# Nonlinear Spectroscopy with Twisted Beams

David L. Andrews[a*], Mohamed Babiker[b], Colin R. Bennett[b] and Luciana C. Dávila Romero[a]

[a]School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.
[b]Department of Physics, University of York, Heslington, York YO10 5DD, U.K.

## ABSTRACT

The propensity of conventional optical beams to convey angular momentum is very well known. As a spin-1 elementary particle any photon can assume a polarisation state with a well defined 'spin' angular momentum of plus or minus 1 in the direction of propagation, corresponding to a circular polarisation of either left or right helicity. The mechanical effects of photonic angular momentum are manifest in a variety of phenomena operating at both the atomic and macroscopic scale. Photon angular momentum also exercises a key role in atomic spectroscopy and a host of other fundamental optical phenomena.

The aim of this work is to study the interaction between matter and Laguerre-Gaussian beams, and others of related structure in which a helical wavefront confers an endowment with 'orbital' angular momentum. Although the principles and methods of production of these twisted beams are already quite well understood, the detailed study of the interactions is a novel subject. We explore changes in selection rules transfer of linear and angular momentum in the context of nonlinear processes, especially harmonic and sum-frequency generation.

Keywords: Spin angular momentum, orbital angular momentum, Laguerre-Gaussian beams, nonlinear optical processes, optical vortices, optical spanners, selection rules.

## 1. THE ELECTROMAGNETIC FIELD DESCRIBED IN TERMS OF TWISTED BEAMS

It has long been known that circularly polarised light beams convey angular momentum. The photons of which any such beam is comprised are spin-1 elementary particles, whose states with angular momentum of plus or minus 1 in the direction of propagation correspond to circular polarisation of either left or right handedness. On the atomic scale, the effects of this angular momentum are manifest in the selection rules governing absorption and emission; mechanical effects are also observable on the macroscopic scale, as in Beth's famous experiment with a suspended half-wave plate.[1]. For circularly polarised light, a well-defined helicity is associated with the associated electromagnetic vector fields.

Recently, another quite distinct type of optical helicity has become the subject of considerable interest. Whilst circularly polarised light comprises photons that convey an intrinsic spin angular momentum, it is also possible to optically engineer *optical vortices,* beams endowed with what has become known as *orbital angular momentum.* [2-8] Here it is the wave-front of the electromagnetic fields that assumes helical form. This new field is rife with synonyms: whilst the radiation itself is also commonly referred to as a *twisted* or *helical beam*, the associated technology has been termed an *optical spanner* (though the latter term is misleading as it has also been applied to systems where a wave-front is mechanically rotated [9-14] Twisted beams may, but need not, comprise circular photons.

[*] Correspondence: Email: david.andrews@physics.org; http://www.uea.ac.uk/~c051/, Tel.: +44 1603 592014

The most commonly studied of the new twisted beams have a Laguerre-Gaussian (LG) profile, and although the principles and methods of their production are quite well understood, the detailed study of their interactions is a subject still in its infancy, and usually based on a classical description of the radiation. A novel approach that pays due heed to the quantum mechanical nature of the photonic interactions is presented by quantum electrodynamics (QED). The fact that the fully quantised theory introduces another tier of complexity in comparison to its classical counterpart might at first be considered undesirable. However by treating interactions at the most fundamental level, this formulation introduces a focus on certain issues that escape attention in the classical development. Recent experimental observations of optical nonlinearity in LG beams provide the grounds to illustrate application of the QED representation through calculation of the rate of second harmonic and sum-frequency generation in suitable media. This approach, which can also be regarded as a test case for dealing in general with the nonlinear optics of twisted beams, reveals rules for linear and angular momentum conservation in a particularly transparent way.

In source-free regions Maxwell's equations governing the electromagnetic (EM) field are conveniently cast in terms of the vector and scalar potentials, **a** and $\phi$ respectively. In the Lorentz gauge, $\nabla\cdot\mathbf{a}+c^{-2}\partial_t\phi=0$, the free fields are expressible in terms of **a** and $\phi$ as $\mathbf{b}=\nabla\times\mathbf{a}$, $\mathbf{e}=-\partial_t\mathbf{a}-\nabla\phi$, and Maxwell's equations reduce to the simple wave equation.[15] The orbital angular momentum (OAM) of experimentally realizable well collimated beams has generally been studied within *the paraxial approximation*, the being assumption that the transverse profile varies only slowly along the direction of propagation.[16] Thus, with the constraint that the beam is only free to propagate in a designated direction, say along the $\hat{\mathbf{z}}$-axis, then the vector field **a** can be described as;

$$\mathbf{a}(\mathbf{r},t)=\boldsymbol{\varepsilon}\, u(x,y,z)\ \ \exp\left[\mathrm{i}\left(kz-\omega t\right)\right] \quad , \tag{1}$$

where $\boldsymbol{\varepsilon}$ is a polarisation vector normal to $\hat{\mathbf{z}}$ and $u(x,y,z)$ is the transverse amplitude.[15, 17, 18] The spatial symmetry associated with the paraxial approximation invites expression of the amplitude $u(x,y,z)$ in cylindrical coordinates $(r,\phi,z)$. Choosing $u(r,\phi,z)$ to be independent of $z$ we can then express the amplitude as,

$$u_{lp}\left(r,\phi,z\right)\equiv u_{lp}\left(r,\phi\right)=f_{lp}\left(r\right)\exp\left(-\mathrm{i}l\phi\right) \ , \tag{2}$$

where $f_{lp}(r)$ must satisfy the conditions imposed by Maxwell's equations within the paraxial approximation. It has been shown that beams possessing a field phase factor $\exp(-\mathrm{i}l\phi)$ exhibit features associated with an orbital angular momentum *L* of eigenvalue $l\hbar$,[18] this signifying the conferred orbital angular momentum per photon. It is this type of beam that we call *twisted*. The additional index *p* introduced as a parameter in the amplitude function $u_{lp}(r,\phi)$ differentiates all possible modes with the same orbital angular momentum, *l*, i.e. its presence accommodates considerations of degeneracy.[18]

The best-known examples of experimentally realizable twisted laser beams, satisfying the characteristics of the paraxial equation, are LG modes.[6, 19] Within the long Rayleigh range, $z_R \gg z$ , the amplitude distribution of such beams, $u_{lp}^{LG}(r,\phi,z)\equiv u_{lp}^{LG}(r,\phi)$, is given by;

$$u_{lp}^{LG}(r,\phi,z) \ = \ \frac{C_p^{|l|}}{w_0}\ \left[\frac{\sqrt{2}\ \ r}{w_0}\right]^{|l|}\exp\left(\frac{-r^2}{w_0^2}\right)L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\times\exp\left[-\mathrm{i}l\phi\right] \ , \tag{3}$$

where; $C_p^{|l|}$ is the normalization constant; $w_0$ is the Gaussian beam-waist at $z=0$; $L_p^l\left(x\right)$ is the *generalized Laguerre polynomial* of order *p* and argument *x*, and $2z_R$ is the Rayleigh range – a measure of $z$ over which collimation is sustained.[16] Under such conditions the amplitude $u_{lp}^{LG}\left(r,\phi\right)$ is independent of *z* and then takes the form given in equation (2).

The most general description of the vector potential is a linear combination of all possible solutions of the type presented in equation (2). In terms of such twisted modes, the vector potential field assumes a structure expressible in the following form;

$$\mathbf{a}(\mathbf{r},t)=\sum_{k,\lambda,l,p}\left\{\boldsymbol{\varepsilon}^{(\lambda)}(k\hat{\mathbf{z}})\,a_{k,\lambda,l,p}\,u_{lp}(r,\phi)\;\exp\left[\mathrm{i}(kz-\omega t)\right]+\;\text{c.c.}\;\right\}\;, \tag{4}$$

with amplitude $u_{lp}(r,\phi)=u_{lp}$ precisely as given by (2). The sum over the wave-vector in equation (4) takes only one degree of freedom, the magnitude *k*, the propagation direction being fixed in the $\hat{\mathbf{z}}$ direction. This mode of expression reflects the imposition of a condition that the wave-vector **k** can vary only in magnitude, not in its direction. The vector field as given by equation (4) nonetheless has obvious structural similarities to the more traditional expansion in terms of plane waves.

From the general equation (4), the electric and the magnetic induction fields associated with all possible twisted mode are readily obtained using the expressions in terms of the vector field $\mathbf{a}$, as follows;

$$\mathbf{e}(\mathbf{r},t)=\sum_{\mathbf{k},\,\lambda,\,l,\,p}\left\{\left[\mathrm{i}ck\,u_{l,p}\,\boldsymbol{\varepsilon}^{(\lambda)}(\mathbf{k})-c\left(\boldsymbol{\varepsilon}^{(\lambda)}(\mathbf{k})\cdot\nabla\right)u_{l,p}\hat{\mathbf{z}}\right]a_{\mathbf{k},\lambda,l,p}\exp(\mathrm{i}kz-\mathrm{i}\omega\;t)\;+\;\text{c.c.}\right\}\;; \tag{5a}$$

$$\mathbf{b}(\mathbf{r},t)=\sum_{\mathbf{k},\lambda,l,p}\left\{\left[\mathrm{i}k\left(\hat{\mathbf{k}}\times\boldsymbol{\varepsilon}^{(\lambda)}(\mathbf{k})\right)u_{l,p}-\left(\boldsymbol{\varepsilon}^{(\lambda)}(\mathbf{k})\times\nabla\right)u_{l,p}\;\;\hat{\mathbf{z}}\right]a_{\mathbf{k},\lambda,l,p}\;\exp(\mathrm{i}k\,z-\mathrm{i}\omega t)\;+\;\text{c.c.}\right\}. \tag{5b}$$

Both fields exhibit a transverse and also a longitudinal part (as defined with respect to the direction of propagation.) The transverse terms are very similar in form to those presented when the EM field is described as an expansion in terms of plane waves. The distinctive longitudinal terms depend on the first derivatives of the amplitude $u_{lp}\equiv u_{lp}(r,\phi)$. This last feature is highly significant since it makes possible the quantisation of the EM field: together with the necessary mode orthogonality, it permits the later promotion of field amplitudes to operators. We note that the 'curvature' represented by the *z*-components in (5) prove not to contribute measurably to the field angular momentum. Full details of the progression to the results given in the above equation can be found in other recent work.[20]

## 2. RADIATION, MATTER AND INTERACTION HAMILTONIAN

The classical Hamiltonian for the free field is given by;

$$H_{rad}=\int\mathcal{H}_{rad}\;d^3r=\frac{\varepsilon_0}{2}\int\left(\mathbf{e}^2+c^2\mathbf{b}^2\right)d^3r\;\;, \tag{6}$$

where $\mathcal{H}_{rad}$ is the Hamiltonian density. Using the EM field expressions, equations (7), it is possible to quantify the field generated by the twisted beams, [20]

$$H=\sum_{k,\lambda,l,p}\hbar\omega\left[\mathrm{a}_{lp}^{\dagger(\lambda)}(k\,\hat{\mathbf{z}})\;\mathrm{a}_{lp}^{(\lambda)}(k\,\hat{\mathbf{z}})+\frac{1}{2}\right]\;\;. \tag{7}$$

where $a_{lp}^{\dagger(\lambda)}(k\hat{z})$ ($a_{lp}^{(\lambda)}(k\hat{z})$) is the creation (annihilation) operator of a photon whose source is the twisted beam. The quantisation rules followed by the creation and annihilation operators are here adopted in order that the quantised Hamiltonian is independent of the normalization constant $A_{lp}$, and the amplitude function $f_{lp}(r)$. Note that the state artificially designated $|0\rangle$ cannot be identified with the usual vacuum state of the EM field; the physical significance of this difference is that it is not possible for a system to spontaneously emit a twisted beam.

The potential vector $\mathbf{a}(\mathbf{r},t)$, and the transverse parts of the electric and magnetic fields $\mathbf{e}(\mathbf{r},t)$ and $\mathbf{b}(\mathbf{r},t)$, are also expressible in terms of the new creation and annihilation operators. From these expressions the interaction Hamiltonian describing the coupling between the light and matter will also invoke the creation and annihilation operators for photons with angular momentum $l$. Therefore, when studying optical processes involving interactions between any EM field and matter, the QED Hamiltonian describing the system can be expressed as a sum of three terms, [21]

$$H = H_{rad} + H_{matter} + H_{int} \quad , \tag{8}$$

where $H_{rad}$ is the EM field Hamiltonian. The matter Hamiltonian comprises the usual Schrödinger operators, summed over the centres $\xi$ that constitute the matter (molecules, atoms, ions, etc.); the sum of the first two terms in (10) is the unperturbed Hamiltonian. Finally, in the electric-dipole approximation the interaction Hamiltonian, $H_{int}$, which represents the interaction between the matter and the EM field, is;

$$H_{int} = -\varepsilon_0^{-1} \sum_{\xi} \boldsymbol{\mu}\left(\mathbf{R}_{\xi}\right) \cdot \mathbf{d}^{\perp}\left(\mathbf{R}_{\xi}\right) \quad , \tag{9}$$

representing dipolar coupling with $\mathbf{d}^{\perp}(\mathbf{R})$, the electric displacement vector associated with the field $\mathbf{e}^{\perp}(\mathbf{R})$.

The Fermi rule determines the probability of the system evolving from an initial state $|i\rangle$ to a final state $|f\rangle$ over time $t$;

$$\Gamma = \frac{d}{dt} P_{TOTAL} = \frac{2\pi}{\hbar} \left| M_{fi} \right|^2 \rho_f \quad , \tag{10}$$

and for processes generating optical output, the density of final states, $\rho_f$, is given by $k^2 \left(2\pi\right)^{-3} \left(\hbar c\right)^{-1} V d\Omega$ ; $M_{fi}$ is the transition matrix element between the states involved. The intensity of an emitted signal can be expressed in terms of the rate $d\Gamma$ per solid angle $d\Omega$. Specifically, with the radiant intensity defined as the energy per unit solid angle and per unit time radiated with polarization $\lambda'$, trivially it follows that;

$$I\left(k'\right) = \hbar c k' \frac{d\Gamma}{d\Omega} \quad . \tag{11}$$

It is the radiant intensity given in (11), as determined from the transition matrix $M_{fi}$, which we need to consider when analysing different optical processes in the following section.

## 3. NONLINEAR OPTICAL PROCESSES

In this section we consider two nonlinear optical processes that occur due to a coupling of matter and radiation. To this end we adopt the QED formulation of nonlinear optics as detailed in a recent review.[22] Our first example is the well-known process of second harmonic generation (SHG) and the second, the more general sum-frequency generation (SFG). Both are parametric, in the sense that there is no uptake or loss of energy by the medium, and coherent output emerges. It is important to recall that the radiation fields as given by equations (4) and (5) are restricted to those cases where all beams involved in the optical process are collinear. The generalisation to cases where twisted beams have different propagation direction is beyond the description given in this work.

### 3.1 Second harmonic generation

If we consider as input a twisted Laguerre-Gaussian beam, then the interaction Hamiltonian given in equation (9) must be deployed with reference to the field expansion, equation (5a). For simplicity and compactness of notation we define a more general polarisation vector given by;

$$\boldsymbol{\varepsilon}_{\lambda,l,p}(\mathbf{k},\mathbf{R})=\frac{C_p^{|l|}}{w_0}\left(\frac{\sqrt{2}r}{w_0}\right)^{|l|}L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\exp\left(-\frac{r^2}{w_0^2}\right)\times\boldsymbol{\varepsilon}^{\lambda}(\mathbf{k}) \quad , \tag{12}$$

accommodating most of the functional form of the LG mode. The initial and final states of the radiation–matter system are now expressible as;

$$|i\rangle=|E_0\rangle\otimes|n(k\hat{\mathbf{z}},\lambda,l,p),0(k'\mathbf{z},\lambda',l',p')\rangle \quad , \tag{13a}$$

$$|f\rangle=\sum_{l',p'}d_{l',p'}|E_0\rangle\otimes|(n-2)(k\hat{\mathbf{z}},\lambda,l,p),1(k'\hat{\mathbf{z}},\lambda',l',p')\rangle \quad . \tag{13b}$$

The leading term of the transition matrix $M_{fi}$ is

$$\begin{aligned}M_{fi}=-i\sum_{l',p'}d_{l',p'}\left(\frac{\hbar c}{2\varepsilon_0 V}\right)^{3/2}\left(\frac{k^2k'n(n-1)}{A_{lp}^2A_{l'p'}}\right)^{1/2}\times\\ \left[\bar{\boldsymbol{\varepsilon}}'_{\lambda',l',p'}(k'\hat{\mathbf{z}},\mathbf{R})\right]_i\left[\boldsymbol{\varepsilon}_{\lambda,l,p}(k\hat{\mathbf{z}},\mathbf{R})\right]_j\left[\boldsymbol{\varepsilon}_{\lambda,l,p}(k\hat{\mathbf{z}},\mathbf{R})\right]_k\beta_{ijk}\exp\left[-i\Delta\theta(\mathbf{R})\right]\end{aligned} \tag{14}$$

where the polarisation product is explicitly;

$$\left[\bar{\varepsilon}'_{\lambda',l',p'}(k'\hat{\mathbf{z}},\ \mathbf{R})\right]_i\left[\varepsilon_{\lambda,l,p}(k\hat{\mathbf{z}},\ \mathbf{R})\right]_j\left[\varepsilon_{\lambda,l,p}(k\hat{\mathbf{z}},\ \mathbf{R})\right]_k=\frac{\left(C_p^{|l|}\right)^2C_{p'}^{|l'|}}{w_0^{\;3}}\left(\frac{\sqrt{2}r}{w_0}\right)^{|l'|+2|l|}\exp\left(-\frac{3r^2}{w_0^2}\right)L_{p'}^{|l'|}\left(\frac{2r^2}{w_0^2}\right)\left[L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\right]^2\times\bar{\varepsilon}_i'^{\lambda'}\varepsilon_j^{\lambda}\varepsilon_k^{\lambda} \quad . \tag{15}$$

The phase difference $\Delta\theta$ introduced in equation (14) is simply given by;

$$\Delta\theta=-(l'-2l)\phi+(k'-2k)z \quad , \tag{16}$$

and $\beta_{ijk}$ is the hyperpolarisability tensor given by;

$$\beta_{ijk}=\sum_{r,s}\left[\frac{\mu_i^{0r}\mu_j^{rs}\mu_k^{s0}}{(E_r-E_0-2\hbar\omega)(E_s-E_0-\hbar\omega)}+\frac{\mu_k^{0r}\mu_i^{rs}\mu_j^{s0}}{(E_r-E_0+\hbar\omega)(E_s-E_0-\hbar\omega)}+\frac{\mu_j^{0r}\mu_k^{rs}\mu_i^{s0}}{(E_r-E_0+\hbar\omega)(E_s-E_0+2\hbar\omega)}\right] \quad . \tag{17}$$

From equation (14), with cognisance of the ($jk$) index symmetry of the polarization vectors, it can be seen that only the corresponding index-symmetric part of the hyperpolarisability, $\beta_{i(jk)}=\frac{1}{2}\left(\beta_{ijk}+\beta_{ikj}\right)$, contributes to $M_{fi}$.

In constructing the harmonic signal from a bulk system the above phase manifests itself in the form of a $\text{sinc}^2$ function, differing from the conventional form through the inclusion of the term involving angular momentum. Optimum conversion efficiency, associated with fully coherent output, thus ensues through satisfaction of the two conditions:

$$\left.\begin{aligned}k'&=2k \quad ,\\ l'&=2l.\end{aligned}\right\} \tag{18}$$

The former condition is the familiar result for wave-vector matching (conservation of photon momentum); the latter signifies conservation of orbital angular momentum. Note that neither conservation principle is enforced by the formalism here applied; however both emerge on an equal footing as natural conditions for coherent output. Under such conditions the transition matrix reduces to;

$$M_{fi}=-\mathrm{i}\sum_{p'}d_{2l,p'}\left(\frac{\hbar c}{2\varepsilon_0 V}\right)^{3/2}\left(\frac{k^2k'n(n-1)}{A_{lp}^2A_{l'p'}}\right)^{1/2}\frac{\left(C_p^{|l|}\right)^2C_{p'}^{|2l|}}{w_0^3}\left(\frac{\sqrt{2}r}{w_0}\right)^{4l}\exp\left(-\frac{3r^2}{w_0^2}\right)L_{p'}^{2l}\left(\frac{2r^2}{w_0^2}\right)\left[L_p^l\left(\frac{2r^2}{w_0^2}\right)\right]^2\times\bar{\varepsilon}_i'^{\lambda'}\varepsilon_j^\lambda\varepsilon_k^\lambda\beta_{ijk}$$

The rate of conversion to the second harmonic now follows, using equation (10) and the given expression for $\rho_f$, the density of final states;

$$d\Gamma=\frac{2\pi}{\hbar}\left|M_{fi}\right|^2\frac{(2k)^2}{(2\pi)^3\hbar c}Vd\Omega\quad. \tag{19}$$

The result in terms of the observable, the radiant intensity of the harmonic signal emitted by the system, $I_{\text{harmonic}}$, is then;

$$I_{\text{harmonic}}=N^2k^6\frac{\hbar^2c^3}{2\pi^2\varepsilon_0^3\;V^2A_{lp}^2}\left(\frac{C_p^{|l|}}{w_0}\right)^4\left(\frac{\sqrt{2}r}{w_0}\right)^{8l}\exp\left(-\frac{6r^2}{w_0^2}\right)\left[L_p^l\left(\frac{2r^2}{w_0^2}\right)\right]^4\left\langle n(n-1)\right\rangle\left\langle\left|\bar{\varepsilon}_i'^{\lambda'}\varepsilon_j^\lambda\varepsilon_k^\lambda\beta_{ijk}\right|^2\right\rangle$$
$$\times\left|\sum_{p'}\frac{d_{2l,p'}}{A_{2l\;p'}}\frac{C_{p'}^{|2l|}}{w_0}L_{p'}^{2l}\left(\frac{2r^2}{w_0^2}\right)\right|^2\quad. \tag{20}$$

where $N$ is the number of molecules involved in the optical process. Given that the mean input irradiance of the fundamental beam is;

$$\frac{\langle n\rangle}{V}\left(\frac{C_p^{|l|}}{w_0}\right)^2\left(\frac{\sqrt{2}r}{w_0}\right)^{2l}\exp\left(-\frac{2r^2}{w_0^2}\right)\left[L_p^l\left(\frac{2r^2}{w_0^2}\right)\right]^2=\frac{\bar{I}_\omega(r)}{\hbar c\omega}\quad, \tag{21}$$

it is immediately evident that $I_{\text{harmonic}}$ correctly varies with the square of $\bar{I}_\omega$ ;

$$I_{\text{harmonic}}=\frac{N^2k^4}{2\pi^2\varepsilon_0^3cA_{lp}^2}\bar{I}_\omega^2\frac{\langle n(n-1)\rangle}{\langle n\rangle^2}\left\langle\left|\bar{\varepsilon}_i'^{\lambda'}\varepsilon_j^\lambda\varepsilon_k^\lambda\beta_{ijk}\right|^2\right\rangle\times\left|\sum_{p'}\frac{d_{2l,p'}}{A_{2l\;p'}}\frac{C_{p'}^{|2l|}}{w_0}\left(\frac{\sqrt{2}r}{w_0}\right)^{2l}\exp\left(-\frac{r^2}{w_0^2}\right)L_{p'}^{|2l|}\left(\frac{2r^2}{w_0^2}\right)\right|^2\quad. \tag{22}$$

One notable feature of the result is that SHG is a process generally allowed with an input conveying orbital angular momentum. However this is subject to the condition that the polarisation is not circular; in an isotropic medium a strict embargo operates on the coherent production of any harmonic with circularly polarised light.[22]

### 3.2 Sum-frequency generation

The generalization of SHG to include sum-frequency generation is straightforward. In this case the initial and final states of the matter-radiation system are;

$$|i\rangle=|E_0\rangle\otimes\left|n_1(k_1\hat{\mathbf{z}},\lambda_1,l_1,p_1),n_2(k_2\hat{\mathbf{z}},\lambda_2,l_2,p_2),0(k_3\hat{\mathbf{z}},\lambda_3,l_3,p_3)\right\rangle\quad; \tag{23a}$$

$$|f\rangle=|E_0\rangle\otimes\left|(n_1-1)(k_1\hat{\mathbf{z}},\lambda_1,l_1,p_1),(n_2-1)(k_2\hat{\mathbf{z}},\lambda_2,l_2,p_2),1(k_3\hat{\mathbf{z}},\lambda_3,l_3,p_3)\right\rangle\quad, \tag{23b}$$

considering that the two absorbed photons originate from two different LG beams which are collinear, $\hat{\mathbf{k}}_1 = \hat{\mathbf{k}}_2$. Note that the two beams could in particular have equal frequency $k_1 = k_2$ but different angular momentum $l_1 \neq l_2$, and therefore be generated by the coupling of two different beams. The matrix element $M_{fi}$ for SFG is;

$$M_{fi} = -\mathrm{i}\left(\frac{\hbar c}{2\varepsilon_0 V}\right)^{3/2}\left[\frac{k_1 k_2 k_3 n_1 n_2}{A_{l_3 p_3} A_{l_2 p_2} A_{l_1 p_1}}\right]^{1/2} \times$$
$$\left[\bar{\boldsymbol{\varepsilon}}_{\lambda_3,l_3,p_3}(k_3\hat{\mathbf{z}},\mathbf{R})\right]_i \left[\boldsymbol{\varepsilon}_{\lambda_1,l_1,p_1}(k_1\hat{\mathbf{z}},\mathbf{R})\right]_j \left[\boldsymbol{\varepsilon}_{\lambda_2,l_2,p_2}(k_2\hat{\mathbf{z}},\mathbf{R})\right]_k \beta_{ijk} \exp\left[-i\Delta\theta(\mathbf{R})\right]. \quad (24)$$

The phase change $\Delta\theta$ is given as;

$$\Delta\theta = \theta_{\mathbf{k}_3,l_3,p_3} - \theta_{\mathbf{k}_1,l_1,p_1} - \theta_{\mathbf{k}_2,l_2,p_2} \ ,$$

$$\therefore \quad \Delta\theta = -(l_3 - l_1 - l_2)\,\phi + (k_3 - k_1 - k_2)\, z\,, \quad (25)$$

and the corresponding hyperpolarisability tensor $\beta_{ijk}$ is now;

$$\beta_{ijk} = \sum_{r,s}\left[\frac{\mu_i^{0r}\mu_j^{rs}\mu_k^{s0}}{(E_r - E_0 - \hbar\omega_2 - \hbar\omega_1)(E_s - E_0 - \hbar\omega_1)} + \frac{\mu_i^{0r}\mu_k^{rs}\mu_j^{s0}}{(E_r - E_0 - \hbar\omega_2 - \hbar\omega_1)(E_s - E_0 - \hbar\omega_2)} + \right.$$
$$\frac{\mu_k^{0r}\mu_i^{rs}\mu_j^{s0}}{(E_r - E_0 + \hbar\omega_3 - \hbar\omega_2)(E_s - E_0 - \hbar\omega_2)} + \frac{\mu_j^{0r}\mu_i^{rs}\mu_k^{s0}}{(E_r - E_0 + \hbar\omega_3 - \hbar\omega_1)(E_s - E_0 - \hbar\omega_1)}$$
$$\left. + \frac{\mu_j^{0r}\mu_k^{rs}\mu_i^{s0}}{(E_r - E_0 - \hbar\omega_1 + \hbar\omega_3)(E_s - E_0 + \hbar\omega_3)} + \frac{\mu_k^{0r}\mu_j^{rs}\mu_i^{s0}}{(E_r - E_0 - \hbar\omega_2 + \hbar\omega_3)(E_s - E_0 + \hbar\omega_3)}\right] .$$

The field factors in (24) take the form,

$$\boldsymbol{\varepsilon}_{\lambda,l,p}(\mathbf{k},\mathbf{R}) = \frac{C_p^{|l|}}{w_0}\left(\frac{\sqrt{2}r}{w_0}\right)^{|l|} L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\exp\left(-\frac{r^2}{w_0^2}\right)\times\boldsymbol{\varepsilon}^{\lambda}(\mathbf{k}) \ ,$$

and thus;

$$\left[\bar{\boldsymbol{\varepsilon}}_{\lambda_3,l_3,p_3}(k_3\hat{\mathbf{z}},\mathbf{R})\right]_i \left[\boldsymbol{\varepsilon}_{\lambda_1,l_1,p_1}(k_1\hat{\mathbf{z}},\mathbf{R})\right]_j \left[\boldsymbol{\varepsilon}_{\lambda_2,l_2,p_2}(k_2\hat{\mathbf{z}},\mathbf{R})\right]_k =$$
$$\frac{C_{p_3}^{|l_3|}C_{p_2}^{|l_2|}C_{p_1}^{|l_1|}}{w_0^3}\left(\frac{\sqrt{2}r}{w_0}\right)^{|l_1|+|l_2|+|l_3|}\exp\left(-\frac{3r^2}{w_0^2}\right)L_{p_1}^{|l_1|}\left(\frac{2r^2}{w_0^2}\right)L_{p_2}^{|l_2|}\left(\frac{2r^2}{w_0^2}\right)L_{p_3}^{|l_3|}\left(\frac{2r^2}{w_0^2}\right)\times\bar{\varepsilon}_i^{\lambda_3}\varepsilon_j^{\lambda_1}\varepsilon_k^{\lambda_2} \ . \quad (26)$$

In obvious analogy to SHG, the optimum conversion efficiency occurs when;

$$\begin{cases} l_3 = l_1 + l_2 \\ k_3 = k_1 + k_2 \quad \text{phase matching condition} \end{cases} \quad (27)$$

It can be seen that these conditions are very similar to those which apply for SHG; moreover by considering the case where $k_1 = k_2$ it is seen that SHG is still valid for the case where the input photons involved have different orbital angular momenta. The intensity of the signal can be found as in the previous section, and emerges as the following result;

$$I_{\mathrm{SFG}}=\frac{N^2k_3^4}{32\pi^2\varepsilon_0^3 c\,A_{l_1p_1}A_{l_2p_2}}\bar{I}_{\omega_1}\bar{I}_{\omega_2}\frac{\langle n_1n_2\rangle}{\langle n_1\rangle\langle n_2\rangle}\left\langle\left|\bar{\varepsilon}_i^{\lambda_3}\varepsilon_j^{\lambda_2}\varepsilon_k^{\lambda_1}\beta_{ijk}\right|^2\right\rangle\times\left|\sum_{p'}\frac{d_{l_3,p_3}}{A_{l_3\ p_3}}\frac{C_{p_3}^{|l_3|}}{w_0}\left(\frac{\sqrt{2}r}{w_0}\right)^{|l_3|}\exp\left(-\frac{r^2}{w_0^2}\right)L_{p_3}^{|l_3|}\left(\frac{2r^2}{w_0^2}\right)\right|^2$$

$$u_{lp}^{LG}(r,\phi,z)\ =\ \frac{C_p^{|l|}}{w_0}\left[\frac{\sqrt{2}\ \ r}{w_0}\right]^{|l|}\exp\left(\frac{-r^2}{w_0^2}\right)L_p^{|l|}\left(\frac{2r^2}{w_0^2}\right)\times\exp\left[-\mathrm{i}l\phi\right]$$

## 4. EXCHANGE OF ORBITAL ANGULAR MOMENTUM

The manifestation of OAM in the interactions of twisted beams with matter has been explored theoretically, leading to predictions that a light-induced torque can be used to control the rotational motion of atoms [23]. More generally, Berry [24] has shown that orbital angular momentum is an intrinsic property of all types of azimuthal phase-bearing light, independent of the choice of axis about which the OAM is defined. O'Neil *et al.* [25] have classified the engagement of twisted beam OAM in terms of *intrinsic* and *extrinsic* interactions, i.e. those relating to electronic transitions, and those concerned with centre of mass motion. On such grounds it might be argued that, in its interaction with an electronically distinct and isolated system such as a free atom or a molecule, intrinsic OAM should be manifest through an exchange of orbital angular momentum between the light and matter, just as photon *spin* angular momentum manifests itself in the selection rules associated with the interactions of circularly polarised light. The QED analysis affords a means of testing this hypothesis.

At the fundamental level, each electric interaction of twisted light with a molecule is associated with a coupling operator given by;

$$H_{int}=-\int d^3\mathbf{r}\quad \mathbf{P}(\mathbf{r})\cdot\mathbf{d}_{kl}(\mathbf{r},t)\ \ , \tag{28}$$

where $\mathbf{P}(\mathbf{r})$ is the multipolar polarisation field, and considering one specific mode of the electric displacement field associated with the fundamental electric field of equation (5a). For simplicity only electrical interactions are considered here. To identify prototypical behaviour, the molecule may be represented by a hydrogenic two-particle system of charges for which we have;

$$\mathbf{P(r)}=\sum_{\alpha=1,2}e_\alpha\int_0^1 d\lambda\left(\mathbf{q}_\alpha-\mathbf{R}\right)\ \ \delta\left[\mathbf{r}-\mathbf{R}-\lambda\left(\mathbf{q}_\alpha-\mathbf{R}\right)\right]\ . \tag{29}$$

From the form of the matrix element it may then be concluded that the exchange of OAM is principally mediated through electric-dipole coupling and involves only the centre of mass motion and the light beam;

$$M_{if}=\left\langle P_z,L_z;e;\{n_{kl}\}\right|H_{int}\left|P_z',L_z';g;\{n_{kl}'\}\right\rangle\ . \tag{30}$$

Crucially, the internal electronic-type motion does not exchange any OAM with the light beam in this leading order of multipole coupling.

On detailed analysis, it transpires that only in the weaker electric quadrupole interaction, or in yet higher order multipoles, is there an exchange involving all three subsystems (the light, the atomic centre of mass and the internal motion). In the electric quadrupole case, one unit of orbital angular momentum is exchanged between the light beam and the internal motion, resulting in the light beam acquiring ($l\pm1$)ħ units of OAM – which are then transferred to the centre of mass motion.

## CONCLUSIONS

In summary, we have developed an internally consistent QED representation of twisted optical beams and their interactions with matter. The application of this formalism has been illustrated in two types of parametric process; one is SHG, the prototypical example of optical nonlinearity; the other is SFG, its non-degenerate counterpart. With experimentally reasonable constraints identified in the mathematical construction of the twisted modes, our results are applicable more widely than to Laguerre-Gaussian modes. In the application to nonlinear optical processes, conservation of orbital angular momentum is seen to arise as a necessary condition for coherent output; hence measurements of SHG using any twisted beam pump are dominated by harmonic signals associated with a twisted output conveying twice the input angular momentum, in accordance with experimental observations by Courtial *et al*. The SFG results, which again signal OAM conservation, can also be applied to the generation of a second harmonic from the coupling of two LG beams of identical frequency, but with different values of $l$. In general, our results rule out any experiments seeking to observe OAM exchange between light beams and molecular systems through modifications in the selection rules governing electric dipole transitions. In *chiral* molecules, the low symmetry enables many optical transitions to be allowed under the selection rules for both electric and magnetic multipoles, and the entanglement of spin and orbital photon angular momentum will require careful extrication; that is the thrust of further work currently in progress.

## ACKNOWLEDGMENTS

This work is supported by the Engineering and Physical Sciences Research Council.

## REFERENCES

1. R. A. Beth, "Mechanical detection and measurement of the angular momentum of light", Physical Review, **50**, 115-125, 1936.
2. S. J. van Enk and G. Nienhuis, "Eigenfunction description of laser-beams and orbital angular-momentum of light", Opt Commun, **94**, 147-158, 1992.
3. S. J. van Enk and G. Nienhuis, "Commutation rules and eigenvalues of spin and orbital angular-momentum of radiation-fields", J Mod Optic, **41**, 963-977, 1994.
4. S. J. van Enk and G. Nienhuis, "Spin and orbital angular-momentum of photons", Europhys Lett, **25**, 497-501, 1994.
5. H. He, M. E. J. Friese, N. R. Heckenberg and H. Rubinsztein-Dunlop, "Direct observation of transfer of angular-momentum to absorptive particles from a laser-beam with a phase singularity", Phys. Rev. Lett., **75**, 826-829, 1995.
6. L. Allen, M. W. Beijersbergen, R. J. C. Spreeuw and J. P. Woerdman, "Orbital angular-momentum of light and the transformation of laguerre-gaussian laser modes", Phys Rev A, **45**, 8185-8189, 1992.
7. J. W. R. Tabosa and D. V. Petrov, "Optical pumping of orbital angular momentum of light in cold cesium atoms", Phys. Rev. Lett., **83**, 4967-4970, 1999.
8. S. M. Barnett, "Optical angular-momentum flux", Journal of Optics B: Quantum and Semiclassical Optics, **4**, S7, 2002.
9. N. B. Simpson, L. Allen and M. J. Padgett, "Optical tweezers and optical spanners with laguerre-gaussian modes", J Mod Optic, **43**, 2485-2491, 1996.
10. M. E. J. Friese, T. A. Nieminen, N. R. Heckenberg and H. Rubinsztein-Dunlop, "Optical alignment and spinning of laser-trapped microscopic particles", Nature, **394**, 348-350, 1998.
11. M. E. J. Friese, H. Rubinsztein-Dunlop, J. Gold, P. Hagberg and D. Hanstorp, "Optically driven micromachine elements", Appl. Phys. Lett., **78**, 547-549, 2001.
12. A. T. O'Neil and M. J. Padgett, "Three-dimensional optical confinement of micron-sized metal particles and the decoupling of the spin and orbital angular momentum within an optical spanner", Opt Commun, **185**, 139-143, 2000.

13. J. Courtial, K. Dholakia, D. A. Robertson, L. Allen and M. J. Padgett, "Measurement of the rotational frequency shift imparted to a rotating light beam possessing orbital angular momentum", Phys. Rev. Lett., **80**, 3217-3219, 1998.
14. I. Bialynicki-Birula and Z. Bialynicki-Birula, "Rotational frequency shift", Phys. Rev. Lett., **78**, 2539-2542, 1997.
15. J. D. Jackson, *Classical electrodynamics*, John Wiley & Sons, 2nd, London, 1975.
16. A. E. Siegman, *Lasers*, Oxford University Press, New York, 1986.
17. M. Lax, W. H. Louisell and W. B. McKnight, Physics Review A, **11**, 1365, 1975.
18. L. Allen, M. J. Padgett and M. Babiker, "The orbital angular momentum of light", Prog Optics, **39**, 291-372, 1999.
19. M. Padgett, J. Arlt, N. Simpson and L. Allen, "An experiment to observe the intensity and phase structure of laguerre-gaussian laser modes", Am J Phys, **64**, 77-82, 1996.
20. L. C. Dávila Romero, D. L. Andrews and M. Babiker, "A quantum electrodynamics framework for the nonlinear optics of twisted beams", Journal of Optics B: Quantum and Semiclassical Optics, **4**, S66, 2002.
21. D. P. Craig and T. Thirunamachandran, *Molecular quantum electrodynamics : An introduction to radiation-molecule interactions*, Dover Publications, Mineola, N.Y., 1998.
22. D. L. Andrews and P. Allcock, *Optical harmonics in molecular systems: Quantum electrodynamical theory*, Wiley-VCH, Weinheim, 2002.
23. M. Babiker, W. L. Power and L. Allen, "Light-induced torque on moving atoms", Phys. Rev. Lett., **73**, 1239-1242, 1994.
24. M. Berry, "Paraxial beams of spinning light", International Conference on Singular Optics, **3487**, 6-11, SPIE - Int.Soc. of Optical Engineering, Bellingham, 1998.
25. A. T. O'Neil, I. MacVicar, L. Allen and M. J. Padgett, "Intrinsic and extrinsic nature of the orbital angular momentum of a light beam", Phys. Rev. Lett., **8805**, art. no.-053601, 2002.