nature portfolio

Peer Review File

Orbital angular momentum control of strong-field ionization in atoms and molecules

Corresponding Author: Dr Jean-Luc Begin

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In the work "Orbital angular momentum control of strong-field physics in gas phase", authors investigate the strong-field ionization of argon atom and two molecules (R(+)-limonene and acetone) under a sinthesized field, in which they start with a standard LG beam with a well-defined OAM and they displace the singularity, what authors called asymmetric OAM beam. They build up a theory beyond dipole approximation that takes into account also second-order spatial changes via the gradient of the electric field. The theory seems to nicely reproduce the experimental data.

Overall, I believe this is a strong work with very interesting results, but the presentation needs to be definitely improved. The paper starts describing the phenomenon of strong-field ionization under beams carrying OAM. But the story is slowly drifting towards the possible applications of the "synthesized OAM" beams, in which the singularity is displaced, and therefore the gradient of the field gains more importance. Hence, one may wonder if the OAM plays any importance at all or it is just a question of producing a synthesized field with strong field gradients. To be more specific, OAM is linked to a phase singularity and therefore to an physical property of photons, which allow us to quantify their angular momentum by looking at the winding number. But I feel the physics underlying this paper is not about the phase, but rather the field gradient. Of course, one may argue that both are linked, indeed, but the main question is whether we can observe similar physics but just tailoring the field gradient of a beam (independently of the phase of the singularity). In this work you have a convenient knob control, which is the displacement of the singularity, but one may wonder if another knob control is still valid and providing similar physics on the strong-field ionization. In order to link both the start and end of the paper, it will be interesting to be able to address some questions such as: the developed theory is beyond OAM beams? Is it essential to have a phase singularity in the theory to be still valid? Or any synthesized field with strong field gradients will be equally interesting?

I would also like to recommend the following points to clarify and improve the presentation:

i) Figure 1 should include an illustration of the main experiment. I do not see any geometry structure of the main systems to be studied (argon, R(+)-limonene and acetone). Figure 1 may also include some schematics of why studying these different systems.

ii) I had difficulties to understand Fig 1b at first glance. When we refer to OAM, we are not thinking in displacing the singularity. Not sure if the probability of ionization corresponds to the transverse profile of the pulse (Fig. S12 for example). If not, it would be also important to illustrate it here. BTW, not sure that the bottom right panel is correct.

iii) If I think in the paraxial approximation, the displaced singularity should be just like a coherent superposition of LG beams, perhaps in the line of what is mentioned before the conclusion (ref 43). If so, it will be nice to elaborate in this to make a proper link with the standard OAM beams.

iv) Related to the previous comment, if the asymmetric OAM beam is a superposition of OAM beams, then I would expect the beam to rotate significantly under propagation. This may be important to consider in the experiment.

v) Some explanations are needed for some essential concepts. When asymmetric OAM beams are introduced and discussed in the Results section, I recommend to explain these beams with Eq. (19) of the SM.

vi) After Eq. (5), it will help to clarify the weighting factor c, how this is taken? is this calculated or from a reference? Clarify please the sentence “Since our theory excludes the Coulomb potential, and thus ignores hyperfine interactions, higher c-values are required for quantitative analysis.” and why “c=200”.

vii) How the normalization of figure 2 is done? If the displacement is large and the pulse resembles a Gaussian beam, then the ionization probability (charged ion yield) is zero? If the pulse has l=0 (Gaussian), should one obtain the same than if the singularity is largely displaced?

viii) Figure 2c, what occurs for l=3 after 2 microns displacement in the experiment? Is that not possible to show?

ix) Please clarify the sentence “The degree of control achieved using asymmetric OAM beams is significantly higher when compared to complex techniques involving manipulating the peak of the laser field by varying the carrier envelope phase of few-cycle pulse, pulse shaping, coherent control, and utilization of bichromatic light fields”. Be more specific.

x) After investigating the argon atom, there is Fig. 3 for two molecules, one chiral and one achiral. But then, there is no experimental results of the main differences of these molecules and how this is linked to chirality. An probably the most interesting feature, that is an asymmetric double bump structure, is barely discussed. Authors should elaborate the link of the experimental results with chirality, if any, and also please clarify/expand the following statement: “For a specific handedness of helical light, both molecules exhibit an asymmetric double bump structure, unlike argon. This is possibly due to differences in their ionization potentials. In molecules, ionization occurs at lower peak fields, leading to less suppression of ion yields relative to argon at $\delta = \pm 1\mu$m.”

xi) Figure 4a do not fit very well with Fig2b,d. Rather than comparing the slopes, it should be more meaningful to look at the maximum points. Those for l=1 are in larger displacements than for l=3, which is not the case for the experiment.

xii) Can you use higher l (OAM) in the experiment?

xiii) There is a change of colours in the labels of Figure 5.

Minor comments:

1) r_{i,j} before Eq. (2), elaborate in its definition of the distance of a positive and negative charge.

2) Before Eq. (2), the vector potential is expanded in R but R is not explained after a later stage.

3) When Fig.4b is explained, there is a paragraph that refer mainly to figure of the SM. I do not have a good solution for this, but it is strange to have such discussion with several figures of the SM.

4) Clarify the following statement if this is a change of the electric field or a change of the induced ionization probability: “This variation in the peak field strength has a direct impact on the ponderomotive energy of the free electron, as depicted in Fig. 5a”

Before recommending this work for publication, strong changes are needed.

Reviewer #2

(Remarks to the Author)
This manuscript demonstrates a new dimension in manipulating nonlinear phenomena in laser-matter interaction. By displacing the phase singularity of the OAM beam, asymmetric helical light pulses have potential applications in strong-field ionization, high harmonic generation, and super-resolution imaging. The manuscript is of general interest, is well-written, and can be considered for publication with the following comments addressed:
1, When the OAM beam intensity was mentioned in the captions of Figure 2, 3, and 4, is it the local peak intensity of OAM beam or the peak intensity of the Gaussian beam before the q-plate is added? This should be clarified in the manuscript.
2, In the introduction, in addition to the structured OAM beam, it would be beneficial to also introduce pulse shaping methods as a conventional approach to control the interaction between light beams and matter, such as the strong-field ionization [ref. 36] and NSDI.
3, The term ε, ellipticity, should be defined when it is first used in Figure 5.
4, Figure 5 shows the ponderomotive energy and force as a function of displacement of the singularity, which could significantly impact high harmonic generation by extending the cut-off harmonics. It would be beneficial to address this point by a quick simulation.
5, Regarding the displacement of the singularity δ, instead of providing the value in μm, it would be better to present the normalized value (normalize to w0).

6, In Figure S4, could the Z=67 peak also be a doubly charged fragment?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I read the new version of the manuscript “Orbital angular momentum control of strong-field physics in gas phase” and the response of authors. Overall, authors have addressed many of the arisen points and they have improved the presentation in the new version of the manuscript. However, the paper is still difficult to follow, it starts describing the phenomenon of strong-field ionization under beams carrying OAM but the story slowly drifts towards the possible applications of the “synthesized OAM” beams. Also, I am still not convinced that this phenomenon is mainly dependent on the OAM. In the response it is claimed:

“Ionization of atoms and molecules with OAM beams is purely a phase effect whereas the applications discussed in the article (such as ponderomotive effects and sub-wavelength microscopy) are a result of intensity variation in structured light beams.”

Also, now after Eq. (1) in the paper, it reads the following:

“Taking a gradient of this field leads to a factor of ± l that either enhances or reduces the potential distortion”

But one could always argue that this is also true if you take an Hermite Gaussian (HG) basis. You can get strong changes in the intensity profile, and now your gradient would depend on other quantum numbers (n,m) that are not related to the transverse angular phase of the beam, i.e. the winding number (l,p). As I was trying to argue in my initial review, you may think this phenomenon of displacing the origin as a quantum coherent superposition, both in the LG or HG basis, and your gradient can be expressed in both basis. And this constraining ourselves in the paraxial approximation, out of the paraxial approximation we may have stronger gradient effects, not necessarily related to the angular phase of the beam. In this work you have a convenient knob control, which is the displacement of the singularity on an initial LG mode, but one could obtain the same phenomenon using for example a superposition of HG modes. To be clear, the theory is purely dependent of the gradient of intensity, it is not related to the transport of angular momenta of photons in the propagation axis. Authors should revise this point.

Reviewer #2

(Remarks to the Author)
I thank the authors for the extensive response and modifications to the manuscript. It's in good shape now.

Minor comments:

1, I am satisfied with the reply to referee #1 with respect to the role played by the strong field gradients. However, I still wonder if it's experimentally feasible to generate synthesized light beams with strong field gradients but without helical phase.

2, Thank you for giving the normalized displacement of singularity (δ-position), but I saw 'ω0/3 μm' in the main text and plots, where the 'μm' is unnecessary.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I read the new response of the authors and I believe they addressed my main concern. In their reply, it is nicely explained how the OAM, or helical phase, somehow controls the asymmetry of the gradient, and this is imprinted when the ionization is measured as a function of the singularity displacement. To be honest, their reply addresses such fundamental question that it would be very interesting to have the discussion of non-OAM and OAM beams with strong gradients and their effects on ionization. I am sure this is not a close point, and it would trigger further investigations. I would suggest authors to consider to add this discussion in the SM at least.

I would also suggest to do a minor change in the title to “Orbital angular momentum control of strong-field ionization in gas phase”

Reviewer #2

(Remarks to the Author)
The updates in the new version of Orbital angular momentum control of strong-field physics in gas phase and the authors' response emphasize that ionization modulation with OAM beams results from the combination of helical phase and field gradients. Detailed explanations and examples have been provided.
All my concerns have been addressed, and I have no further comments.

Response to Reviewer #1:

Thank you for positive response to our work and we appreciate the detailed review of the manuscript. Below is the response to your comments and the changes made to improve the delivery of our research. (Comments in red, responses in blue).

General comments:

(1) The paper starts describing the phenomenon of strong-field ionization under beams carrying OAM. But the story is slowly drifting towards the possible applications of the "synthesized OAM" beams, in which the singularity is displaced, and therefore the gradient of the field gains more importance. Hence, one may wonder if the OAM plays any importance at all or it is just a question of producing a synthesized field with strong field gradients.

We realize that the influence of phase and gradients on strong field ionization with OAM beams was not clearly identified. As a result, the article gave the impression that field gradients are more important when potential applications were discussed. However, phase singularity and field gradients are linked together, as rightly pointed, and one cannot observe similar physics by simply tailoring the field gradient of a beam. Helical phase gives rise to OAM dependent ionization and field gradients in an asymmetric OAM beam further amplifies it by enhancing or reducing the distortion of the atomic potential. Asymmetric OAM beams enable to overcome the spatial averaging effects so that OAM dependence can be observed in the total ion yields. To summarize, the combination of helical phase and field gradient lead to the observed modulation in ionization.

In beams with no helical phase, tailoring the field gradient can lead to some modulation of ionization because the peak field varies but the change would be limited compared to OAM beams. Tailored non-OAM beams would produce results similar to conventional pulse shaping methods where only an order of magnitude change was observed. However, with OAM beams the modulation can be significantly enhanced by increasing the l-value and position of the singularity resulting in complete suppression of ionization by changing the handedness of helical phase. For l=3, we observed two orders of magnitude differences in ionization between the left- and right-helical light.

To address these issues, we modified the beginning of the results section to emphasize the influence of helical phase on ionization and how it gets enhanced by the field gradient obtained by shifting the phase singularity.

(2) To be more specific, OAM is linked to a phase singularity and therefore to an physical property of photons, which allow us to quantify their angular momentum by looking at the winding number. But I feel the physics underlying this paper is not about the phase, but rather the field gradient. In this work you have a convenient knob control, which is the displacement of the singularity, but one may wonder if another knob control is still valid and providing similar physics on the strong-field ionization. In order to link both the start and end of the paper, it will be interesting to be able to address some questions such as: the developed theory is beyond OAM beams? Is it essential to have a phase singularity in the theory to be still valid? Or any synthesized field with strong field gradients will be equally interesting?

Ionization of atoms and molecules with OAM beams is purely a phase effect whereas the applications discussed in the article (such as ponderomotive effects and sub-wavelength microscopy) are a result of intensity variation in structured light beams. However, as demonstrated, these effects can be scaled with l-value so helical phase and field gradient effects cannot be separated in OAM beams. In contrast, synthesized light beams with no helical phase would only lead marginal changes to ionization and ponderomotive effects, but more importantly cannot be scaled up.

The interplay between the helical phase and the field gradient can be clearly seen in the transition amplitude describing the tunnel ionization probability (Eq. 4 in new version). It consists of two effects; the electric quadrupole and magnetic dipole both in the pre-exponent and in the classical action via the vector potential gradient. The electric quadrupole (E1E2) in the preexponent affects only ionization and survives averaging for asymmetric beams. The non-dipole terms of the classical action in the exponential changes the electron trajectory

- not important for ionization but for HHG and acceleration. There are three scenarios when dipole approximation breaks down.

1. Short wavelength limit, such as x-rays, when the wavelength of the laser field approaches the atomic size.
2. Long wavelength limit and high laser intensities, due to the magnetic field component. Either the magnetic dipole transitions play a prominent role and/or the electron trajectories are altered by the Lorentz force at relativistic (~ 10^{18} W/cm2) and non-relativistic (~10^{14} W/cm^2) intensities, when electron displacement perpendicular to the field polarization direction approaches Bohr radius. This breakdown is mostly due to changes to the pulse envelope.
3. When electric quadrupole transitions become important due to the helical phase and field gradients of the structured light. In this case the phase singularity violates the dipole approximation where the carrier wave modifies the envelope profile on sub-wavelength scale. The presence of non-dipole terms in classical action indicates changes to the carrier wave affects the ponderomotive energy more efficiently than changes to envelope (scenario 2 above) suggesting phase singularity is critical. As a result, synthesized light beams with strong field gradients but without helical phase cannot reproduce the experimental results.

<u>Specific comments:</u>

i) Figure 1 should include an illustration of the main experiment. I do not see any geometry structure of the main systems to be studied (argon, R(+)-limonene and acetone). Figure 1 may also include some schematics of why studying these different systems.

Figure 1 now includes an illustration of the experimental setup. We have separated the symmetric and asymmetric ionization profiles to highlight the significance of helical phase of OAM beam and the influence of field gradient in enhancing/suppression ionization. For a better understanding of the effects of asymmetric OAM beams on ionization, we included the transverse ionization probability profiles for (l=$\pm$1 at ($\pm\delta$)-positions. Figure 3 was modified to include the geometrical structures of S(+)-limonene and acetone. The main text includes a section explaining the rationale behind using these systems, and we elaborate on the importance of chirality in the discussion of Figure 3.

ii) I had difficulties to understand Fig 1b at first glance. When we refer to OAM, we are not thinking in displacing the singularity. Not sure if the probability of ionization corresponds to the transverse profile of the pulse (Fig. S12 for example). If not, it would be also important to illustrate it here. BTW, not sure that the bottom right panel is correct.

Typically, OAM beams are symmetric with the phase singularity at the center. The intensity profile is independent of the handedness of helical phase, depicted in new Fig. 1c or Fig S11a. However, the transverse ionization probability displays an asymmetry due to local distortion of the atomic potential when the handedness of the helical phase is changed. This is purely a phase effect and can be observed by locally probing ionization. However, when the total ion yields are monitored this effect vanishes due to spatial averaging across the beam cross-section. The averaging effects can be overcome by displacing the singularity. The resultant field gradients enhance/supress the distortion of the atomic potential when the handedness of helical phase is changed leading to modulation in the total ion yields. To make this distinction clear we modified the figure to show the transverse ionization profiles for both l=$\pm$1 for $\pm\delta$-positions. There seems to be some confusion about the bottom panels depicting the ionization profiles for asymmetric beams. There is nothing wrong with plots shown. To avoid potential confusion, we modified the figure (Fig. 1d) to show that ionization can be manipulated either by changing the handedness of OAM beam or the position of the singularity in the beam. This is in fact the unique feature of strong field ionization with OAM beams.

iii) If I think in the paraxial approximation, the displaced singularity should be just like a coherent superposition of LG beams, perhaps in the line of what is mentioned before the conclusion (ref 43). If so, it will be nice to elaborate in this to make a proper link with the standard OAM beams.

The phase singularity in an OAM beam can be experimentally displaced either by translating the phase plate used to generate the OAM beam or by a coherent superposition of Gaussian and LG beams. The latter method was used by us to displace and split the singularities, enabling to manipulate the position of nanocone within the ablation craters on silicon [Rahimian et al, Scientific Reports, 2020]. We now clearly state the alternate method of displacing the singularity in the main text and elaborate further in the experimental methods section. Whichever method is used to shift the singularity, the physics remains the same. However, the phase singularity is crucial, it is not possible to obtain the observed results with synthesized light beams that do not carry the helical phase or with coherent superposition of non-OAM beams.

iv) Related to the previous comment, if the asymmetric OAM beam is a superposition of OAM beams, then I would expect the beam to rotate significantly under propagation. This may be important to consider in the experiment.

It is possible for the beam to undergo rotation after propagation. However, this is monitored in the experiment and can be quickly corrected. During the experiment, the direction of displacement of the singularity was monitored by observing the null intensity region in the defocused beam. This allowed us to make on the fly corrections to the position of the singularity along a particular orientation. Consequently, any rotation of the singularity could be corrected provided the center is well defined, which was identified by identical ion yields for left- and right-handed helical light.

v) Some explanations are needed for some essential concepts. When asymmetric OAM beams are introduced and discussed in the Results section, I recommend to explain these beams with Eq. (19) of the SM.

We agree and introduce the symmetric and asymmetric LG beam equations in cartesian coordinates in the main text.

vi) After Eq. (5), it will help to clarify the weighting factor c, how this is taken? is this calculated or from a reference? Clarify please the sentence "Since our theory excludes the Coulomb potential, and thus ignores hyperfine interactions, higher c-values are required for quantitative analysis." and why "c=200".

The weighting factor is derived from the contributions of hyperfine interactions between the electron and the magnetic dipole and the electric quadrupole of the nuclei, $H_{HFI} = H_{\mu} + H_{Q}$. This results in a small shift in the otherwise degenerate electronic state. The total induced quadrupole moment of the atom consists of nuclear, magnetic and quadrupole contributions and is given by $Q = Q_N + Q_{\mu} + Q_Q$. For argon, the nuclear moment, Q_N, is 0.01(4) barn (ref). The weighting factor c is obtained by determining the contribution of the hyperfine interaction, $c = Q/Q_N$. The c-value for a 3p state varies within the order of $10^2 - 10^3$for a total atomic angular momentum of $F = I \pm \frac{1}{2}$ and $F = I \pm \frac{3}{2}$. The range of c-values alter the shape of ionization probability as a function of position of the singularity, as show in supplementary Fig S1b. We choose c = 200 to show the double bump feature, which also depends on the laser intensity (Fig. S1a), observed in molecules and expect to exist in atoms at higher laser intensity.

Our theoretical model is based on strong field approximation which ignores the influence of coulomb potential on the ionized electron and uses the single active electron approximation. In addition, within the Born-Oppenheimer approximation, our model considers only the electron wavefunction and does not consider the influence of nucleus on the energy level, thereby ignoring hyperfine interactions. These approximations lead to discrepancies between theory and experiment, necessitating the use of a weighting factor c for a full quantitative analysis. A section has been added to the article.

vii) How the normalization of figure 2 is done? If the displacement is large and the pulse resembles a Gaussian beam, then the ionization probability (charged ion yield) is zero? If the pulse has l=0 (Gaussian), should one obtain the same than if the singularity is largely displaced?

The ion yields were normalized with respect to the maximum yields obtained at a specific $\pm\delta = \frac{w_0}{3}$ position for the left- or right-handed OAM beam. When the singularity is far away from the center (~w_0), the intensity profile resembles a Gaussian beam. So, the resultant ion yields of the OAM beam would be similar to that of a Gaussian beam. The yields are not zero at high $\pm\delta$-positions but are small. This is done on purpose to avoid saturating the yields at $\pm\delta = \frac{w_0}{3}$. Ion yield measurements for argon were accumulated over 100,000 laser shots. The maximum yield was typically about 80,000 counts.

viii) Figure 2c, what occurs for l=3 after 2 microns displacement in the experiment? Is that not possible to show?

The incident Gaussian beam was 10mm and the q-plate aperture was ~ 15mm. So, experimentally, we were limited by how much the q-plate could be shifted without clipping the incident beam. This translated to a displacement of singularity by about 2μm in the interaction region. It is possible to conduct experiments with displacements beyond 2μm by using an alternate method of displacing the singularity such as coherent superposition of OAM beams with tunable amount of Gaussian beam, achieved by varying the voltage on the q-plate (as per your suggestion, this alternate method is now mentioned in the methods sections).

ix) Please clarify the sentence "The degree of control achieved using asymmetric OAM beams is significantly higher when compared to complex techniques involving manipulating the peak of the laser field by varying the carrier envelope phase of few-cycle pulse, pulse shaping, coherent control, and utilization of bichromatic light fields". Be more specific.

Conventional pulse shaping techniques can modulate the ionization signal by up to an order of magnitude. In contrast, OAM beams provide more than two orders of magnitude modulation of the ion yields and more importantly scale up with higher l-values.

x) After investigating the argon atom, there is Fig. 3 for two molecules, one chiral and one achiral. But then, there is no experimental results of the main differences of these molecules and how this is linked to chirality. An probably the most interesting feature, that is an asymmetric double bump structure, is barely discussed. Authors should elaborate the link of the experimental results with chirality, if any, and also please clarify/expand the following statement: "For a specific handedness of helical light, both molecules exhibit an asymmetric double bump structure, unlike argon. This is possibly due to differences in their ionization potentials. In molecules, ionization occurs at lower peak fields, leading to less suppression of ion yields relative to argon at $\delta = \pm 1\mu$m."

In chiral systems, the two enantiomers that are non-superimposable mirror images, are discernible only when they interact with another chiral system. A typical optical probe exploits the broken symmetry of circularly polarized light resulting, in differential absorption of left- and right-handed polarizations, leading to circular dichroism. However, we have recently demonstrated enhanced chiral sensitivity in liquids and solids *[Nature photonics 2023, Nature Comm. 2024]* by transferring this broken symmetry to the helical phase of the light rather than its polarization. In achiral systems, the conventional understanding is that dichroism does not exist due to the existing Sn symmetry. However, achiral liquids and solids exhibited dichroism when irradiated with asymmetric OAM beams, where the symmetry is broken spatially in the beam profile and the phase of light. This raises the question of whether helical dichroism can also be observed in the gas phase. This was the rationale to show results for a chiral and achiral molecule. For a specific enantiomer, left- and right-handed helical light produced different ion yields. However, for a specific helicity of light, the ion yields remained similar for the two enantiomers within the experimental errors, in contrast to the enhanced chiral sensitivity observed in liquids and solids. This is possibly because of the intensities used in the experiments, where tunnel ionization is predominant. Electron transitions mostly from the ground state to continuum without involving the chiral sensitive excited states. Therefore, the ionization rates are expected to be similar for both the enantiomers, albeit in different directions. So, probing the electron angular distributions would provide more chiral sensitivity than the total ion yields.

The double bump structure observed in molecules for a specific handedness of helical light, is likely due to differences in their ionization potentials (8.5 eV for limonene, 9.7 eV for acetone) compared to argon (15.6 eV). The double bump feature is influenced by the laser intensity and the strength of the E1E2 coupling term (see Supplementary Fig. S1a,b) and becomes more pronounced with increasing intensity approaching saturation. Strong field ionization with OAM beams is a consequence of the interplay between peak field strength and field gradients. The latter gives rise to helicity dependent ionization while the former determines the overall ionization rate. At laser intensities approaching saturation, the peak field strength dominates the gradient contribution leading to higher ionization rates but reduced differences in ionization between the left- and right-handed helical light (see Supplementary Fi.g S5 insets) due to ground state depletion. At intensities well below saturation, the field gradient contribution dominates and has a greater impact on the helicity-dependent ionization rate. As a result, one handedness of helical light can completely suppress ionization eliminating the asymmetrical double bump feature. In molecules, the experimental intensities used were closer to their saturation intensities compared to argon.

xi) Figure 4a do not fit very well with Fig2b,d. Rather than comparing the slopes, it should be more meaningful to look at the maximum points. Those for l=1 are in larger displacements than for l=3, which is not the case for the experiment.

We believe the simulation results agree well the experiment. Unfortunately, figure 4a legend had an error with the wrong labelling of the curves, possibly leading to some confusion. The error has been fixed and also represented $l = 3$ with dashed curves in Fig. 4a,b. Experimentally, the maximum differential signal occurs at ~wo/3 and ~wo/2 for l=1, 3, respectively. Numerical results deviate from experiment, but the trend remains the same. Also, a careful look at $\delta = 0$ suggests a slight change in slope for l=3 as observed in the experiments.

xii) Can you use higher l (OAM) in the experiment?

Yes, gas-phase experiments allow the use of higher l-values compared to liquid- or solid-state measurements due to the negligible influence of propagation effects (nonlinearities in materials with high density). However, as l-value increases, the size of the singularity gets bigger requiring higher laser powers, affecting the operation of the q-plate. Moreover, the difference between minimum and maximum ion yields would increase significantly leading to signal to either saturate or fall below error threshold making measurements difficult. We believe l=9 is feasible experimentally. This is the reason we carried out simulations at that value and not beyond.

xiii) There is a change of colours in the labels of Figure 5.

Agreed and implemented.

<u>Minor comments:</u>

1) r_{i,j} before Eq. (2), elaborate in its definition of the distance of a positive and negative charge.

r_{i,j} is the coordinates of the quadrupole moment.

2) Before Eq. (2), the vector potential is expanded in R but R is not explained after a later stage.

R represents the coordinates of the laser beam profile and was defined in the paragraph prior to the equation.

3) When Fig.4b is explained, there is a paragraph that refer mainly to figure of the SM. I do not have a good solution for this, but it is strange to have such discussion with several figures of the SM.

We understand the dilemma. Moving the figures referenced in the supplementary to the main text would distract the readers from the key experimental and theoretical results. However, they provide additional information that would be beneficial for a comprehensive understanding of how the position of the singularity influences ionization and the effect of laser intensity and c-value on the shape of the ionization probability.

4) Clarify the following statement if this is a change of the electric field or a change of the induced ionization probability: “This variation in the peak field strength has a direct impact on the ponderomotive energy of the free electron, as depicted in Fig. 5a”

This is a change in the electric field due to the displacement of singularity.

Response to Reviewer #2:

Thank you for your positive evaluation of our work and recognizing its importance in providing new insights into light-matter interactions. Below we respond to your comments. (Comments in red, responses in blue).

1, When the OAM beam intensity was mentioned in the captions of Figure 2, 3, and 4, is it the local peak intensity of OAM beam or the peak intensity of the Gaussian beam before the q-plate is added? This should be clarified in the manuscript.

The intensity represents the peak intensity of the OAM beam at the interaction region. It is now specified in the main text.

2, In the introduction, in addition to the structured OAM beam, it would be beneficial to also introduce pulse shaping methods as a conventional approach to control the interaction between light beams and matter, such as the strong-field ionization [ref. 36] and NSDI.

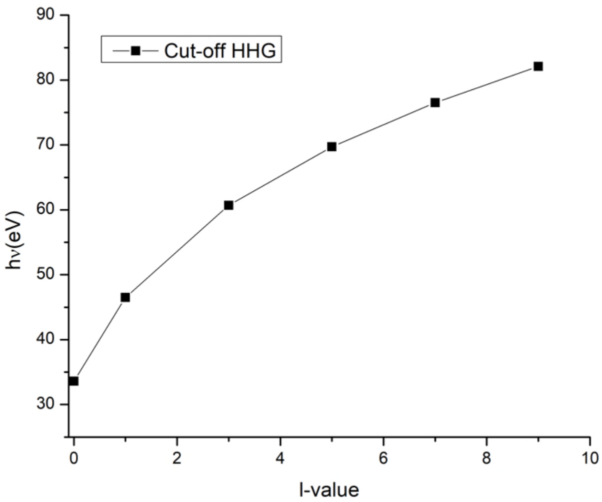
We agree and added a section in the introduction section.

3, The term ε, ellipticity, should be defined when it is first used in Figure 5.

We agree and implemented it in the figure caption.

4, Figure 5 shows the ponderomotive energy and force as a function of displacement of the singularity, which could significantly impact high harmonic generation by extending the cut-off harmonics. It would be beneficial to address this point by a quick simulation.

We believe a quick classical simulation that supported our claim on higher high harmonics was shown in Figure S12 of the old supplementary. However, we agree that the location is more impactful with the ponderomotive figure in Fig 5a). Therefore, we moved the classical trajectories curve to the main text as fig 5c). Below we include an additional curve to demonstrate the influence of higher l-value on the harmonic cut-off.



5, Regarding the displacement of the singularity δ, instead of providing the value in μm, it would be better to present the normalized value (normalize to w0).

We agree and changed all plots containing the displacement of singularity (δ-position) in the main text to the normalized beam waist, w_0.

6, In Figure S4, could the Z=67 peak also be a doubly charged fragment?

The peak at $\frac{m}{z} = 67$ cannot be a doubly charged fragment because there is no stable singly charged fragment ion at $\frac{m}{z} = 134$. However, it is possible to have a doubly charged fragment ion at $\frac{m}{z} = 67.5$, which we do not observe.

Response to Reviewer #1:

Thank you once again for reviewing the second draft of our article. We value your input and discussion, and we believe the revisions does enhance the presentation of our research and address your concerns. (Comments in red, responses in blue)

Comment 1 part 1 (**bold**):

I read the new version of the manuscript "Orbital angular momentum control of strong-field physics in gas phase" and the response of authors. Overall, authors have addressed many of the arisen points and they have improved the presentation in the new version of the manuscript. **However, the paper is still difficult to follow, it starts describing the phenomenon of strong-field ionization under beams carrying OAM but the story slowly drifts towards the possible applications of the "synthesized OAM" beams.** Also, I am still not convinced that this phenomenon is mainly dependent on the OAM. In the response it is claimed:

"Ionization of atoms and molecules with OAM beams is purely a phase effect whereas the applications discussed in the article (such as ponderomotive effects and sub-wavelength microscopy) are a result of intensity variation in structured light beams."

The layout of the paper is based three key results

(1) Influence of OAM on ionization (Fig. 1).
(2) Influence of field gradients in amplifying the OAM-dependent ionization (Fig. 2-4).
(3) Possible applications of OAM-dependent ionization (Fig. 5-6). *This is where there seems to be some confusion, and we would like to clarify.*

OAM-dependent ionization of atoms in strong fields is the main result, enabling the control of ionization (Figures 1-4). Since ionization is the first step in attosecond science and strong field physics, our results can have profound impact on these fields. To highlight this, we discussed two possible applications (Fig 5-6) of using light beams carrying orbital angular momentum. We agree that some form of structured light beams with no helical phase can reproduce results in figure 5-6 which are presented as two applications. However, the degree of control on ionization demonstrated in Fig. 2-4 requires both helical phase and field gradients.

Ponderomotive energy (Fig. 5) depends on the laser intensity. So, in-principle one can enhance it by using structured non-OAM light beams. Similarly, field localization can be achieved with structured non-OAM light beams or by coherent superposition of beams to create a hot spot. For example, both the asymmetric hallow Gaussian and the coherent superposition of $aHG_{10} + aHG_{00}$ beams (see comment 1 part 2) have no OAM but can generate higher peak field strength compared to a lowest order Hermite-Gaussian. So, displacing the singularity will lead to greater intensity variation in the beam profile and hence the enhancement. This will correspond to a specific curve shown in figure 5. <u>In this respect, any structured or synthesized light with significant gradients in the intensity distribution could be used for such applications and we agree OAM provides a convenient knob to alter the intensity effectively.</u> With commercial availability of tunable q-plates or spatial light modulators it is an efficient method to enhance the ponderomotive energy or localize the peak intensity. However, this does not take away the fact that OAM beams can control strong-field ionization and the associated phenomena.

We have clarified thise point in the article which should help with the transition from results to applications on page 8.

Comment 1 part 2 (**bold**):

I read the new version of the manuscript "Orbital angular momentum control of strong-field physics in gas phase" and the response of authors. Overall, authors have addressed many of the arisen points and they have improved the presentation in the new version of the manuscript. However, the paper is still difficult to follow, it starts describing the phenomenon of strong-field ionization under beams carrying OAM but the story slowly drifts towards the possible applications of the "synthesized OAM" beams**. Also, I am still not convinced that this phenomenon is mainly dependent on the OAM. In the response it is claimed:**

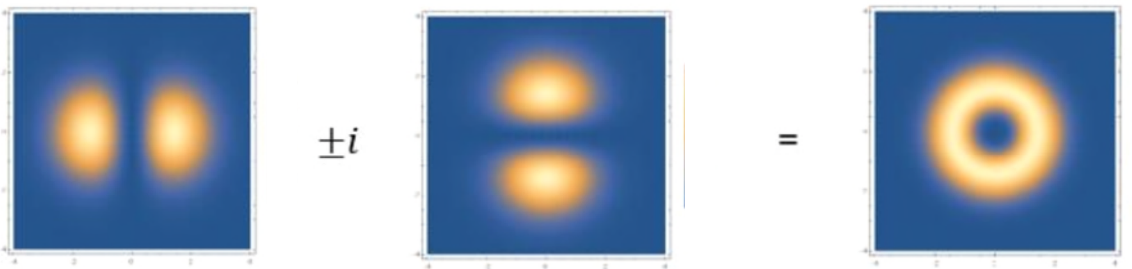
"Ionization of atoms and molecules with OAM beams is purely a phase effect whereas the applications discussed in the article (such as ponderomotive effects and sub-wavelength microscopy) are a result of intensity variation in structured light beams."

The transition from symmetric OAM beams to asymmetric OAM beams is essential to experimentally observe strong OAM-dependent modulation of ionization yields. This is because with symmetric OAM beams, though the ionization probability exhibits an OAM-dependent asymmetry that can only be observed by probing the ionization locally, global probing of ionization upon spatial averaging leads to the total ionization probability/yields being independent of OAM due to their symmetry in the field gradients. The averaging effects are offset by displacing the singularity to introduce asymmetrical field gradients.

While OAM and field gradient effects are intertwined in the experiments, they can be isolated theoretically by simulating ionization with synthesized light fields that mimic the asymmetric OAM beams with or without the helical phase vis-à-vis OAM. As you rightly pointed out, a coherent superposition of Hermite-Gaussian (HG) and Laguerre-Gaussian (LG) basis will result in various intensity distributions with increasing field gradients. Depending on the superposition states, the resulting beam may or may not carry OAM.

Helical light can be generated by a coherent superposition of Hermite-Gaussian beam of orthogonal states HG_{10} and HG_{01} by introducing a $\pi/2$ phase difference between such states to generate LG_0^1. The handedness of the LG beam is changed from +1 to -1 when an extra π phase shift is introduced between the orthogonal states.

$$LG_0^1 = HG_{10} + HG_{01}e^{\pm i\pi/2}$$



This method can also be used to generate asymmetrical LG if the orthogonal states contain an asymmetric parameter δ.

$$HG_{mn} = E_0 e^{-\frac{x^2+y^2}{w_0^2}}\left[H_m\left(\frac{\sqrt{2}x}{w_0}\right)H_n\left(\frac{\sqrt{2}y}{w_0}\right)\right] \Longrightarrow aHG_{mn} = E_0 e^{-\frac{x^2+y^2}{w_0^2}}\left[H_m\left(\frac{\sqrt{2}(x\pm\delta\eta)}{w_0}\right)H_n\left(\frac{\sqrt{2}(y\pm\delta\zeta)}{w_0}\right)\right]$$

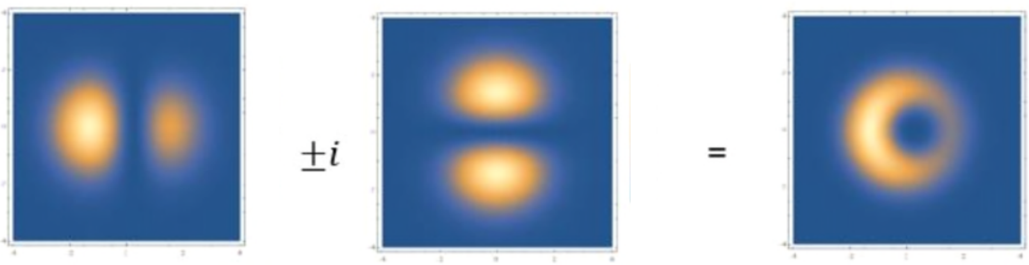
$$aLG_0^1 = aHG_{10} + aHG_{01}e^{\pm i\pi/2}$$

$$aLG_0^1 = E_0 e^{-\frac{x^2+y^2}{w_0^2}} \left[aH_1\left(\frac{\sqrt{2}(x \pm \delta\eta)}{w_0}\right) aH_0\left(\frac{\sqrt{2}(y \pm \delta\zeta)}{w_0}\right) \pm i\, aH_0\left(\frac{\sqrt{2}(x \pm \delta\eta)}{w_0}\right) aH_1\left(\frac{\sqrt{2}(y \pm \delta\zeta)}{w_0}\right)\right]$$

Using the properties of the Hermite polynomials, the above expression can be reduced to the equation derived in the supplementary file (equation 20).

$$aLG_0^1 = \frac{\sqrt{2}E_0}{w_0} e^{-\frac{x^2+y^2}{w_0^2}} [(x \pm \delta\eta) \pm i\,(y \pm \delta\zeta)]$$

The sign of the phase delay between both orthogonal Hermite-Gaussian states results in handedness of the helical light ($\pm l$) and the $\pm$ in front of the δ-position determines the direction of displacement.



Our experimental and simulation results shown in figures 1-4 exhibit a distinctive asymmetrical features in ionization probability as a function of the position of the singularity. This is possible only when light contains both orbital angular momentum and field gradients. To differentiate the effect of gradients and helical phase on our results, we calculated the ionization probability of argon for structured light with no helical phase but with strong intensity distribution. Below we consider two examples of such non-OAM structured light beams.

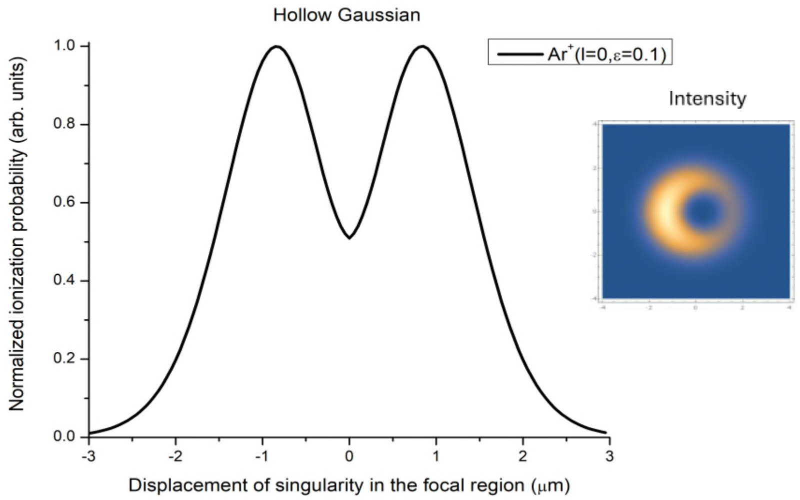
Example 1: Hollow Gaussian beam which is a coherent superposition in the LG basis (or HG basis). The electric field is expressed below

$$E(\rho, \phi) = \left(\frac{\rho}{w_0}\right)^{|l_1|+|l_2|} e^{i(l_1+l_2)\phi} e^{-\left(\frac{\rho}{w_0}\right)^2}$$

Where $\phi = \arctan\left(\frac{y}{x}\right)$ and $\rho = \sqrt{x^2+y^2}$, the OAM order l_1 and l_2 are for the two vortex beams. If $l = l_1 = -l_2$ the resulting electric field is a hollow Gaussian field.

$$E(\rho, \phi) = \left(\frac{\rho}{w_0}\right)^{2l} e^{-\left(\frac{\rho}{w_0}\right)^2}$$

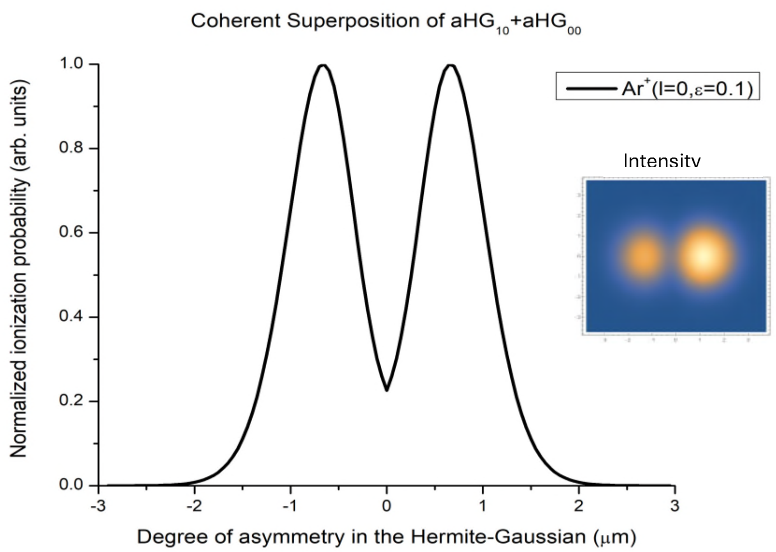
Furthermore, by introducing the shifting parameter δ in x and y one can generate asymmetrical hollow Gaussian. This non-OAM structured beam, which is a coherent superposition of two aLG beams with opposite handedness, exhibits strong intensity variation due to the presence of singularity.



The ionization yields as a function of displacement of the singularity exhibits a symmetrical double bump shape, as one would expect. As the singularity is displaced from the center, the peak intensity increases leading to higher ionization probability. Beyond a certain position of the singularity, the peak intensity and the ionization probability decreases as the beam starts to resemble a Gaussian.

Such a symmetric double pump feature is due to lack of OAM. In the presence of helical phase, the handedness of OAM would further influence the bending of the atomic potential as a function of δ-position leading to asymmetry in ionization probability as shown in the experimental and theoretical curves of Figures 2-4. Therefore, helical phase has a strong influence on ionization and leads to enhanced modulation of total ion yields. A pure gradient effect cannot produce such strong modulation and results in a symmetric variation of ionization probability as shown above.

Example 2: Consider coherent superposition of asymmetric Hermite-Gaussian $aHG_{10} + aHG_{00}$ resulting in a beam with no OAM and null intensity but with strong field distributions. The result is again a symmetric double bump however with narrower peaks due to the change in the beam profile and a slightly deeper modulation.



To summarize:

(1) Ionization can be influenced by OAM alone but is amplified by the asymmetry in the beam resulting in asymmetric field gradients.
(2) Strong field gradients in the intensity distribution alone can alter the distortion of atomic potential leading to some modulation in the ionization probability/yields. However, the degree of control is limited. Moreover, the modulation is symmetric as function of position of the singularity.
(3) OAM enables to further manipulate the distortion of the potential by either suppressing or enhancing the distortion leading to asymmetric distribution of the ionization probability/yields. Therefore, structured light with OAM provides an additional control to turn on/off the ionization (example: Fig. 2c at higher l-values).

We believe, the above explanation is convincing enough to show that our results on strong-field ionization are influenced by the field gradients and dependent on the OAM value.

Comment 2:

"Taking a gradient of this field leads to a factor of ± l that either enhances or reduces the potential distortion"

But one could always argue that this is also true if you take an Hermite Gaussian (HG) basis. You can get strong changes in the intensity profile, and now your gradient would depend on other quantum numbers (n,m) that are not related to the transverse angular phase of the beam, i.e. the winding number (l,p). As I was trying to argue in my initial review, you may think this phenomenon of displacing the origin as a quantum coherent superposition, both in the LG or HG basis, and your gradient can be expressed in both basis. And this constraining ourselves in the paraxial approximation, out of the paraxial approximation we may have stronger gradient effects, not necessarily related to the angular phase of the beam. In this work you have a convenient knob control, which is the displacement of the singularity on an initial LG mode, but one could obtain the same phenomenon using for example a superposition of HG modes. To be clear, the theory is purely dependent of the gradient of intensity, it is not related to the transport of angular momenta of photons in the propagation axis. Authors should revise this point.

We agree non-OAM synthesized light can produce strong changes in the intensity profile, via superposition in the HG and LG basis, as shown in the two examples discussed above. These gradients can lead to a dependence on the m,n quantum numbers that are not related to the angular phase of the beam. However, they cannot control the ionization yields to the same degree as an LG beam with OAM. In the absence of OAM, field gradients in the intensity distribution can also change the amount of distortion of the atomic potential but does not allow for control (on/off switch) of the atomic potential. This control is a result of the handedness of helical light combined with the asymmetric parameter. By changing the handedness of the helical light from $+l \rightarrow -l$ (at a specific δ-position) the bending of the atomic potential can further be enhanced or decreased (see figure 1) which correlates to the control and suppression of ionization yields expressed by the asymmetric ion yield distribution in figure (2-4) of the article.

The applications discussed in the article (Figures 5-6) do not necessarily require orbital angular momentum. As rightly pointed out, a coherent superposition position of beams can indeed generate fields with strong gradients that can mimic the gradients produced by asymmetric OAM beams. This was now clearly stated in the article on page 8. However, the asymmetric modulation of ionization probability/yields is due to the helical phase which can be associated with the transport of angular momenta of photons.

Response to Reviewer #2:

Thank you once again for reviewing the second draft of our article. We appreciate the meticulous read of our article. We have implemented your comments and below is a response to your question. (Comments in red, responses in blue)

Comment 1:

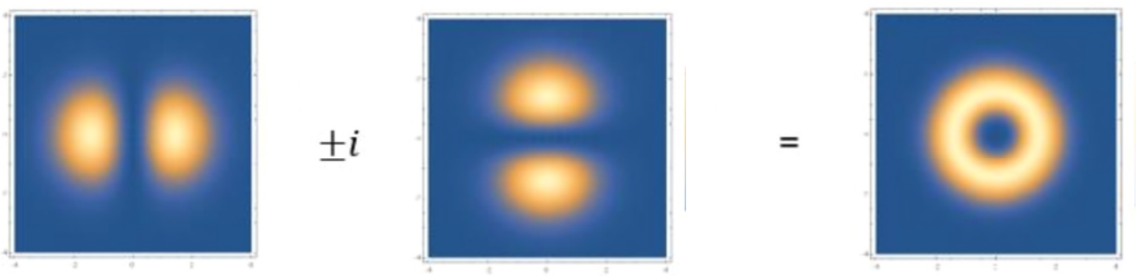
(1) I am satisfied with the reply to referee #1 with respect to the role played by the strong field gradients. However, I still wonder if it's experimentally feasible to generate synthesized light beams with strong field gradients but without helical phase.

Yes, it is feasible to generate synthesized light beams with strong field gradients without helical phase. Consider a coherent superposition of Hermite-Gaussian (HG) and Laguerre-Gaussian (LG) basis than can lead to various intensity distributions with increasing field gradients. Depending on the superposition states, the resulting beam may or may not carry OAM.

First consider structured beams with OAM:

Helical light can be generated by a coherent superposition of Hermite-Gaussian beam of orthogonal states HG_{10} and HG_{01} by introducing a $\pi/2$ phase difference between such states to generate LG_0^1. The handedness of the LG beam is changed from +1 to -1 when an extra π phase shift is introduced between the orthogonal states.

$$LG_0^1 = HG_{10} + HG_{01}e^{\pm i\pi/2}$$



This method can also be used to generate asymmetrical LG if the orthogonal states contain an asymmetric parameter δ.

$$HG_{mn} = E_0 e^{-\frac{x^2+y^2}{w_0^2}}\left[H_m\left(\frac{\sqrt{2}x}{w_0}\right)H_n\left(\frac{\sqrt{2}y}{w_0}\right)\right] \Rightarrow aHG_{mn} = E_0 e^{-\frac{x^2+y^2}{w_0^2}}\left[H_m\left(\frac{\sqrt{2}(x \pm \delta\eta)}{w_0}\right)H_n\left(\frac{\sqrt{2}(y \pm \delta\zeta)}{w_0}\right)\right]$$

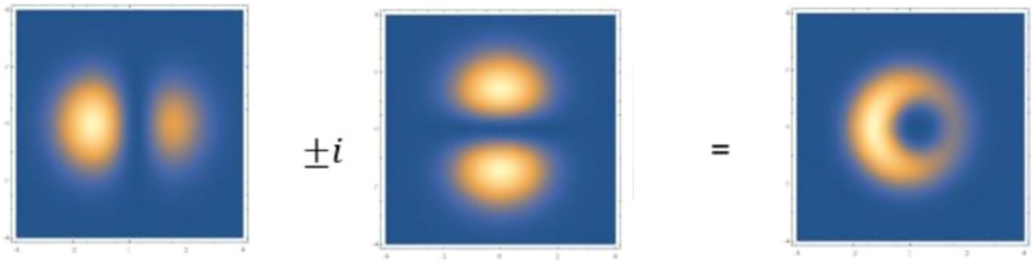
$$aLG_0^1 = aHG_{10} + aHG_{01}e^{\pm i\pi/2}$$

$$aLG_0^1 = E_0 e^{-\frac{x^2+y^2}{w_0^2}}\left[aH_1\left(\frac{\sqrt{2}(x \pm \delta\eta)}{w_0}\right)aH_0\left(\frac{\sqrt{2}(y \pm \delta\zeta)}{w_0}\right) \pm i\, aH_0\left(\frac{\sqrt{2}(x \pm \delta\eta)}{w_0}\right)aH_1\left(\frac{\sqrt{2}(y \pm \delta\zeta)}{w_0}\right)\right]$$

Using the properties of the Hermite polynomials, the above expression can be reduced to the equation derived in the supplementary file (equation 20).

$$aLG_0^1 = \frac{\sqrt{2}E_0}{w_0} e^{-\frac{x^2+y^2}{w_0^2}} [(x \pm \delta\eta) \pm i\,(y \pm \delta\zeta)]$$

The sign of the phase delay between both orthogonal Hermite-Gaussian states results in handedness of the helical light ($\pm l$) and the $\pm$ in front of the δ-position determines the direction of displacement.



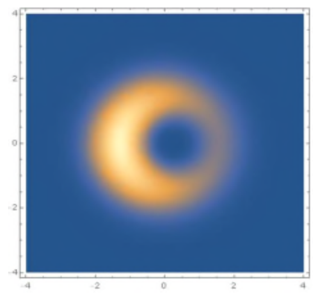
Second, here are two examples of structured beams without OAM:

Example 1: Generation of a Hollow Gaussian beam which is a coherent superposition of LG. The electric field is expressed below

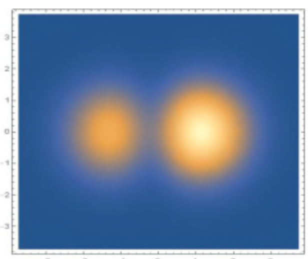
$$E(\rho,\phi) = \left(\frac{\rho}{w_0}\right)^{|l_1|+|l_2|} e^{i(l_1+l_2)\phi} e^{-\left(\frac{\rho}{w_0}\right)^2}$$

Where $\phi = \arctan\left(\frac{y}{x}\right)$ and $\rho = \sqrt{x^2+y^2}$, the OAM order l_1 and l_2 are for the two vortex beams. If $l = l_1 = -l_2$ the resulting electric field is a hollow Gaussian field.

$$E(\rho,\phi) = \left(\frac{\rho}{w_0}\right)^{2l} e^{-\left(\frac{\rho}{w_0}\right)^2}$$



Furthermore, by introducing the shifting parameter δ in x and y one can generate asymmetrical hollow Gaussian. This non-OAM structured beam, which is a coherent superposition of two aLG beams, exhibits strong intensity variation due to the presence of singularity. The resultant intensity profile is shown to the right mimicking an asymmetric OAM beam without helical phase.



Example 2: Consider coherent superposition of asymmetric Hermite-Gaussian $aHG_{10} + aHG_{00}$ resulting in a beam with no OAM and null intensity but with strong field distributions.

Comment 2:

Thank you for giving the normalized displacement of singularity (δ-position), but I saw 'ω0/3 μm' in the main text and plots, where the 'μm' is unnecessary.

Thanks for pointing it out. We have made the corrections.