Structuring the local handedness of synthetic chiral light: global chirality versus polarization of chirality

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Abstract
Synthetic chiral light enables ultrafast and highly efficient imaging of molecular chirality. Unlike standard circularly polarized light, the handedness of synthetic chiral light does not rely on the spatial structure of the light field: it is encoded locally, in the chiral trajectory that the tip of the electric-field vector draws in time, at each point in space. Synthetic chiral light that is both locally and globally chiral (Ayuso et al 2019 Nat. Photon. 13 866) allows us to selectively quench the nonlinear response of a selected molecular enantiomer while maximizing it in its mirror twin at the level of total signal intensities. Synthetic chiral light that exhibits polarization of chirality (Ayuso et al 2021 Nat. Commun. 12 3951) allows us to realize a chiral version of Young’s double-slit experiment that leads to enantio-sensitive light bending. Here we connect these new concepts, and show how one can structure the local and global handedness of synthetic chiral light in space to create optical fields which can be both globally chiral and chirality polarized. Using state-of-the-art computational modeling, we show how these local and global properties are imprinted in the enantio-sensitive response of chiral molecules, creating exciting opportunities for ultrafast, all-optical and highly efficient imaging of molecular chirality.

The capability of structuring the physical properties of light in space at will has opened tremendous possibilities for sculpting light-matter interactions [1–3]. Vortex beams, which exhibit a twisted phase profile and carry orbital angular momentum [4], are a typical example of structured light. Such structured light has found unique applications across a number of fields, including particle manipulation [5, 6], information transfer [7], phase contrast [8] and super-resolution microscopies [9], or quantum information [10]. Likewise, light beams with structured polarization [11–13] have been proven to be unique tools at the nanoscale [14–16] due to their superior focusing properties [17].

In the last decade, structured vortex light has been successfully applied to drive highly non-linear interactions in matter, such as structured high-order harmonic generation (HHG), leading to the creation of ultrashort structured pulses in the extreme-ultraviolet domain [18–27]. An interesting aspect of this capacity is that it allows us to spatially separate HHG radiation with different properties, enabling control over the polarization of ultrashort pulses [27, 28] or their spectral content [29].

However, it is not necessary to resort to orbital angular momentum to create structured light. For instance, it is well known that the polarization of a Gaussian beam becomes spatially structured upon tight focusing [30, 31], or when overlapping two laser pulses that propagate non-collinearly [31–33]. Interestingly, non-collinear optical setups [34–41] and tightly focused laser beams [42–44] create unique opportunities for imaging molecular chirality on ultrafast timescales.

Chiral molecules exist in pairs of non-superimposable mirror images: the left- and right-handed enantiomers, which have identical physical and chemical properties, e.g. melting and boiling points, energy levels, etc, and thus behave identically, unless they interact with something that is also chiral. Not surprisingly, structured light is finding interesting applications for detecting and even separating opposite
molecular enantiomers [45–47], although these applications are limited by the weakness of non-electric-dipole interactions. Indeed, the enantio-sensitive response of chiral molecules to an elliptically or circularly polarized field usually relies on weak magnetic or quadrupole effects which arise beyond the electric-dipole approximation [48]. These effects can be enhanced using short-wavelength radiation [49–51], or intense laser fields to drive chiral HHG [52–57].

Alternatively, one can create chiral measurement setups [58, 59], so that the enantio-sensitive response of the molecules is driven by purely electric-dipole interactions. This can be achieved by recording the photoelectron angular distributions upon ionization with circular [60–73], elliptical [74], or two-color [75–78] driving fields, measuring the phase of induced nonlinear polarization [79–85], creating chiral optical centrifuges [86–88], or recording the orbital momentum of photoelectron vortex beams [89].

Another way around this limitation is to create fields which are chiral already within the electric-dipole approximation [36–42, 90–95].

*Synthetic* chiral light [36] can be seen as an upgrade with respect to circularly polarized light as a chiral photonic reagent [59]. Such light is *locally* chiral: the tip of the electric-field vector draws a chiral Lissajous figure in time, in every point in space. The enantio-sensitive response of chiral molecules is driven by purely electric-dipole interactions, and thus it is stronger than with traditional optical fields. Here we show how, by structuring the local handedness of synthetic chiral light in space, we can imprint the handedness of isotropic chiral matter into different macroscopic observables: the total intensity of harmonic emission [36], and the direction of enantio-sensitive light bending [37].

This paper is structured in four different sections.

- **Section 1** provides a tutorial-style analysis of the local handedness of synthetic chiral light, which is encoded in the relative phase between its frequency components [36]. We highlight the key differences between locally chiral light and circularly polarized light (section 1.1), and review the formalism of chiral correlation functions (1.2), which characterize the local handedness of synthetic chiral light and its nonlinear interaction with chiral matter.

- We continue our analysis in section 2, providing a comprehensive description of the macroscopic properties of synthetic chiral light. We start by describing how we can create locally chiral light using a non-collinear laser configuration that allows us to control its local and global properties. We shall see that we can create locally chiral fields which are:

  * perfectly globally chiral and chirality unpolarized (2.1), as in [36],
  * globally achiral but perfectly chirality polarized (2.2), as in [37],
  * something in between, i.e. light which is both globally chiral and chirality polarized (2.3).

We explicitly show how to control the chirality properties of the field through the two-color phase delays in the proposed optical setup (2.4).

- In section 3, we present numerical results based on a prototypical chiral model: the hydrogen peroxide molecule. Using state-of-the-art computational modeling (3.1), we show how the local and global chirality properties of the field are imprinted in the nonlinear optical response of randomly oriented chiral molecules (3.2). We provide a recipe for creating synthetic chiral light with controlled local and global properties, which can imprint medium’s handedness into different macroscopic observables: the total intensity of harmonic emission (3.3), and the direction of enantio-sensitive light bending (3.4).

- **Section 4** concludes the paper by discussing the unique opportunities enabled by structuring the local handedness of synthetic chiral light in space.

Each section uses concepts introduced in previous sections. However, while sections 1 and 2 contain a comprehensive analysis of the local and global properties of synthetic chiral light, the main ideas are introduced at the beginning of each section. Therefore, readers should feel free to jump to section 3 (numerical results) after reading the first parts of sections 1 and 2, and come back to them afterwards.

### 1. The local handedness of synthetic chiral light

A laser field is locally chiral if the Lissajous figure characterizing the temporal evolution of its electric-field vector is chiral [36]. To fulfil this requirement, the field needs to be three-dimensional, and thus contain at least two frequencies. Here we use the locally chiral field introduced in [36], where the electric-field vector $\mathbf{E}$ is elliptically polarized at frequency $\omega$ in the $xy$ plane and it has a $2\omega$ frequency component along $z$,

$$
\mathbf{E}(t) = E_\omega \left[ \cos(\omega t) \hat{x} + \varepsilon \sin(\omega t) \hat{y} \right] + E_{2\omega} \cos(2\omega t + \phi) \hat{z}.
$$

(1)
The field handedness depends on the two-color phase delay $\phi$ and on the sign of the ellipticity $\varepsilon$. Figure 1 shows the Lissajous figure that $E$ draws in time, for different values of $\phi$. Note that changing $\phi$ by $\pi$ is equivalent to reflecting the field on the $xy$ plane, and thus this operation reverses the field's handedness. Therefore, the fields with, e.g. $\phi = 0$ (upper left in figure 1) and $\phi = \pi$ (lower left) can be seen as field enantiomers. Likewise, changing the sign of $\varepsilon$ is equivalent to reflection on the $xz$ plane and it also reverses the field’s chirality.

### 1.1. Locally chiral light vs circularly polarized light

Locally chiral light is fundamentally different from circularly polarized light. First, because its chirality is defined locally, at each point in space—it does not rely on the spatial structure of the wave. As a result, the enantio-sensitive response of the molecules arises already within the electric-dipole approximation. Second, because its handedness cannot be characterized by a real scalar quantity. Let us illustrate this by considering a monochromatic plane wave $E = [E_x, E_y] e^{i \omega t} | e^{-i \mathbf{k} \cdot \mathbf{r}}$, whose handedness is characterized via its ellipticity $-1 < \varepsilon < 1$. A circularly polarized wave is the limit case with $\varepsilon = \pm 1$.

There are two ways of reversing the wave’s chirality in a smooth, continuous way. The first way is to gradually change the amplitude of one of the two field components, e.g. $E_y$, from $E_{y,0}$ to $-E_{y,0}$, leading to a change of $\varepsilon$ from $\varepsilon_0$ to $-\varepsilon_0$. Bolzano’s theorem tells us that, in this continuous transition, the value of $\varepsilon$ will inevitably go through zero, meaning that at some point during this transition the field will be linearly polarized, i.e. achiral. The second way involves changing the relative phase between $E_x$ and $E_y$, from $\theta = \theta_0$ to $\theta = \theta_0 + \pi$, which will also take us from $\varepsilon = \varepsilon_0$ to $\varepsilon = -\varepsilon_0$ via an achiral field with $\varepsilon = 0$. This is not the case in synthetic chiral light.

We can reverse the handedness of our locally chiral field (figure 1) by changing the sign of ellipticity $\varepsilon$, or by shifting the two-color delay $\phi$ by $\pi$. A continuous transition from $\varepsilon = \varepsilon_0$ to $\varepsilon = -\varepsilon_0$ passes through $\varepsilon = 0$, i.e. through a planar field which is achiral. This situation is somewhat equivalent to the case of the elliptical wave. However, the second way of reversing the field’s handedness, shifting $\phi$ by $\pi$, takes us through an infinite set of fields with different chirality, see figure 1. That is, here we have a continuous trajectory in the space of field configurations which takes us from a locally chiral field to its mirror twin without going through an achiral field. This implies that the handedness of synthetic chiral light cannot be characterized by a real scalar quantity.

### 1.2. Characterizing light’s local handedness: chiral correlation functions

Chiral correlation functions [36] are complex-valued quantities which characterize the local handedness of synthetic chiral light and its enantio-sensitive interaction with isotropic chiral matter. This interaction is nonlinear, as the medium needs to record the phase delay between the different field components in its optical response.

The enantio-sensitive response of chiral matter to our locally chiral field appears at even-order harmonic frequencies [36], and relies on the interference between two multiphoton pathways, see figure 2. We assume weak $\varepsilon$ and $E_{2\omega}$, so the molecules can absorb several photons from $E_{\omega}$, but their response to $E_{\omega}$ and $E_{2\omega}$ is linear. The chiral pathway (figure 2(a)) involves absorption of $2N + 1$ photons from $E_{\omega}$ and emission of 1
photons from \(E_x\). This pathway is exclusive of chiral media, and it leads to polarization at frequency \(2N\omega\) along \(z\), which has opposite phase to molecular enantiomers,

\[
P_e(2N\omega) = \sigma \chi^{(2N+2)}I[F(\omega) \cdot F(\omega)]N[F^*(\omega) \times F(\omega)],
\]

where \(\sigma = \pm 1\) for right-/left-handed molecules, \(\chi^{(2N+2)}I\) is the corresponding \((2N+2)\)-order molecular susceptibility of randomly oriented right-handed molecules, and \(F\) is the Fourier component of the field (equation (1)). In the achiral pathway (figure 2(b)), which is not sensitive to the medium’s handedness, the molecules absorb \(2N-2\) photons from \(E_a\) and 1 photon from \(E_{2\omega}\), also leading to polarization at frequency \(2N\omega\) along \(z\),

\[
P_a(2N\omega) = \chi_a^{(2N-1)}[F(\omega) \cdot F(\omega)]^{N-1}F(2\omega)
\]

Note that \(P_a\) is not sensitive to the medium’s handedness, whereas \(P_e\) has equal amplitude and opposite phase in opposite molecular enantiomers. As a result, the induced polarization \(P = P_e + P_a\) is enantio-sensitive, and the intensity of harmonic emission is proportional to

\[
|P(2N\omega)|^2 = \frac{1}{2}|P_a(2N\omega)|^2 + \frac{1}{2}|P_e(2N\omega)|^2 + \sigma \chi^{(2N-1)}\chi^{(2N+2)}h^{(4N+1)} + c.c.
\]

where \(c.c.\) denotes complex conjugation. The interference term is both enantio-sensitive and dichroic, as it depends on the molecular handedness, \(\sigma = \pm 1\), and on the \((4N+1)\)-order chiral correlation function \(h^{(4N+1)}\), which characterizes the field’s local handedness:

\[
h^{(4N+1)} = [F^*(\omega) \cdot F^*(\omega)]^{N-1} \{F^*(2\omega) \cdot [F^*(\omega) \times F(\omega)]\} \{F(\omega) \cdot F(\omega)\}N.
\]

By adjusting the field parameters, we can control the amplitude and phase of \(h^{(4N+1)}\), and thus the enantio-sensitive interference. The lowest-order chiral correlation function of our field, \(h^{(2)}\), controls enantio-sensitive polarization and emission at frequency \(2\omega\),

\[
h^{(2)} = \{F^*(2\omega) \cdot [F^*(\omega) \times F(\omega)]\} \{F(\omega) \cdot F(\omega)\} \simeq 2i\varepsilon E_{2\omega}E_{2\omega}e^{i\phi}.
\]

Note that equation (6) is the special case of equation (5) with \(N = 1\).

### 2. Structuring light’s local handedness in space

Our locally chiral field can be created using a non-collinear optical setup [36–38] with two laser beams that propagate in the \(xy\) plane, at small angles \(\pm \alpha\) with respect to the \(y\) axis, see figure 3(a). Each beam \((n = 1, 2)\) carries the fundamental \(\omega\) frequency, polarized in the \(xy\) propagation plane, and its second harmonic, polarized along \(z\),

\[
E_n(r, t) = E^{(0)}_\omega R \{f_{n,\omega}(r, t)e^{i k_r \cdot r - \alpha t} - f_{n,\omega}(r, t)e^{i k_r \cdot r + \alpha t}\} \hat{e}_z + E^{(2)}_{2\omega} R \{f_{n,2\omega}(r, t)e^{i k_r \cdot r - \alpha t - \phi_\omega} - f_{n,2\omega}(r, t)e^{i k_r \cdot r + \alpha t + \phi_\omega}\} \hat{e}_z
\]

where \(E^{(0)}_\omega\) and \(E^{(2)}_{2\omega}\) are the field amplitudes, \(f_{n,\omega}\) and \(f_{n,2\omega}\) are envelope functions describing the temporal and spatial Gaussian profiles [96], \(k_{1,2} = \pm k \sin(\alpha) \hat{x} + k \cos(\alpha) \hat{y}\), with \(k = 2\pi/\lambda\) and \(\lambda\) being the fundamental wavelength, \(\phi_\omega\) is the two-color phase delay in each beam, and \(\hat{e}_1 = \cos(\alpha) \hat{x} + \sin(\alpha) \hat{y}\).

If the beams propagate non-collinearly \((\alpha \neq 0)\), the \(\omega\)-field components are not parallel \((\hat{e}_1 \neq \hat{e}_2)\). As a result, in the overlap region, the total electric-field vector becomes elliptically polarized at frequency \(\omega\) in the \(xy\) plane. The combination of this elliptical polarization with the linearly polarized \(2\omega\) components creates three-dimensional chiral Lissajous figures like the ones depicted in figure 1. Note that \(\alpha \neq 0\) also means that

Figure 2. Multiphoton diagrams describing the enantio-sensitive response of isotropic chiral matter to synthetic chiral light in the perturbative regime, see main text.
the projection of \( \mathbf{k}_n \) over the x axis is different for each beam, i.e. \( \mathbf{x} \cdot \mathbf{k}_1 \neq \mathbf{x} \cdot \mathbf{k}_2 \), and thus the relative phase between frequency components in different beams changes along \( x \), creating amplitude and ellipticity gratings in this direction. As we show in this section, control over such gratings enables control over the global properties of the locally chiral field.

We consider the interaction of our field with randomly oriented molecules in the gas phase, where the two frequency components propagate with approximately the same velocity \( |\omega_1 - \omega_2| \gg |\alpha| \) or in a flat liquid microjet [100–103]. For simplicity, we set \( y = z = 0 \), and write the total electric field resulting from adding the two beams (equation (7)) as

\[
\mathbf{E}(x, t) = E_\omega(x, t) \left[ \cos(\omega t) \mathbf{\hat{x}} + \varepsilon \sin(\omega t) \mathbf{\hat{y}} \right] + E_{2\omega}(x, t) \cos(2\omega t + \phi_{\pm}) \mathbf{\hat{z}},
\]

with

\[
E_\omega(x, t) = 2E^{(0)}_\omega A_\omega(t) e^{-x^2/\omega^2} \cos(\alpha) \cos(k_\omega x),
\]

\[
E_{2\omega}(x, t) = 2E^{(0)}_{2\omega} A_{2\omega}(t) e^{-x^2/\omega^2} \cos(2k_\omega x + \phi_{\pm}),
\]

\[
\varepsilon(x) = -\tan(\alpha) \tan(k_\omega x),
\]

where \( A_\omega \) and \( A_{2\omega} \) are envelope functions, \( \omega \) is the beam waist, \( k_\omega = k \sin(\alpha) \), and

\[
\phi_{\pm} = \frac{\phi_2 \pm \phi_1}{2}.
\]

We have neglected the Gouy phase and the wavefront curvature. Direct comparison of equations (8)–(12) and equation (1) shows that the non-collinear setup realizes the locally chiral field of figure 1.

The relative phase delays \( \phi_{\pm} \) (equation (12)) simplify the analysis of the field properties. Loosely speaking, \( \phi_{\pm} \) controls the shape of the projection of \( \mathbf{E} \) over the \( xy \) plane, which can look like an infinite symbol \( \infty \), a smile \( \sim \), or something in between. Note that this shape is maintained in space, although its orientation changes, as \( E_\omega \) and \( E_{2\omega} \) change sign along \( x \) with different spatial periodicity. However, the field’s chirality depends on \( E_{2\omega} \) and \( \varepsilon \) (not on \( E_\omega \)), which change sign along \( x \) with the same periodicity. As we show

![Figure 3](image-url)

Figure 3. Synthetic chiral light that is globally chiral. (a) Non-collinear setup for creating synthetic chiral light that maintains the same handedness in space: the two beams are linearly polarized at frequency \( \omega \) in the \( xy \) plane of propagation, and have a \( 2\omega \) frequency component orthogonal to this plane, with opposite two-color phase delay in the two beams, \( \phi_2 = \phi_1 + \pi \). (b) Forward ellipticity in the \( \omega \)-field component (green curve) and normalized \( 2\omega \)-field amplitude (purple curve) along the transverse coordinate \( x \), for \( \phi_1 = -\pi/2 \) and \( \phi_2 = \pi/2 \). These ellipticity and amplitude gratings change sign exactly at the same positions. (c) Amplitude (black line) of field component (green curve) and normalized 2\( \omega \)-field amplitude (purple curve) along the transverse coordinate \( t \), for \( \phi_1 = -\pi/2 \) and \( \phi_2 = \pi/2 \). These ellipticity and amplitude gratings change sign exactly at the same positions. (d)–(f). Changing the two-color phase delays in the two beams by \( \pi \) (d) changes the sign of \( \pm \) and equation (12) simplifies the analysis of the field properties. Loosely speaking, \( \phi_{\pm} \) controls the shape of the projection of \( \mathbf{E} \) over the \( xy \) plane, which can look like an infinite symbol \( \infty \), a smile \( \sim \), or something in between. Note that this shape is maintained in space, although its orientation changes, as \( E_\omega \) and \( E_{2\omega} \) change sign along \( x \) with different spatial periodicity. However, the field’s chirality depends on \( E_{2\omega} \) and \( \varepsilon \) (not on \( E_\omega \)), which change sign along \( x \) with the same periodicity. As we show
in the following, we can control whether \( E_{2\omega} \) and \( \epsilon \) change sign at the same positions or not by adjusting the value of \( \phi_- \).

### 2.1. Global chirality

The key to create locally chiral light that maintains the same handedness in space is to impose that \( E_{2\omega} \) (equation (10)) and \( \epsilon \) (equation (11)) change sign at the same positions, which is achieved by setting \( \phi_- = \pi/2 \), see figure 3. Note that \( \phi_- = \pi/2 \) means having opposite two-color delay in the two beams, i.e. \( \phi_2 = \phi_1 + \pi \) (figure 3(a)). As a result, the \( \epsilon \) and \( E_{2\omega} \) gratings are perfectly aligned (figure 3(b)), and thus the field’s local handedness, characterized by the phase of \( h^{(5)} \), is maintained in space (figure 3(c)).

If we change the two-color delay in the two beams by \( \pi \) (figure 3(d)), \( E_{2\omega} \) flips sign at every point in space (figure 3(e)), and thus the field’s local handedness is reversed globally (figure 3(f)), in a way that the overall structure remains globally chiral. For illustration purposes, we call a locally chiral field with \( \arg\{h^{(5)}\} = -0.5\pi \) left-handed, and a field with \( \arg\{h^{(5)}\} = 0.5\pi \) right-handed, although this is an arbitrary choice, as \( \arg\{h^{(5)}\} \) is a continuous variable, and thus we have an infinite set of field configurations with different local chirality.

Setting \( \phi_- = \pi/2 \) imposes that the field maintains the same handedness in space. Then, by varying \( \phi_+ \), while keeping \( \phi_- = \pi/2 \) constant (i.e. by varying \( \phi_1 \) and \( \phi_2 \) synchronously while keeping \( \phi_2 = \phi_1 + \pi \)), we can tailor the shape of the chiral Lissajous figure (figure 1) in a way that it has exactly the same chirality everywhere in space.

We can quantify the global handedness our field by integrating \( h^{(5)} \) in space [36],

\[
h_0 = \int h^{(5)}(x)dx.
\]

The amplitude of \( h_0 \) maximizes when \( \phi_2 = \phi_1 \pm \pi \) because, in these situations, the field has the same local chirality (\( \arg\{h^{(5)}\} \)) everywhere in space, as shown in figure 3.

### 2.2. Polarization of chirality

Naively, one could think that synthetic chiral light that is not globally chiral could not be used for enantio-discrimination. Indeed, a locally chiral field that changes handedness periodically in space and is, overall, achiral, can maximize/minimize the response of the L/R enantiomers in some spatial regions, but it will produce the opposite effect in the regions where it has opposite local handedness. However, this does not mean that the macroscopic response of the medium cannot be enantio-sensitive.

If we set \( \phi_1 = \phi_2 \) in our setup, see figure 4, then \( \epsilon \) and \( E_{2\omega} \) change sign at different positions, with a spatial phase delay of \( \pi/2 \) (figure 4(b)). As a result, the field’s chirality changes periodically in space (figure 4(c)), and the overall structure is globally achiral (\( h_0 = 0 \)). Note that the field is symmetric with respect to reflection on the xz plane (up to a global temporal delay).

While the field in figures 4(a)–(c) is not globally chiral, its handedness is spatially structured, and we find pairs of field components with opposite handedness, see figure 4(c). Each of these ‘dimers’ realizes a ‘dipole of chirality’ [37]: a pseudo-vector that points from the left-handed field to the right-handed field (figure 4(c)). Crucially, these dipoles of chirality are oriented, always pointing to the left, and we find the following distribution of handedness as we move towards positive values of \( x \) ... RL RL RL...

As a result, the overall structure acquires polarization of chirality [37].

The amplitude and direction of polarization of chirality can be controlled by controlling the two-color phase delays in our setup. If we change the phase delay in the two beams by \( \pi \) (figure 4(d)), we change the sign of \( E_{2\omega} \) in every point in space (figure 4(e)), reversing the field’s handedness (figure 4(f)). As a result, the dipole of chirality flips direction, and we find the opposite distribution of handedness: ... LR LR LR...

Polarization of chirality can be quantified using chiral correlation functions in the reciprocal space, see [37]. For the locally chiral field considered in this work, we can use a definition that is analogous to the polarization of electric charge [37],

\[
h_x = \int h^{(5)}(x)dx.
\]

\( |h_x| \) maximizes for \( \phi_1 = \phi_2 \), when there is the same amount of left- and right-handed field and the overall structure is globally achiral (\( h_0 = 0 \)), as shown in figure 4.

### 2.3. Global chirality versus polarization of chirality

We now show how, by controlling the two-color phase delays in our setup, we can create light that is both globally chiral (\( h_0 \neq 0 \)) and chirality polarized (\( h_x \neq 0 \)). Figure 5 shows the amplitude (figure 5(a)) and
Figure 4. Synthetic chiral light that is globally achiral, but chirality polarized. (a) Schematic representation of the non-collinear setup to create synthetic chiral light that changes handedness periodically in space and it has the same amount of opposite field enantiomers: the two beams are linearly polarized at frequency $\omega$ in the $xy$ plane of propagation, and have a $2\omega$ frequency component orthogonal to this plane, with the same two-color phase delay in the two beams $\phi_1 = \phi_2$. (b) Forward ellipticity in the $\omega$-field component (green curve) and normalized $2\omega$-field amplitude (purple curve) along the transverse coordinate $x$, for $\phi_1 = \phi_2 = 0$. These ellipticity and amplitude gratings change sign at different positions. (c) Amplitude (black line) and phase (color) of $h(5)$, which characterizes the field’s local chirality. The red color indicates $\arg(h(5)) = \pi/2$ and the blue color indicates $\arg(h(5)) = -\pi/2$. In this configuration, the field changes chirality periodically in space, creating dipoles of chirality, and the overall field has polarization of chirality. (d)–(f). Changing the two-color phase delays in the two beams by $\pi$ (d) changes the sign of $E_{2\omega}$ at each point in space (e), reversing the field’s local handedness (f). As a result, the field remains globally achiral and chirality polarized, and the polarization of chirality changes direction.

Figure 5. Structuring the local handedness of synthetic chiral light. Amplitude (a) and phase (b) of $h(5)$ (equation (6)), which characterizes the field’s local handedness, across the transverse coordinate $x$, as functions of $\phi_-$, for $\phi_+ = 0$ (equation (12)). To obtain $\arg(h(5))$ for a different choice of $\phi_+$ one needs to add $\phi_+$ to the values shown in panel b (|$h(5)$| does not depend on $\phi_+$). If $\phi_- = \pm \pi/2$, the field has the same chirality everywhere in space (b), and thus $|h_0|$ (c, equation (13)) maximizes whereas $h_x = 0$ (d, equation (14)). If $\phi_- = 0$ or $\pi$, the field’s local handedness changes periodically in space, and the overall structure is achiral: $h_0 = 0$, with maximum $|h_x|$. For other values of $\phi_-\phi_-$, the field is both globally chiral and chirality polarized.

Varying $\phi_-$ moves the $2\omega$ amplitude grating (equation (10)) in a way that the shape of the chiral Lissajous figure of our field is not modified as we move along $x$ other than by changes in the amplitude and sign of $E_{2\omega}$. As a result, the phase of $h(5)$ remains constant up to $\pi$ jumps (figure 5(b)). If $\phi_- = \pm \pi/2$ ($\phi_2 = \phi_1 \pm \pi$), the $E_{2\omega}$ and $\xi$ gratings are perfectly aligned (as in figure 3), and thus the field’s chirality is maintained globally in space. In these cases, $|h_0|$ (figure 5(c)) maximizes whereas $h_x = 0$ (figure 5(d)). Otherwise, if $\phi_2 \neq \phi_1 \pm \pi$, the field’s chirality is reversed periodically in space: $\arg(h(5))$ exhibits $\pi$ jumps as
Figure 6. Global handedness and polarization of chirality. Amplitude (a), (b) and phase (c), (d) of \( h_0 \) (a), (c), see equation (13), which characterizes the field's global chirality, and of \( h_x \) (b), (d), see equation (14), which characterizes the polarization of chirality, as functions of the two-color phase delays in the individual beams \( \phi_1 \) and \( \phi_2 \) (equation (7)).

we move along \( x \). For \( \phi_1 = \phi_2 \) (\( \phi_2 = 0 \) or \( \pi \)), we have the same amount of left- and right-handed field, which leads to \( h_0 = 0 \) and maximizing \( |h_x| \). The phase of \( h_x \) captures the direction of polarization of chirality, which is opposite e.g. for \( \phi_2 = \phi_1 \) and \( \phi_2 = \pi \).

Note that, for a given field configuration, the definition of \( \phi_{\pm} \) is not unique. Let us consider, for instance, the field defined by setting \( \phi_1 = 0 \) and \( \phi_2 = \pi \). Its local chirality can be characterized by taking the corresponding values of \( \text{arg}(h(5)) \) from figure 5(b), which assumes \( \phi_+ = 0 \), and then adding \( \phi_+ \) to these values. Figure 5(b) shows that, for \( \phi_+ = \pi/2 \), we have \( \text{arg}(h(5)) = 0.5\pi \) everywhere in space. Adding \( \phi_+ \) to this value, we obtain \( \text{arg}(h(5)) = \pi \). Since phase definitions are arbitrary up to \( \pm 2n\pi \) (\( n \in \mathbb{Z} \)), we can represent the exact same field using \( \phi_+ = 2\pi \) instead and keeping \( \phi_2 = \pi \). In this case, the we have \( \phi_- = \pi/2 \) and \( \phi_+ = 1.5\pi \), and thus value that we need take from figure 5(b) is different: \( \text{arg}(h(5)) = -0.5\pi \). However, when we add \( \phi_+ = 1.5\pi \) to this value, we obtain the same result: \( \text{arg}(h(5)) = \pi \) everywhere in space. Despite this ambiguity, characterizing the field's chirality in terms of \( \phi_{\pm} \) is advantageous because, as described above, \( \phi_- \) unequivocally determines whether the field is globally chiral and/or chirality polarized or not, whereas \( \phi_+ \) controls the shape of the chiral Lissajous figure everywhere in space.

The lines with slope -1 in figure 6 connect points with equal \( \phi_+ \) and different \( \phi_- \), and thus the amplitude of \( h_0 \) and \( h_x \) changes along these lines, whereas their phase remains constant up to \( \pi \) jumps. This reflects that,
by varying $\phi$, we control the global chirality properties of the field without changing the shape of the field’s chiral Lissajous figure, other than by flips in the direction of the $2\omega$-field component.

3. Enantio-sensitive control over the nonlinear response of chiral molecules

We now show how the local and global properties of synthetic chiral light can be imprinted in the macroscopic nonlinear response of randomly oriented chiral molecules. We have computed the ultrafast electronic response of the prototypical chiral molecule $\text{H}_2\text{O}_2$. The potential energy surface of the electronic ground state has two minima at dihedral angles 112.5° and 247.5°, which correspond to opposite enantiomers [104]. Here we label these configurations left- (112.5°) and right-handed (247.5°). However, because the interconversion energy barrier is small, the molecule exists as a racemic mixture in standard conditions. Still, the relatively small number of nuclei (4) and electrons (18) makes it a convenient 'toy model' to investigate ultrafast chiral light-matter interactions using reasonable computational resources [38].

3.1. Computational method

We have computed the ultrafast evolution of the electron density in $\text{H}_2\text{O}_2$ driven by locally chiral light using real-time time-dependent density functional theory (TDDFT) in Octopus [105–108], as described in [38]. We used pseudo-potentials to model the 1s orbitals of the oxygen atoms, and applied the local-density approximation [109–111] to describe electronic exchange and correlation effects, together with the averaged-density self-interaction correction [112]. The Kohn–Sham orbitals and the electronic density were expanded onto a uniform real-space grid enclosed in a sphere of radius $30.7$ a.u., with $0.4$ a.u. of spacing between neighboring grid points. To avoid spurious reflection effects, we used a complex absorbing potential expanded onto a uniform real-space grid enclosed in a sphere of radius $30.7$ a.u., with $0.4$ a.u. of spacing.

We assumed the fixed-nuclei approximation because we are interested in ultrafast electronic processes driven by ultrashort laser pulses. While the nuclear motion is expected to give rise to rich dynamics upon photo-excitation, these are expected to take place on a longer timescale, and thus do not significantly affect our results.

We considered 200 different molecular orientations in order to describe the physical situation of randomly oriented molecules. The induced polarization in the randomly oriented ensemble was obtained by averaging over the contribution from all orientations:

\[
P(t,x) = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} P_{\phi \theta \chi}(t,x) \sin(\theta) \, d\phi \, d\theta \, d\chi,
\]

where $\phi$, $\theta$ and $\chi$ are the three Euler angles and $P_{\phi \theta \chi}$ is the induced polarization in a particular molecular orientation in the laboratory frame. We used the Lebedev quadrature [113] of order 11 to integrate over $\phi$ and $\theta$, and the trapezoid method to integrate over $\chi$.

We run TDDFT simulations for the equilibrium geometry of $\text{H}_2\text{O}_2$ with dihedral angle $112^\circ$, and the results for the opposite enantiomer were obtained using symmetry considerations. In our modeling, we assume that the phase of the achiral contribution to light-induced polarization depends linearly on the phase of the $2\omega$ component of the locally chiral field, see figure 2(b).

We considered the following laser parameters: fundamental wavelength $\lambda = 400$ nm, peak intensity in each beam of $I_0 = 2.5 \times 10^{13}$ W cm$^{-2}$, beam waist $w = 50 \mu$m, non-collinear angle $\alpha = 10^\circ$, and a sine-squared flat-top envelope of eight laser cycles of the fundamental frequency, with two cycles to rise up, four cycles of constant intensity, and two cycles to go down. The total peak intensity in the overlap region reaches $10^{14}$ W cm$^{-2}$. The fundamental wavelength was chosen so the relatively low-order harmonic processes that we are interested in are close to electronic resonances. We used ultrashort laser pulses to reduce the computational cost of the simulations, but our findings do not rely on the ultrashort nature of the driving field. That is, we do not expect that increasing the pulse duration would lead to significant changes in our results, other than a spectral narrowing of the harmonic peaks in the induced polarization associated with the spectral narrowing of the driving field.

The amplitude of the $2\omega$-field component was adjusted so the achiral contribution to the induced polarization at frequency $6\omega$ (figure 2(b)) has the same amplitude as the chiral contribution (figure 2(a)), in order to balance the enanti-o-sensitive interference. Our simulations show that this condition is achieved by setting $\sqrt{I_{2\omega}/I_0} = 0.0125$ in each beam.

The amplitude of emission in the far field was evaluated using Fraunhofer diffraction,

\[
\mathbf{E}(N\omega, \kappa) \propto \int_{-\infty}^{\infty} [\mathbf{P}_x(N\omega, x)\mathbf{x} + \mathbf{P}_y(N\omega, x)\mathbf{y}] e^{-iN\omega x \kappa / c} \, dx.
\]
where $N$ is the harmonic number, $c$ is the speed of light in vacuum, $\hat{\mathbf{P}} = \hat{P}_x \mathbf{\hat{x}} + \hat{P}_y \mathbf{\hat{y}} + \hat{P}_z \mathbf{\hat{z}}$ is the second derivative of the induced polarization in the frequency domain, and

$$\kappa = \arctan \left( \frac{\dot{N}_x}{\dot{N}_z} \right)$$

is the angle of emission, or divergence, where $z_f$ is the position of the detector relative to the chiral medium, and $x_f$ is the transverse coordinate in the far-field plane.

### 3.2. Angularly resolved harmonic spectra

The amplitude of harmonic light emitted from the L and R enantiomers of H$_2$O$_2$ upon interaction with synthetic chiral light that is globally chiral and chirality unpolarized (a)–(d), and globally achiral and chirality polarized (e)–(h), as a function of the harmonic order and the divergence angle $\kappa$ (equation (17)). To maximize $|h_0|$ and suppress $|h_0|$ (a)–(d), we impose $\phi_1 = \phi_1 + \pi (\phi_- = \pi/2)$. Setting $\phi_1 = 0.17\pi$ and $\phi_2 = 1.17\pi (\phi_+ = 0.67\pi)$ quenches emission at frequency $\omega_0$ in the left-handed molecule (a) while maximizing it in the right-handed molecule (b). Shifting $\phi_1$ and $\phi_2$ by $\pi (\phi_1 = 1.17\pi$ and $\phi_2 = 0.17\pi$) changes the field’s local handedness in every point in space, leading to enhancement of emission at frequency $\omega_0$ if the left-handed molecule (c) and suppression in the right-handed molecule (d). To suppress $|h_0|$ and maximize $|h_0|$ (e)–(h), we impose $\phi_1 = \phi_2 (\phi_- = 0)$. Setting $\phi_1 = \phi_2 = 1.17\pi (\phi_+ = 1.17\pi)$ bends the emission of harmonic 6 to the left in the left-handed molecule (e) and to the right (f) in the right-handed molecule. Changing $\phi_1$ and $\phi_2$ by $\pi (\phi_1 = \phi_2 = 0.17\pi$) changes the field’s local handedness at every point in space, reversing the direction of polarization of chirality, and thus the direction of enantio-sensitive light bending (g), (h).

![Figure 7](image-url) Enantio-sensitive harmonic emission. Amplitude of the $z$-polarized component of the harmonic light emitted from H$_2$O$_2$ upon interaction with synthetic chiral light that is globally chiral and chirality unpolarized (a)–(d), and globally achiral and chirality polarized (e)–(h), as a function of the harmonic order and the divergence angle $\kappa$ (equation (17)). To maximize $|h_0|$ and suppress $|h_0|$ (a)–(d), we impose $\phi_1 = \phi_1 + \pi (\phi_- = \pi/2)$. Setting $\phi_1 = 0.17\pi$ and $\phi_2 = 1.17\pi (\phi_+ = 0.67\pi)$ quenches emission at frequency $\omega_0$ in the left-handed molecule (a) while maximizing it in the right-handed molecule (b). Shifting $\phi_1$ and $\phi_2$ by $\pi (\phi_1 = 1.17\pi$ and $\phi_2 = 0.17\pi$) changes the field’s local handedness in every point in space, leading to enhancement of emission at frequency $\omega_0$ if the left-handed molecule (c) and suppression in the right-handed molecule (d). To suppress $|h_0|$ and maximize $|h_0|$ (e)–(h), we impose $\phi_1 = \phi_2 (\phi_- = 0)$. Setting $\phi_1 = \phi_2 = 1.17\pi (\phi_+ = 1.17\pi)$ bends the emission of harmonic 6 to the left in the left-handed molecule (e) and to the right (f) in the right-handed molecule. Changing $\phi_1$ and $\phi_2$ by $\pi (\phi_1 = \phi_2 = 0.17\pi$) changes the field’s local handedness at every point in space, reversing the direction of polarization of chirality, and thus the direction of enantio-sensitive light bending (g), (h).
The macroscopic response of H$_2$O$_2$ to synthetic chiral light that is globally achiral ($h_0 = 0$), but chirality polarized ($|h_x| \neq 0$), is presented in figures 7(e)–(h). Here, we maximize $|h_x|$ by setting $\phi_1 = \phi_2 = 0$. The total intensity of emission is no longer enantio-sensitive because $h_0 = 0$. However, because $h_x \neq 0$, the molecular handedness is imprinted in the direction of harmonic emission. Setting $\phi_1 = \phi_2 = 1.17\pi$ ($\phi_+ = 1.17\pi$) bends the nonlinear response of the L and R enantiomers to the left and to the right, respectively (figures 7(e) and (f)). If we shift $\phi_1$ and $\phi_2$ by $\pi$, we reverse the direction of polarization of chirality in the driving field, and thus the directions of harmonic emission (figures 7(g) and (h)).

This analysis shows how, by adjusting $\phi_1$ and $\phi_2$ in a way that $\phi_2 = \phi_1 \pm \pi$, we can tailor the field’s local handedness to maximize the enantio-sensitive response of the medium at the level of total intensity signals. If we impose $\phi_1 = \phi_2$, instead, we can achieve full control over the direction enantio-sensitive light bending. The two enantio-sensitive observables rely on the interference between two contributions to light-induced polarization (figure 2): $P_c$ (chiral) and $P_a$ (achiral). However, the interference mechanism is different, and thus the values of $\phi_+$ which optimize each enantio-sensitive observable are different.

To maximize the enantio-sensitivity in the total intensity of emission when the field is globally chiral (figures 7(a)–(d)), we need to adjust $\phi_+$ so that $P_c$ and $P_a$ are in phase in one enantiomer (and thus out of phase in the other) in the near field, at each point in space. As a result, the intensity of the optical response is enantio-sensitive already at the single-molecule level. However, when the field has polarization of chirality (figures 7(e)–(h)), enantio-sensitive light bending relies on the far-field interference of the radiation emitted from $P_c$ and $P_a$, which is optimized when $P_c$ and $P_a$ radiate with a phase delay of $\pm \pi/2$. That is, in this case, the two contributions to light-induced polarization do not produce an enantio-sensitive intensity at the single-molecule response level, but in the macroscopic harmonic emission. As a result, the optimum values of $\phi_+$ when light is globally chiral and unpolarized are shifted by $\pm \pi/2$ with respect to optimum values when light is globally achiral and polarized.

### 3.3. Control over the total intensity of the harmonic radiation

We now show how the total intensity of harmonic emission can be controlled by controlling the individual two-color phase delays $\phi_1$ and $\phi_2$ in our setup. Figure 8 shows the total intensity emitted from the L ($I_L$, figure 8(a)) and R ($I_R$, figure 8(b)) enantiomers at frequency $6\omega$, integrated over the divergence angle, as functions of $\phi_1$ and $\phi_2$. To quantify the enantio-sensitive response, we use a standard definition of the dissymmetry factor,

$$\gamma = \frac{2I_L - I_R}{I_L + I_R}.$$  \hspace{1cm} (18)

As shown in figure 8, we can achieve full control over the total intensity of harmonic emission by adjusting $\phi_1$ and $\phi_2$, and the dissymmetry factor (figure 8(c)) reaches its maximum values: $\pm 200\%$. These phase scans record the properties of the field and provide valuable information about the ultrafast electronic response of the molecules.
If $\phi_1 = \phi_2$, then the field is not globally chiral ($h_0 = 0$, see figure 6(a)) and thus $I_L = I_R$. This is the origin of the white ($\gamma = 0$) line with slope 1 in figure 8(c), which is characteristic of the field configuration and will be present when recording the enantio-sensitive response of any chiral molecule, at any (even) harmonic order. However, the white line with slope -1 is a molecule-specific feature. It records the relative phase between the two contributions to light-induced polarization ($P_c$ and $P_a$). If their phase delay is $\pm \pi/2$, the total intensity emitted from the L and R enantiomers is identical, yielding $\gamma = 0$.

Note that $\gamma = 0$ does not mean that the molecular response is not enantio-sensitive. While the total intensity emitted from opposite enantiomers is the same when the field is globally achiral ($h_0 = 0$), these field configurations exhibit polarization of chirality ($h_c \neq 0$), which leads to enantio-sensitive light bending.

3.4. Control over the enantio-sensitive light bending

We now show how the direction of harmonic emission can be controlled by adjusting the individual phase delays $\phi_1$ and $\phi_2$ in our setup (see equation (7)). We quantify the degree of enantio-sensitive light bending by calculating the average angle of harmonic emission,

$$\langle \phi \rangle = \frac{\int |\phi| \kappa d\phi}{\int |\phi| d\phi},$$

where $\kappa$ is the divergence angle in the far field (equation (17)). Figure 9 presents the average angle of emission at frequency $6\omega$ from the L (figure 9(a)) and R (figure 9(b)) enantiomers, as a function of $\phi_1$ and $\phi_2$. By adjusting these parameters, we achieve full control over enantio-sensitive light bending, and $|\langle \phi \rangle|$ exceeds 1.5°.

Enantio-sensitive light bending is optimized in the phase regions where the total intensity of emission is not enantio-sensitive ($\gamma = 0$ in figure 8(c)), as in these regions: (i) the field is globally achiral, but has maximum polarization of chirality ($\phi_\perp = 0$), and (ii) $\phi_\perp$ favors enantio-sensitive light bending. We find the opposite situation, $|\langle \kappa \rangle| = 0$ and maximum $|\gamma|$, in the regions where (i) the field is perfectly globally chiral, but chirality unpolarized, and (ii) $\phi_\perp$ favors the enantio-sensitive interference at the single-molecule level.

The $\langle \phi \rangle$ scans in figure 9 contain white lines with $\langle \kappa \rangle = 0$. As in the $\gamma$ scan in figure 8(c), these nodal lines record the field configuration and the ultrafast chiral response of the chiral medium. Here, the white lines of slope 1 appear at $\phi_2 = \phi_1 \pm \pi/2$, where the field is globally chiral ($h_0 \neq 0$) and unpolarized ($h_c = 0$), see figure 6. These lines are characteristic of the field configuration and independent of the molecular properties, just like the white lines of slope 1 the $\gamma$ scan (figure 8(c)).

Also like in the $\gamma$ scan, the white lines of slope -1 record the ultrafast electronic response of the chiral medium, and are molecule-specific features. Here, the nodal lines appear in the regions where $P_c$ and $P_a$ are exactly in phase in one enantiomer and out of phase in the other, because the enantio-sensitive light bending relies on a far-field interference which maximizes when $P_c$ and $P_a$ radiate with a phase delay of $\pm \pi/2$. If $P_c$ and $P_a$ are exactly in or out of phase, then they can efficiently interfere in the near field, but radiate symmetrically with respect to $\kappa$, yielding $\langle \kappa \rangle = 0$.  

Figure 9. Control over enantio-sensitive light bending. Average angle of harmonic emission $\langle \kappa \rangle$ (equation (19)) at frequency $6\omega$ from left- (a) and right-handed (b) H$_2$O$_2$, as a function of the two-color phase delay in the two beams $\phi_1$ and $\phi_2$. $|\langle \kappa \rangle|$ maximizes for $\phi_2 = \phi_1$, when the field’s polarization of chirality, quantified by $h_c$ (equation (14)), maximizes. For $\phi_2 = \phi_1 + \pi$, the field is chirality unpolarized ($h_c = 0$), and thus the direction of harmonic emission is not enantio-sensitive.
4. Conclusion and outlook

Synthetic chiral light is a powerful optical tool for chiral recognition, which allows us to bypass two fundamental limitations of (standard) circularly polarized light. The first limitation is related to the strength of the chiro-optical signals. Circularly polarized light is not chiral within the electric-dipole approximation: the Lissajous figure that the tip of the electric-field vector draws in time, in a given point in space, is a (planar) circle. This circle becomes chiral once we include the propagation vector of the light wave and its magnetic-field component, but non-electric-dipole interactions are weak for small to medium-size molecules, and lead to weak enantio-sensitivity. In contrast, the enantio-sensitive response of chiral matter to synthetic chiral light is solely driven by the electric-field vector of the light field.

The second constraint of standard chiral light is that it offers limited opportunities for control: we can change between left and right circular or elliptical polarization, but the phase between the electric and magnetic components of the wave is fundamentally locked. As a result, the enantio-sensitive response of the molecules is not only weak, but also harder to control. In contrast, the handedness of synthetic chiral light depends on the phase delay between its frequency components, which is a continuous and controllable parameter. By adjusting the phase delays in the proposed non-collinear setup, we can shape the Lissajous figure that the tip of the electric-field vector draws in time, at every point in space, in order to maximize the enantio-sensitive response of the chiral medium.

This paper provides a recipe for structuring the local handedness of synthetic chiral light in space, and thus for creating optical fields with tailored local and global chirality properties. Using state-of-the-art computational modeling to evaluate the ultrafast electronic response of a prototypical chiral system, we have shown how these local and global properties are imprinted into enantio-sensitive macroscopic observables. Because the enantio-sensitive signals rely on the interference between two multiphoton pathways which are ubiquitous in chiral molecules driven by locally chiral light, our findings are general and the conclusions of this work remain valid for more complex chiral systems.

We have shown how locally and globally chiral light can enhance the nonlinear response of a selected molecular enantiomer while quenching it in its mirror twin at the level of total intensity signals. However, global chirality is not necessarily needed to produce strongly enantio-sensitive signals. If the driving field is globally achiral, but chirality polarized, it can send the nonlinear response of opposite molecular enantiomers in different directions. In contrast with previous works \cite{36–38}, we have shown how one can engineer synthetic chiral light that is both globally chiral and chirality polarized. Here, the intensity of harmonic emission is enantio-sensitive at the level of total intensity signals, and sent in different directions from opposite molecular enantiomers, although the enantio-sensitivity of both macroscopic observables is reduced.

Our analysis reveals the presence of enantio-sensitive molecule-specific fingerprints in the spectra of harmonic emission. Indeed, the nodal lines in the scans which record the dissymmetry factor (figure 8(c)) and the average emission angles (figure 9), as functions of the two-color phase delays in the incident beams, contain valuable information about the laser field configuration, which could be used for calibration purposes, but also about the enantio-sensitive interplay between the chiral and achiral components of the ultrafast dynamics induced in the molecules.

The possibility of creating synthetic chiral light with controllable local handedness, controllable global handedness, and controllable polarization of chirality, opens exciting avenues for efficient chiral recognition on ultrafast time scales. New opportunities may arise from the possibility of sculpting the local handedness of synthetic chiral light using vortex beams, taking advantage of the structured phase profiles characteristic of such waveforms.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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