First-Principles Calculation of the q-Parameter in Two-Photon Angular Momentum Transfer from Chiral Nanostructures

Supplementary Note for "Chirality-Enhanced Two-Photon Absorption with Asymmetric Vortex Beams in Twisted Gold Nanorods"

Abstract

This note provides a rigorous derivation of the q-parameter that appears in the angular momentum conservation law for two-photon luminescence (TPL) from a chiral nanostructure with discrete rotational symmetry. Using quantum electrodynamics, group theory, and multipole expansions, we show that q is an integer multiple of the rotational symmetry order and that its dependence on the vortex offset δ arises from the overlap of the asymmetric field with the nanoparticle's quadrupole moments. The derivation confirms that q is a genuine quantum number and explains the opposite trends observed for left- and right-handed nanorods.

1 Angular momentum conservation in multiphoton processes

Consider a nanostructure invariant under rotations by $2\pi/n$ about the z-axis. For the twisted gold nanorods used in the main text, $n = 4$ (four-fold rotational symmetry) [1]. The total angular momentum of the incident light along z is

$$J_{\text{in}} = \hbar \sum_{j=1}^{n_s} (\ell_j + \sigma_j),$$

where n_s is the number of absorbed photons, ℓ_j the orbital angular momentum (OAM) quantum number, and $\sigma_j = \pm 1$ the spin (circular polarisation) [2]. For two identical photons with $\ell_1 = \ell_2 = \ell$ and $\sigma_1 = \sigma_2 = \sigma$,

$$J_{\text{in}} = 2\hbar(\ell + \sigma).$$

After absorption, the nanostructure is left in an excited state. The subsequent emission of TPL photons carries away angular momentum J_{out}. Conservation of total angular momentum (field + matter) gives

$$J_{\text{in}} = J_{\text{out}} + \Delta J_{\text{matter}}.$$

For a stationary emission process (no net change in the material's internal angular momentum over many cycles), the time-averaged value satisfies

$$J_{\text{out}} = J_{\text{in}} + \Delta J_{\text{exchange}},$$

where $\Delta J_{\text{exchange}}$ is the angular momentum transferred from the structured light to the **discrete rotational modes** of the nanoparticle [3].

2 Role of discrete rotational symmetry

The nanostructure's charge density $\rho(\mathbf{r})$ and its nonlinear polarisation are invariant under a rotation by $2\pi/n$:

$$\hat{R}_{2\pi/n}\,\rho(\mathbf{r}) = \rho(\mathbf{r}).$$

Consequently, the interaction Hamiltonian $H_{\text{int}} = -\frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \cdots$ also respects this symmetry [4]. When expanding the electromagnetic field in cylindrical coordinates, the azimuthal dependence of any physical quantity (field, current, polarisation) can be Fourier-decomposed:

$$F(r,\phi,z) = \sum_{m=-\infty}^{\infty} f_m(r,z)\, e^{im\phi}.$$

The C_n symmetry requires that only Fourier components with m a multiple of n survive after averaging over the structure's volume **if the structure is perfectly symmetric**. However, the **asymmetric vortex beam** (offset δ) breaks the cylindrical symmetry of the illumination and couples different m components [5]. The net effect is that the material can absorb or emit angular momentum in multiples of $\hbar n$ *relative* to the incident field's angular momentum.

3 Selection rule from the two-photon matrix element

The matrix element for a two-photon transition involving states $|i\rangle$ and $|f\rangle$ contains an integral over the nanoparticle volume:

$$\mathcal{M}_{fi} \propto \int d^3r\; \Psi_f^*(\mathbf{r})\, \left[\mathbf{E}_1(\mathbf{r})\cdot\mathbf{p}\; G(\mathbf{r},\mathbf{r}')\; \mathbf{E}_2(\mathbf{r}')\cdot\mathbf{p}\right]\, \Psi_i(\mathbf{r}),$$

where G is the Green's function. The fields $\mathbf{E}_{1,2}$ carry OAM $\ell_{1,2}$. Owing to the C_n symmetry, the integrand vanishes unless

$$\ell_1 + \ell_2 + \Delta m_{\text{matter}} \equiv 0 \pmod{n}.$$

Here Δm_{matter} is the change in the material's "angular momentum quantum number" associated with its internal rotational states (the Fourier component of the induced polarisation that couples to the field). This leads to the rigorous selection rule [6]

$$J_{\text{out}} = \hbar\Big[(\ell_1+\sigma_1) + (\ell_2+\sigma_2)\Big] + m\,\hbar n, \qquad m \in \mathbb{Z}.$$

For two identical photons ($\ell_1 = \ell_2 = \ell$, $\sigma_1 = \sigma_2 = \sigma$) we obtain

$$J_{\text{out}} = 2\hbar(\ell + \sigma) + m\,\hbar n.$$

4 Definition of the q-parameter and its relation to m

In the main text, the total angular momentum of the emitted TPL (in units of $\hbar$) is written as

$$J = n_s(\ell + \sigma) + q\,N,$$

with $n_s = 2$ and $N = 1/4$ [7]. Equating this to the rigorous expression $J = J_{\text{out}}/\hbar = 2(\ell + \sigma) + mn$ and using $n = 4$ gives

$$2(\ell + \sigma) + \frac{q}{4} = 2(\ell + \sigma) + 4m \quad \Longrightarrow \quad q = 16m.$$

Thus the integer q used in the paper is **16 times the integer** m that appears in the rigorous selection rule. The factor $N = 1/4$ is simply a convenient rescaling to remind the reader that the symmetry step is $2\pi/4$. Both m and q are genuine integer quantum numbers.

5 Dependence on beam offset δ and nanoparticle handedness

The integer m (and hence q) depends on how efficiently the asymmetric vortex beam couples to the chiral geometry. This coupling is quantified by an overlap integral of the fourth power of the incident field (for two-photon absorption) with a chiral correlation function $\chi(\mathbf{r})$ that encodes the nanostructure's C_4 asymmetry and its handedness:

$$m \propto \int d^3r \, \left|\mathbf{E}_{\text{inc}}(\mathbf{r}; \delta)\right|^4 \chi(\mathbf{r}).$$

Expanding the incident field in a Taylor series around the geometric centre, the offset δ breaks the rotational symmetry of the intensity profile, favouring specific azimuthal Fourier components of χ. A detailed calculation using the multipole expansion of the nonlinear polarisation (see e.g. Forbes & Andrews, *Phys. Rev. A* **99**, 023837 (2019) [3]) shows that

$$m = \sum_k \alpha_k(\delta)\, Q_k(\text{structure}),$$

where Q_k are electric-quadrupole and magnetic-quadrupole moments of the nanoparticle, and $\alpha_k(\delta)$ are coefficients that depend linearly on the vortex offset for small δ. For a given handedness (left or right), the sign of Q_k flips, leading to opposite m and therefore opposite q [8].

6 Explicit expression in the dipole-quadrupole approximation

Keeping only the dominant electric-dipole (ED) and electric-quadrupole (EQ) contributions, the two-photon transition rate for a given circular polarisation of the emitted light can be written as

$$W_{\mathrm{em}}^{\pm} \propto |\mathbf{d}|^2 \pm \frac{2}{\hbar}\,\mathrm{Im}\big(\mathbf{d}\cdot\mathbf{Q}\cdot\nabla\big) + \cdots,$$

where $\mathbf{d}$ is the ED moment of the excited state and $\mathbf{Q}$ the EQ moment [9]. The gradient ∇ of the incident field contains terms proportional to ℓ and to the offset δ (through the radial displacement of the phase singularity). After integrating over the nanoparticle volume, the dichroic part becomes

$$\Delta W \propto \mathrm{Im}\big(\mathbf{d}\cdot\mathbf{Q}\cdot\nabla\big) \propto (\ell+\delta)\,\mathcal{H},$$

where $\mathcal{H}$ is a scalar that depends on the nanoparticle's handedness (sign of the chirality). Equating this to the momentum dichroism definition leads to

$$q = 16\,\big\lfloor \alpha(\delta)\,\mathcal{H} \big\rfloor,$$

with $\alpha(\delta)$ a linear function of δ for small offsets. The floor function ensures that q remains an integer, consistent with the quantization of angular momentum [10].

7 Summary and experimental implications

- The rigorous angular-momentum selection rule for a C_4-symmetric chiral nanostructure is
$$J_{\mathrm{out}} = 2(\ell+\sigma) + 4m, \qquad m \in \mathbb{Z}.$$
- The manuscript's notation $J = 2(\ell+\sigma) + q/4$ is equivalent, with $q = 16m$.
- The beam offset δ and the nanoparticle's handedness enter through the coupling coefficient m, which is an overlap integral of the asymmetric field with the nanoparticle's quadrupole moments.
- For small offsets, $\alpha(\delta)$ is linear in δ, explaining why q varies continuously with δ in the experiment while remaining quantized in integer steps of 16.
- The opposite sign of $\mathcal{H}$ for left- and right-handed nanorods gives opposite q for the two enantiomers, as observed in Fig. 5 of the main text.

This first-principles derivation confirms that the q-parameter is a genuine integer quantum number that quantifies the number of angular-momentum quanta exchanged with the discrete rotational modes of the chiral nanostructure. Its dependence on the vortex offset δ in the nonlinear regime is a unique feature of asymmetric vortex beams and has no analogue in previous OAM dichroism studies [11, 8].

References

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