langle M_{fi}^\mu \bar{M}_{fi}^q \rangle$ does not retain any information of the handedness of the optical vortex, therefore independent of l .

It remains to consider $\langle M_{fi}^m \bar{M}_{fi}^q \rangle$, given by;

$$\begin{aligned}
\langle M_{fi}^\mu \bar{M}_{fi}^q \rangle &= - \left(\frac{\hbar k}{2A_{lp} \varepsilon_o V} \right) |f_{lp}|^2 \varepsilon_{i_1 i_4 i_5}(\hat{\mathbf{k}})_{i_4} e_{i_5}^{(\lambda)}(\mathbf{k}) \bar{e}_{i_2}^{(\lambda)}(\mathbf{k}) [\bar{G}_{lp}(r, \phi)]_{i_3} I_{i_1 i_2 i_3; \lambda_1 \lambda_2 \lambda_3}^{(3)} m_{\lambda_1}^{ba} \bar{q}_{\lambda_2 \lambda_3}^{ba} \\
&= \left(\frac{\hbar k}{2A_{lp} \varepsilon_o V} \right) \frac{|f_{lp}|^2}{6} [\bar{G}_{lp}(r, \phi)]_z \varepsilon_{\lambda_1 \lambda_2 \lambda_3} m_{\lambda_1}^{ba} \bar{q}_{\lambda_2 \lambda_3}^{ba}
\end{aligned} \tag{28}$$

As $[\bar{G}_{lp}(r, \phi)]_z = -ik$, the result is independent of the signature of l . Thus it is confirmed, by explicit calculation, that the helicity of a Laguerre-Gaussian beam cannot engage in any enantiomerically specific sense in its absorption by a chiral molecule.

4 Conclusion

Through rigorous analysis of the grounds for chiroptical behaviour involving electric and magnetic dipole interactions, it transpires that the helicity of twisted beams cannot engage through any parametric or non-parametric optical process with the chirality of a molecular system – other than through any circularity of its photons. Thus, the manifestations of orbital angular momentum differ markedly from those associated with photon spin angular momentum. The analysis is comprehensive, within the scope of the assumptions given, with recent experimental verification confirming our theoretical results. [22] It remains to study those optical processes invoking electric quadrupole and other higher multipole interactions; the analysis reported here excludes the possibility of any magnetic dipole contributions to such chiral specificity. In the specific case of electric quadrupole interactions, the analysis carried out for circular dichroism illustrates the difficulties that higher order multipole considerations introduce, where the simplest symmetry arguments are not sufficient to attest enantiomeric specificity. Assessing the possible chiral selectivity of the *mechanical* interactions of such twisted beams is an issue that merits separate attention, and which is the subject of other recent and ongoing work. [21,23]

Appendix 1 LG Functions, Generalised Laguerre Polynomials and their Properties

The positive frequency, un-normalised electric field of an LG mode as expressed by equation (15) can be written as;

$$\mathbf{e}^\perp(\mathbf{r}) = i\boldsymbol{\varepsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}})f_{lp}(r)a_{lp}^{(\lambda)}(k\hat{\mathbf{z}})\exp[i\theta_{klp}(k\hat{\mathbf{z}})] \quad (\text{A1.1})$$

The position-dependent polarisation functions $\boldsymbol{\varepsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}})$ and $\theta_{klp}(k\hat{\mathbf{z}})$ are, respectively, the mode amplitude distribution function and phase function, which are explicitly given by; [20]

$$\boldsymbol{\varepsilon}_{lp}^{(\lambda)}(k\hat{\mathbf{z}}) = \varepsilon_{k00} \frac{C_{lp}}{(1+z^2/z_R^2)^{1/2}} \left(\frac{\sqrt{2}r}{w(z)} \right)^{|l|} L_p^{|l|} \left(\frac{2r^2}{w^2(z)} \right) \exp[-r^2/w^2(z)] \quad , (\text{A1.2})$$

$$\theta_{klp}(k\hat{\mathbf{z}}) = \frac{kr^2z}{2(z^2+z_R^2)} + l\phi + (2p+l+1)\tan^{-1}(z/z_R) + kz \quad . \quad (\text{A1.3})$$

Here ε_{k00} is the amplitude for a plane wave of wave-vector \mathbf{k} ; $C_{lp} = \sqrt{p!/(|l|+p)!}$ is a normalisation factor; $L_p^{|l|}(x)$ is the generalised Laguerre polynomial of indices $|l|$ and p . The width $w(z)$ of the beam is defined in terms of the Rayleigh range, z_R , by $w^2(z) = 2(z^2+z_R^2)/kz_R$. The generalised Laguerre polynomials $L_p^l(x)$ are well-known functions whose properties can be found in the established literature. [24,25] Different works of reference give explicit expressions which differ by a constant factor. Table A1 gives the expressions as used in our work.

Table A1: Properties of generalized Laguerre Polynomials [24,25].

Explicit expression:	$L_p^l(x) = \sum_{m=0}^p (-1)^m \binom{p+l}{p-m} \frac{1}{m} x^m$
Orthogonality relationship	$\int_0^\infty e^{-x} x^l L_p^l(x) L_m^l(x) dx = \frac{(l+p)!}{p!} \delta_{p,m}$

The products of two identical generalized Laguerre polynomials are also tabulated in the literature, as;

$$\left[L_p^l(x) \right]^2 = \frac{\Gamma(1+l+p)}{p!} \sum_{k=0}^\infty \frac{(2p-2k)!(2k)!}{\Gamma(1+l-k)(n-k)!} I_{2k}^{2l}(2x) \quad (\text{A1.4})$$

In passing we note that in reference [24] there is a typographical error in the gamma function in the denominator of the expression (A1.4). However, even with correction the above formula is incorrect. We have found a different expression, which also is a linear combination of $L_{2k}^{2l}(2x)$ polynomials;

$$\left[L_p^l(x)\right]^2 = \sum_{n=0}^p c_{p,n}^l L_{2n}^{2l}(2x) \quad (\text{A1.5})$$

Here the coefficients c_{np}^l are more complicated and different to those in equation (A1.4);

$$c_{p,n}^l = \begin{cases} \frac{(2p)!}{(2p+2l)!} \sum_{t=0}^{2(n+p)} \sum_{m=0}^{2n} \sum_{k=0}^n \frac{1}{2^m} d_{2p,t-m}^{2l} d_{n,k}^l d_{n,m-k}^l (2l+t)! & \text{for } 0 \leq n \leq p, \\ 0 & \text{otherwise,} \end{cases} \quad (\text{A1.6})$$

with;

$$d_{n,k}^l = \begin{cases} \frac{(-1)^k}{k!} \binom{n+l}{n-k} & \text{for } 0 \leq k \leq n, \\ 0 & \text{otherwise.} \end{cases}$$

For $p=0$, a trivial example, the results given by both expressions, (A1.4) and (A1.5) are identical. However, for $p=1$ there is a difference by a numerical factor between the two equations. For $p=2$ the difference is more than just a factor, and as the p index increases this difference is accentuated. We have verified that the expression given in (A1.5), obtained by using the properties listed in Table A1, is correct and should be used instead of (A1.4).

Appendix 2 Optical Interaction Tensors and Rotational Averages

For any chiroptical process taking place in a fluid, or otherwise microscopically disordered system, it is required to evaluate:

$$\left\langle \left| M_{fi} \right|^2 \right\rangle = \left\langle \sum_{\xi, \xi'}^N M_{fi}^{\xi} \bar{M}_{fi}^{\xi'} \right\rangle \quad (\text{A2.1})$$

see, for example, equation (12). Using the specific expression for the transition matrix given in equation (9) we have;

$$\begin{aligned}
\left\langle |M_{fi}|^2 \right\rangle &= \sum_{\xi}^N \sum_{e,m,e',m'=0}^n \mathbf{S}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi} \otimes \left\langle \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi} \right\rangle + \\
&\sum_{\xi \neq \xi'}^N \sum_{e,m,e',m'=0}^n \exp\left[i\Delta\mathbf{k} \cdot (\mathbf{R}_{\xi} - \mathbf{R}_{\xi'})\right] \mathbf{S}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi'} \otimes \left\langle \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \right\rangle \left\langle \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi'} \right\rangle \\
&= N \sum_{e,m,e',m'=0}^n \mathbf{S}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi} \otimes \left\langle \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi} \right\rangle + \\
&\sum_{\xi \neq \xi'}^N \sum_{e,m,e',m'=0}^n \exp\left[i\Delta\mathbf{k} \cdot (\mathbf{R}_{\xi} - \mathbf{R}_{\xi'})\right] \mathbf{S}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi'} \otimes \left\langle \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \right\rangle \left\langle \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi'} \right\rangle \quad (\text{A2.2})
\end{aligned}$$

The first term on the right of equation (A2.2) signifies an incoherent contribution, and the second term a coherent response. The latter dominates if the process is parametric, and evaluation of the corresponding term requires the implementation of a rotational average over $\mathbf{T}^{(r)}$. However if the process is *non*-parametric the coherent term vanishes (through the interference of the different phase factors for each molecular centre) and the response derives solely from the incoherent term, where the rotational average is effected over $|\mathbf{T}^{(r)}|^2$, invoking tensors of rank $(r+r')$. In each case the rotational average involves the molecular tensors alone, since it is considered that the radiation components are fixed with respect to a laboratory-anchored cartesian frame. Since $\mathbf{T}^{(r)}$ refers to a molecular property it is convenient to express it with respect to a molecule fixed frame through the relation;

$$\begin{aligned}
\left\langle \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \right\rangle &= \mathbf{T}_{e;m;n-e-m}^{(r);\xi} I^{(r)} \\
&= \left(T_{\lambda_1 \lambda_2 \dots \lambda_r} \right)_{e;m;n-e-m}^{(r);\xi} I_{\lambda_1 \dots \lambda_r; i_1 \dots i_r}^{(r)} \quad (\text{A2.3})
\end{aligned}$$

where $I^{(r)}$ is the rotational average tensor of rank $(2r)$. The Latin and Greek indices refer to space-fixed and molecule-fixed frames respectively. Then the rotational average of the molecular tensor is given by;

$$\begin{aligned}
\left\langle |M_{fi}|^2 \right\rangle &= N \sum_{e,m,e',m'=0}^n \mathbf{S}_{e;m;n-e-m}^{(r)} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r')} I^{(r+r')} \mathbf{T}_{e;m;n-e-m}^{(r)} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r')} + \\
&\sum_{\xi \neq \xi'}^N \sum_{e,m,e',m'=0}^n \exp\left[i\Delta\mathbf{k} \cdot (\mathbf{R}_{\xi} - \mathbf{R}_{\xi'})\right] \mathbf{S}_{e;m;n-e-m}^{(r);\xi} I^{(r)} \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi'} I^{(r')} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi'}
\end{aligned}$$

Thus for a parametric process, $\Delta\mathbf{k} = 0$, we have;

$$\begin{aligned}
\left\langle |M_{fi}|^2 \right\rangle^{\text{coherent}} &= N^2 \left\langle M_{fi}^{\xi} \right\rangle^2 \\
&\approx N^2 \sum_{e,m,e',m'=0}^n \mathbf{S}_{e;m;n-e-m}^{(r);\xi} I^{(r)} \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi'} I^{(r')} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi'} \quad (\text{A2.4})
\end{aligned}$$

On the other hand if $\Delta\mathbf{k} \neq 0$ then;

$$\begin{aligned}
\left\langle \left| M_{\bar{f}\bar{i}} \right|^2 \right\rangle^{incoherent} &\simeq N \left\langle \left| M_{\bar{f}\bar{i}}^{\xi} \right|^2 \right\rangle \\
&\simeq N \sum_{e,m,e',m'=0}^n \mathbf{S}_{e;m;n-e-m}^{(r)} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r')} \mathbf{I}^{(r+r')} \mathbf{T}_{e;m;n-e-m}^{(r)} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r')} \quad (\text{A2.5})
\end{aligned}$$

To evaluate the result in either case, using equation (A2.4) or (A2.5) as appropriate, it is necessary to engage the double tensor $I^{(k)}$, which is explicitly the rotational average of a direction cosine product;

$$I^{(k)} \equiv \left\langle l_{i_1 \lambda_1} l_{i_2 \lambda_2} \dots l_{i_k \lambda_k} \right\rangle = \int \int \int l_{i_1 \lambda_1} l_{i_2 \lambda_2} \dots l_{i_k \lambda_k} \sin \theta \, d\phi \, d\theta \, d\psi \quad (\text{A2.6})$$

where each $l_{i_k \lambda_k}$ is the cosine of the angle between the space-fixed axis and the molecule-fixed axis. The rotational average tensor $I^{(k)}$ can be expressed as a linear combination of isotropic tensors, *i.e.* tensors that are invariant under rotation. It is important to notice that the way that the tensor $I^{(k)}$ is defined in equation (A2.6) implies that the rank of the tensor is $2k$. Each member of the linear combination is a product of two isotropic tensors, one referred to the space-fixed frame and the other to the molecule-fixed frame. An important property of these products is that the Latin and Greek indices do not mix; explicitly;

$$I^{(k)} = \sum_{st} m_{st}^{(k)} \mathbf{f}_s^{(k)} \mathbf{g}_t^{(k)} \quad (\text{A2.7})$$

Here $\mathbf{f}_s^{(k)}$ ($\mathbf{g}_t^{(k)}$) is a k -rank tensor in the space-fixed (molecule-fixed) frame, and the tensor indices $i_1 \dots i_k$ ($\lambda_1 \dots \lambda_k$) are suppressed for convenience. Then the rotational average of the quantum amplitude product emerges as;

$$\begin{aligned}
\left\langle \left| M_{\bar{f}\bar{i}} \right|^2 \right\rangle &= N \sum_{e,m,e',m'=0}^n \sum_{ts} m_{ts}^{(r+r')} \left[\mathbf{f}_t^{(r+r')} \mathbf{S}_{e;m;n-e-m}^{(r)} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r')} \right] \left[\mathbf{g}_s^{(r+r')} \mathbf{T}_{e;m;n-e-m}^{(r)} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r')} \right] \\
&+ N(N-1) \sum_{e,m,e',m'=0}^n \sum_{ts} m_{ts}^{(r+r')} \left[\mathbf{f}_t^{(r)} \mathbf{S}_{e;m;n-e-m}^{(r);\xi} \right] \left[\mathbf{g}_s^{(r)} \mathbf{T}_{e;m;n-e-m}^{(r);\xi} \right] \sum_{t's'} m_{t's'}^{(r')} \left[\mathbf{f}_{t'}^{(r')} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r);\xi'} \right] \left[\mathbf{g}_{s'}^{(r')} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r);\xi'} \right] \quad (\text{A2.8})
\end{aligned}$$

Finally, for calculational implementation a simpler notation can be adopted, where the rotational average of the molecular and radiation tensors is implied;

$$\begin{aligned}
\left\langle \left| M_{\bar{f}\bar{i}} \right|^2 \right\rangle &= N \sum_{e,m,e',m'=0}^n \sum_{ts} m_{ts}^{(r+r')} \left\langle \mathbf{S}_{e;m;n-e-m}^{(r)} \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r')} \right\rangle \left\langle \mathbf{T}_{e;m;n-e-m}^{(r)} \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r')} \right\rangle + \\
&N(N-1) \sum_{e,m,e',m'=0}^n \sum_{ts} m_{ts}^{(r+r')} \left\langle \mathbf{S}_{e;m;n-e-m}^{(r)} \right\rangle \left\langle \mathbf{T}_{e;m;n-e-m}^{(r)} \right\rangle \times \\
&\times \sum_{t's'} m_{t's'}^{(r')} \left\langle \bar{\mathbf{S}}_{e';m';n-e'-m'}^{(r')} \right\rangle \left\langle \bar{\mathbf{T}}_{e';m';n-e'-m'}^{(r')} \right\rangle \quad (\text{A2.9})
\end{aligned}$$

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