Discriminatory optical force for chiral molecules

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Abstract
We suggest that the force \( F \) exerted upon a chiral molecule by light assumes the form \( F = a \nabla w + b \nabla h \) under appropriate circumstances, where \( a \) and \( b \) pertain to the molecule whilst \( w \) and \( h \) are the local densities of electric energy and helicity in the optical field; the gradients \( \nabla \) of these quantities thus governing the molecule’s centre-of-mass motion. Whereas \( a \) is identical for the mirror-image forms or enantiomers of the molecule, \( b \) has opposite signs; the associated contribution to \( F \) therefore pointing in opposite directions. A simple optical field is presented for which \( \nabla w \) vanishes but \( \nabla h \) does not, so that \( F \) is absolutely discriminatory. We then present two potential applications: a Stern–Gerlach-type deflector capable of spatially separating the enantiomers of a chiral molecule and a diffraction grating to which chiral molecules alone are sensitive; the resulting diffraction patterns thus encoding information about their chiral geometry.

1. Introduction

It was Kelvin who introduced the word *chiral* [1, 2] to refer to any geometrical figure or group of points that cannot be brought into coincidence with its image as seen in a plane mirror, thus possessing a sense of handedness. Chirality pervades the natural world [3], from the enigmatic preferences of the weak interaction [4, 5] to the helices traced out by the arms of spiral galaxies [6].

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Figure 1. The left-handed (a) and right-handed (b) enantiomers of hexahelicene, a chiral molecule with a shape resembling that of a finite cylindrical helix. The normalized pitch $\gamma$ of hexahelicene is a pseudoscalar: it assumes opposite signs for the molecule’s enantiomers [7–9].

Under ‘normal’ circumstances, an atom is essentially achiral as it possesses the high degree of symmetry associated with a sphere [7]. In contrast, many types of molecule are chiral owing to the nature and arrangement in space of their constituent atoms [3]. The separate and seemingly stable existence of mirror-image forms, or enantiomers, of certain chiral molecules is a remarkable example of symmetry breaking [7]: see figure 1. Whilst they are similar in many respects, the enantiomers of a chiral molecule can, for example, exert drastically different influences upon living things, the inner workings of which are themselves invariably chiral [3, 10]. The development of means to detect and discriminate between the enantiomers of a chiral molecule is a task of utmost importance and, indeed, constitutes a vibrant field of modern research [11, 12].

It is well established that chiral molecules can exert discriminatory mechanical forces upon each other [13–15]. In recent years, interest has been expressed regarding the possibility of using light, such as that produced by a laser, to exert a mechanical force of discriminatory character upon a single chiral molecule [16–21]. The present paper is concerned with this possibility. Specifically, we suggest that the centre-of-mass motion of a chiral molecule is, under appropriate circumstances, sensitive to gradients in the helicity of an optical field and observe that the force associated with these gradients points in opposite directions for the molecule’s enantiomers (section 2). We present a simple optical field for which this phenomenon is brought to prominence (section 3) and propose two potential applications, namely a Stern–Gerlach-type deflector capable of spatially separating the enantiomers of a chiral molecule (section 4) and a diffraction grating to which chiral molecules alone are sensitive, the resulting diffraction patterns thus encoding information about their chiral geometry (section 5). Our approach differs, it seems, from others that have been presented in the literature [16–20] in that we make no critical assumptions regarding the energy-level structure of our molecule but rather, rely upon the sign of a certain polarizability. Whilst drafting the present paper for submission, however, another paper of closely related content was published, independently, on the arXiv [21]. We believe that our contributions are complementary.

In what follows, we consider ourselves to be in an inertial frame of reference and adopt a right-handed Cartesian coordinate system ($x$, $y$ and $z$), employing SI units.

2. Force exerted by light upon a chiral molecule

Consider a ‘small’, neutral, non-polar, non-magnetic, chiral molecule irradiated by monochromatic light of angular frequency $\omega$ that is (otherwise) freely propagating. We shall
presume that the Coulomb field binding the molecule together is ‘sufficiently’ stronger than the optical field [13], that the molecule is ‘essentially’ transparent at \( \omega \), which we take to be far off-resonance (in the near infrared, perhaps), and that the molecule has come into contact with the optical field in an adiabatic manner [22]. A simple, classical picture then emerges in which the optical field drives steady oscillations of the molecule’s charge and current distributions, also at angular frequency \( \omega \), the radiation attributable to these oscillations constituting Rayleigh scattered light [7, 13]. During the course of their interactions, the optical field will, in general, exchange linear momentum with the molecule, giving rise to a force which governs the molecule’s centre-of-mass motion.

We derive an expression for the force using only classical electromagnetism. The electric field \( \mathbf{E} = \mathbf{E}(r, t) \) and magnetic flux density \( \mathbf{B} = \mathbf{B}(r, t) \) that comprise the light, which we treat as an externally imposed influence acting upon the molecule, evolve as functions of space \( r \) and time \( t \) in accord with the charge-free Maxwell equations:

\[
\nabla \cdot \mathbf{E} = 0, \tag{2.1}
\]
\[
\nabla \cdot \mathbf{B} = 0, \tag{2.2}
\]
\[
\nabla \times \mathbf{E} = -\dot{\mathbf{B}}, \tag{2.3}
\]
\[
\nabla \times \mathbf{B} = \varepsilon_0 \mu_0 \dot{\mathbf{E}}. \tag{2.4}
\]

Here \( \nabla \) is the gradient operator with respect to \( r \), an overdot is used to indicate (partial) differentiation with respect to \( t \), \( \varepsilon_0 \) and \( \mu_0 \) are the electric and magnetic constants and \( c = 1/\sqrt{\varepsilon_0 \mu_0} \) is the speed of light [23–25]. As the optical field is presumed monochromatic, it is convenient to introduce complex (denoted by a tilde) quantities \( \tilde{\mathbf{E}} = \tilde{\mathbf{E}}(r) \) and \( \tilde{\mathbf{B}} = \tilde{\mathbf{B}}(r) \) defined such that

\[
\mathbf{E} = \Re(\tilde{\mathbf{E}} \exp(-i\omega t)), \tag{2.5}
\]
\[
\mathbf{B} = \Re(\tilde{\mathbf{B}} \exp(-i\omega t)). \tag{2.6}
\]

where the function \( \Re \) yields the real part of its argument [24, 25]. It should be noted that we are not restricting ourselves to the consideration of a single plane wave or even a single beam of light. Instead, we work with the presumed forms (2.5) and (2.6) in direct accord with the charge-free Maxwell equations (2.1)–(2.4), which are general and exact. We are thus free in what follows to consider, in particular, any suitable superposition of plane electromagnetic waves of angular frequency \( \omega \). This freedom allows us to construct rather exotic optical fields [26], the unusual properties of which open the door to novel possibilities, as we shall see. We consider the molecule to consist of a collection of non-relativistic point particles (labelled \( n = 1, 2, \ldots \)) of charge \( q_n \), mass \( m_n \) and position \( \mathbf{r}_n = \mathbf{r}_n(t) \). Some of these particles are electrons, the remainder are nuclei. It is convenient, albeit artificial, to suppose, at present, that the centre of mass \( \mathbf{R} = \mathbf{R}(t) = \sum_n m_n \mathbf{r}_n / \sum_n m_n \) of the molecule is fixed at some position \( \hat{X} \hat{x} + \hat{Y} \hat{y} + \hat{Z} \hat{z} \) in the optical field, where \( \hat{x}, \hat{y} \) and \( \hat{z} \) are unit vectors for the \( x, y \) and \( z \) axes. We neglect the forces experienced by the particles due to their own electromagnetic fields, which give rise, in particular, to radiation reaction effects [23–25]. Moreover, we approximate the true electromagnetic interactions between the particles by non-retarded Coulomb interactions [23], the forces associated with which cancel for any given pair of particles. Thus, the net electromagnetic force \( \mathbf{F} = \mathbf{F}(t) \)
experienced by the molecule derives solely from the Lorentz forces \[23–25\] exerted upon the individual particles by the optical field

\[
\mathbf{F} = \sum_n q_n [\mathbf{E}(\mathbf{r}_n, t) + \mathbf{r}_n \times \mathbf{B}(\mathbf{r}_n, t)]
\]

\[
= \int (\rho \mathbf{E} + \mathbf{J} \times \mathbf{B}) \, dV,
\]

where \(\rho = \rho(\mathbf{r}, t)\) and \(\mathbf{J} = \mathbf{J}(\mathbf{r}, t)\) are the charge and current densities attributable to the molecule

\[
\rho = \sum_n q_n \delta(\mathbf{r} - \mathbf{r}_n),
\]

\[
\mathbf{J} = \sum_n q_n \hat{\mathbf{r}}_n \delta(\mathbf{r} - \mathbf{r}_n)
\]

with \(\delta(\mathbf{r})\) the three-dimensional Dirac delta function. Introducing the associated electric polarization \(\mathbf{P} = \mathbf{P}(\mathbf{r}, t)\) and magnetization \(\mathbf{M} = \mathbf{M}(\mathbf{r}, t)\) fields\(^4\)

\[
\mathbf{P} = \sum_n q_n (\mathbf{r}_n - \mathbf{R}) \int_0^1 \delta(\mathbf{r} - \mathbf{R} - u(\mathbf{r} - \mathbf{r}_n)) \, du,
\]

\[
\mathbf{M} = \sum_n q_n (\mathbf{r}_n - \mathbf{R}) \times \hat{\mathbf{r}}_n \int_0^1 u \delta(\mathbf{r} - \mathbf{R} - u(\mathbf{r} - \mathbf{r}_n)) \, du,
\]

through the relations \(\rho = -\nabla \cdot \mathbf{P}\) and \(\mathbf{J} = \dot{\mathbf{P}} + \nabla \times \mathbf{M}\) \([13, 23]\), we find that

\[
\mathbf{F} = \int \left[ (-\nabla \cdot \mathbf{P}) \mathbf{E} + (\dot{\mathbf{P}} + \nabla \times \mathbf{M}) \times \mathbf{B} \right] \, dV
\]

\[
= \int \sum_{a=x,y,z} \left( P_a \nabla E_a + M_a \nabla B_a \right) \, dV + \frac{d}{dt} \int \mathbf{P} \times \mathbf{B} \, dV,
\]

where we have performed integrations by parts and have made use of the Faraday–Lenz law (2.3) \([27]\). Being a total derivative with respect to \(t\), the third term here contributes nothing when averaged in time over an optical period \(2\pi/\omega\).\(^5\) Expanding \(\delta(\mathbf{r} - \mathbf{R} - u(\mathbf{r}_n - \mathbf{R}))\) about \(\mathbf{r} - \mathbf{R}\) in \(\mathbf{P}\) and \(\mathbf{M}\) on the second line of (2.12) yields a multipole expansion of \(\mathbf{F}\): a sum of terms in which the electric-multipole moments (from \(\mathbf{P}\)) and mechanical magnetic-multipole moments (from \(\mathbf{M}\)) \([7, 13, 23]\) of the molecule’s charge and current distributions couple to various spatial derivatives of the components of \(\mathbf{E}\) and \(\mathbf{B}\). The contributions to these multipole moments that are induced by the optical field can be related to the latter through the use of appropriate polarizability tensors and pseudotensors \([7, 31]\).

We imagine that the molecule is ‘tumbling’ freely in the optical field\(^6\) and content ourselves accordingly with an examination of the cycle-averaged (denoted by an overbar),

\(^4\) We have expressed \(\mathbf{P}\) and \(\mathbf{M}\) with respect to \(\mathbf{R}\). A different position within or near to the molecule may be more convenient, however, and can be used instead.

\(^5\) We note that this does play an important part, however, in resolving the Abraham–Minkowski dilemma \([28–30]\). Indeed it is this term that accounts for the difference between the Abraham and Minkowski linear momenta.

\(^6\) In reality, the molecule might, for example, initially occupy a suitable thermal mixed state of ‘high’ temperature that spans many rotational levels.
rotationally averaged (denoted by angular brackets) form \( \langle \mathbf{F} \rangle \) of the multipolar expansion of \( \mathbf{F} \), restricting our attention to those terms that are of leading order under ‘typical’ circumstances. To arrive at our desired result, we consider the molecule’s electric-dipole moment \( \mu = \mu(t) \), its symmetric and traceless electric-quadrupole moment \( \Theta = \Theta(t) \) and its mechanical magnetic-dipole moment \( \mathbf{m}' = \mathbf{m}'(t) \). The rotationally averaged forms \( \langle \mu \rangle = \langle \mu \rangle(t) \), \( \langle \Theta \rangle = \langle \Theta \rangle(t) \) and \( \langle \mathbf{m}' \rangle = \langle \mathbf{m}' \rangle(t) \) are, to the order of present interest, expressible as

\[
\langle \mu \rangle = \Re (\langle \hat{\mu} \rangle \exp(-i\omega t)),
\]

\[
\langle \Theta \rangle = 0,
\]

\[
\langle \mathbf{m}' \rangle = \Re (\langle \hat{\mathbf{m}} \rangle \exp(-i\omega t))
\]

with the complex quantities \( \langle \hat{\mu} \rangle \) and \( \langle \hat{\mathbf{m}} \rangle \) related to the optical field via

\[
\langle \hat{\mu} \rangle = \alpha(\mathbf{E})_0 - iG'(\mathbf{B})_0,
\]

\[
\langle \hat{\mathbf{m}} \rangle = iG' \langle \mathbf{E} \rangle_0.
\]

The vanishing of \( \langle \Theta \rangle \) seen in (2.14) is a direct consequence of the rotational averaging procedure\(^7\) [7, 13]. A subscripted zero accompanying a pair of brackets indicates evaluation at \( \mathbf{R} \) whilst \( 3\alpha = \alpha_{xx}(f_w) + \alpha_{yy}(f_w) + \alpha_{zz}(f_w) \) and \( 3G' = G'_{xx}(f_w) + G'_{yy}(f_w) + G'_{zz}(f_w) \) are the traces of the dispersive pieces of the molecule’s unprimed electric-dipole/electric-dipole polarizability tensor \( \alpha_{ab}(f_w) \) and primed electric-dipole/magnetic-dipole polarizability pseudotensor \( G'_{ab}(f_w) \), where \( f_w \) is the molecule’s dispersion lineshape evaluated at \( \omega \) [7]. The forms seen in (2.13)–(2.17) may be justified through appropriate semi-classical calculations, for example: see [7], where explicit quantum-mechanical expressions for \( 3\alpha \) and \( 3G' \) are presented. In adopting the forms seen in (2.16) and (2.17), we have presumed the relevant unperturbed energy eigenstate wavefunctions of the molecule to be real, as may be done in the absence of externally imposed time-odd influences such as a static magnetic flux density, provided these eigenstates are non-degenerate [7, 22]. Taking the rotationally averaged electric polarization \( \langle \mathbf{P} \rangle = \langle \mathbf{P} \rangle(\mathbf{r}, t) \) and magnetization \( \langle \mathbf{M} \rangle = \langle \mathbf{M} \rangle(\mathbf{r}, t) \) fields to be

\[
\langle \mathbf{P} \rangle = \langle \mu \rangle \delta^3(\mathbf{r} - \mathbf{R}),
\]

\[
\langle \mathbf{M} \rangle = \langle \mathbf{m}' \rangle \delta^3(\mathbf{r} - \mathbf{R}),
\]

we find that \( \langle \mathbf{F} \rangle \) is conservative and is comprised of two distinct pieces

\[
\langle \mathbf{F} \rangle = -\langle \nabla U_w \rangle_0 - \langle \nabla U_h \rangle_0,
\]

where the potential energies \( U_w = U_w(\mathbf{r}) \) and \( U_h = U_h(\mathbf{r}) \) are introduced below.

Note that in obtaining the result seen in (2.20) we supposed \( \mathbf{R} \) to be fixed. In what follows, however, we employ this result to describe scenarios in which \( \mathbf{R} \) may be changing with time. In doing so, we neglect certain phenomena that are attributable directly to the centre-of-mass

\(^7\) The spins of the individual particles may be accounted for heuristically here by incorporating their associated magnetic dipole moments in \( \mathbf{m}' \) [7, 23].

\(^8\) In the present context, it is permissible to work with the rotationally averaged forms of \( \mu \), \( \Theta \) and \( \mathbf{m}' \) from the outset. There are, however, contexts in which it is not appropriate to perform a rotational averaging at this early stage: when calculating scattering intensities, for example, where electromagnetic waves attributable to different multipole moments interfere with each other [7].
motion of the molecule (Röntgen current, Doppler shifts, etc [13, 32]), the effects of which will be ‘small’ for realistic molecular speeds.

The potential energy $U_w$ seen in the first term of (2.20) is the familiar ‘dipole’ potential energy [31, 32]:

$$U_w = -\alpha \overline{w}_E/\epsilon_0,$$

where $w_E = w_E(r,t)$ is an electric energy density of the optical field [24, 25]:

$$w_E = \epsilon_0 \mathbf{E} \cdot \mathbf{E}/2.$$

Except for a factor of twice the speed of light $c$, $\overline{w}_E$ is often referred to loosely as the ‘intensity’ of an optical field, although this nomenclature is not appropriate in general. It seems natural that $3\alpha$ should appear in connection with $w_E$. The former is a time-even scalar associated with the interference of electric-dipole transition moments within a molecule [7] whilst the latter is a time-even scalar field that is also of apparent electric character [24]. For $\omega$ far off-resonance, $3\alpha$ may be well-approximated by its static value, which is usually positive [7, 33]. In general, $w_E$ is also positive although it may, of course, vanish at certain points in space at certain times [26]. $U_w$ thus attracts the molecule towards those regions in the optical field where $\overline{w}_E$ is maximum. The employment of the dipole potential energy to manipulate molecules has been pursued in a wealth of theoretical [33–49] and experimental [50–67] contexts.

The potential energy $U_h$ seen in the second term of (2.20) is

$$U_h = \omega G' \overline{h}/\epsilon_0 c,$$

where $h = h(r,t)$ is a helicity density of the optical field [26, 70–73]

$$h = \epsilon_0 c (\mathbf{A}^\perp \cdot \mathbf{B} - \mathbf{C}^\perp \cdot \mathbf{E}) /2,$$

with $\mathbf{A}^\perp = \mathbf{A}^\perp (r,t)$ and $\mathbf{C}^\perp = \mathbf{C}^\perp (r,t)$ the transverse, gauge-invariant pieces [23] of the familiar magnetic vector potential [24, 25] and an analogous electric pseudovector potential [68, 69] defined here such that $\mathbf{E} = -\mathbf{A}^\perp = -\nabla \times \mathbf{C}^\perp/\epsilon_0 \mu_0$ and $\mathbf{B} = \nabla \times \mathbf{A}^\perp = -\mathbf{C}^\perp$. Helicity is a property of light that is familiar from particle physics, where it is recognized as being the value taken by the component of a photon’s spin angular momentum in the direction of propagation: the helicity $\mathcal{H} = \int h \, dV$ of an optical field assumes a value equivalent to $\pm \hbar$ per circularly polarized plane-wave-mode photon, in particular [26, 70–73]. Locally, $h$ is found to be time independent for a strictly monochromatic optical field and may exhibit other interesting characteristics besides [26]. It seems natural that $3G'$ should appear in connection with $h$. The former is a time-even pseudoscalar associated with the mutual interference of electric-dipole and magnetic-dipole transition moments within a molecule [7] whilst the latter is a time-even pseudoscalar field that embodies the electric-magnetic symmetry inherent to freely propagating light [73–77]. Moreover, such transformation properties are the hallmarks of true chirality [7, 78–81] and indeed, $3G'$ possesses equal magnitudes but opposite signs for the enantiomers of a chiral molecule [13, 15, 22] whilst $\mathcal{H}$ itself possesses equal magnitudes but opposite signs for the enantiomorphs of an optical field [26, 71–73]. Thus, the force associated with $U_h$ is entirely discriminatory, pointing in opposite directions for the enantiomers of the molecule: $U_h$ attracts the enantiomer for which $3G' > 0$ towards those regions in the optical field where $\overline{h}$ is minimum whilst the opposite enantiomer, with $3G' < 0$, is instead attracted to those regions in the optical field where $\overline{h}$ is maximum. We suggest, therefore, that $U_h$ represents something of a marriage between the chirality of the molecule and the chirality of the optical field. This, in essence, is our main result.
It seems that the explicit identification of $\vec{h}$ in $U_h$ is only possible because we are restricting our attention to a monochromatic, optical field. In this context, it appears, in fact, that we could equally well have identified any one of an infinite number of lower- and higher-order extensions of $h$ [71, 73, 82], amongst them, the 00-zilch density $Z^{000}$ [83, 84], which was re-introduced into the literature recently in connection with fluorescence-detected circular dichroism [85] and has since been considered in a sizeable body of research [21, 86–97]. A similar ambiguity prevails when considering the explicit identification of $\overline{w}_E$ in $U_w$ and we observe more generally that it does not appear possible to identify every term in the complete form of $\langle \vec{F} \rangle$ with the density of a familiar quantity in a convincing manner. This fact becomes clear, perhaps, when one considers those contributions to our molecule’s response that are nonlinear in our optical field. Thus, such identifications can hardly be said to be of any fundamental significance. They do, however, provide us with useful pictures.

Although the derivation given in the present section and indeed, the concept of a force, is classical in nature, we note that the forms of $U_w$ and $U_h$ can also be justified by an appropriate calculation in the quantum domain.

3. Bringing the discriminatory optical force to prominence

In section 2, we found that the cycle-averaged, rotationally averaged force $\langle \vec{F} \rangle$ exerted upon the molecule by the optical field could be expressed as

$$\langle \vec{F} \rangle = \alpha \langle \nabla \overline{w}_E \rangle_0 / \epsilon_0 - \omega G' \langle \nabla \overline{h} \rangle_0 / \epsilon_0 c. \quad (3.1)$$

The first term here points in the same direction for the enantiomers of the molecule whereas the second term points in opposite direction and is, therefore, the contribution to $\langle \vec{F} \rangle$ that we envisage using to manipulate the centre-of-mass motion of the molecule in a discriminatory manner. A simple estimate reveals that the ratio $|\alpha / G'|$ is ‘typically’ of the order of $1 \times 10^3$ [7, 13, 14] and so it may appear that the first term dominates. However, this need not be the case: we can, in fact, eliminate the first term so that $\langle \vec{F} \rangle$ is in turn entirely discriminatory, by constructing the optical field such that the cycle-averaged electric energy density $\overline{w}_E$ is homogeneous (and, therefore, $\langle \nabla \overline{w}_E \rangle_0 = 0$) whilst the cycle-averaged helicity density $\overline{h}$ is not (and $\langle \nabla \overline{h} \rangle_0 = 0$).

To demonstrate this, we consider one such optical field [26] which is constructed by superposing two linearly polarized plane electromagnetic waves of equal amplitude $E_0 > 0$ and angular frequency $\omega$, propagating such that their wavevectors lie in the $x$-$z$-plane making angles of $\pm \theta$ ($\theta > 0$) with the $+z$-axis. We take the electric fields of the $\pm \theta$ waves to be oscillating in the $x$-$z$-plane and parallel to the $y$-axis, respectively: see figure 2. We suppose that $\theta \ll 1$ but work in an exact manner at present nonetheless, taking the complex quantity $\vec{E}$ to be

$$\vec{E} = E_0 (\hat{x} \cos \theta - \hat{z} \sin \theta) \exp (i \omega (z \cos \theta + x \sin \theta) / c) + E_0 \hat{y} \exp (i \omega (z \cos \theta - x \sin \theta) / c). \quad (3.2)$$

From (2.22), we find that $\overline{w}_E$ is homogeneous

$$\overline{w}_E = \epsilon_0 E_0^2 / 2, \quad (3.3)$$

which is unsurprising given that the waves possess orthogonal polarizations and so do not interfere. From (2.24), we find, however, that $\overline{h}$ undulates in $x$

$$\overline{h} = - \epsilon_0 E_0^2 \cos^2 \theta \sin (\kappa x) / \omega, \quad (3.4)$$
a characteristic attributable to the undulation, in \( x \), of the relative phase of the waves, with associated wavenumber \( \kappa = 2\omega \sin \theta / c \). We refer to these undulations in \( h \) as *helicity fringes* [26]. Optical fields of this character have been produced experimentally in various contexts [98–100]. From (2.21), (2.23), (3.3) and (3.4) we have that \( U_w \) and \( U_h \) are

\[
U_w = -\alpha E_0^2 / 2, \quad (3.5)
\]

\[
U_h = -G' E_0^2 \cos^2 \theta \sin(\kappa x) / c. \quad (3.6)
\]

From (2.20), \( \langle \bar{F} \rangle \) is then

\[
\langle \bar{F} \rangle = \kappa G' E_0^2 \cos^2 \theta \cos(\kappa X) \hat{x} / c, \quad (3.7)
\]

which is non-vanishing, in general, and points in opposite directions for the enantiomers of the molecule by virtue of the opposite signs of the trace \( 3G' \), as claimed. See figure 3.

It is possible, of course, to conceive of many other optical fields for which \( \bar{w}_E \) is homogeneous whilst \( \bar{h} \) is not. We emphasize that \( \langle \bar{F} \rangle \) is entirely discriminatory in *all* such cases. The simple examples of which we are aware are obtained, as above, from various superpositions of electromagnetic waves that possess orthogonal polarizations [26, 101].

4. Newtonian molecular optics: chiral Stern–Gerlach deflector

The field of Newtonian molecular optics is concerned with the manipulation of the centre-of-mass motion of a molecule in a regime where the motion can be viewed classically [32], as we have presumed to be the case so far. The dipole potential energy \( U_w \) seen in (2.21) and
Figure 3. Plots pertaining to the optical field presented in section 3. We consider $2\pi/\kappa \geq x \geq -2\pi/\kappa$, the specific values of $y$ and $z$ being irrelevant. (a) The potential energies $U_w$ and $U_h$ seen in (3.5) and (3.6), the latter being depicted for positive and negative values of the trace $3G'$. (b) The $x$-component $\langle F_x \rangle$ of the associated cycle-averaged, rotationally averaged force $\langle \vec{F} \rangle$ seen in (3.7), again depicted for positive and negative values of $3G'$. (c) A two-dimensional section of the optical field with regions of negative helicity and positive helicity depicted in dark purple and light green. The influence of $\langle \vec{F} \rangle$ is indicated here for the enantiomers of hexahelicene (see figure 1) by black arrows. Not to scale.

its contribution to the force $\langle \vec{F} \rangle$ seen in (2.20) have been utilized successfully in this regime in a multitude of experiments [50, 51, 53, 55, 56, 58–61, 65–67]. It is natural, therefore, to investigate the novel possibilities offered for our molecule in the regime of Newtonian molecular optics by the discriminatory potential energy $U_h$ seen in (2.23) and its contribution to $\langle \vec{F} \rangle$.

The use of an optical field akin to the one presented in section 3 to deflect the centre-of-mass trajectory of the molecule in a discriminatory manner with a single helicity fringe, say, presents itself as one possibility: see figure 4. Such a device may, for example, be employed to spatially separate the enantiomers of a chiral molecule. In apparent analogy to a traditional Stern–Gerlach deflector [102], we refer to it as a chiral Stern–Gerlach deflector. Closely related devices have been proposed theoretically elsewhere [16, 18–20], albeit making use of seemingly different mechanisms.
We perform a simple estimate to gauge the feasibility of our chiral Stern–Gerlach deflector. We suppose that the molecule, of mass $M$, resides, at some initial time $t = 0$, at the origin of the optical field presented in section 3, moving in the $+z$ direction with speed $V_z$. We suppose, moreover, that its subsequent centre-of-mass motion is governed by Newton’s second law and the cycle-averaged, rotationally averaged force $\langle F \rangle$ seen in (3.7). Considering an interaction time $0 < t \ll \sqrt{Mc/\kappa^2}|G'|E_0^2$ such that the molecule does not reach its nearest helicity trough or peak and $|X(t)| \ll \pi/2\kappa$, we deduce that its angular deflection $\phi = \phi(t)$, as measured with respect to the $+z$-axis, is given approximately by

$$\phi = \kappa G' E_0^2 t/MV_z c$$  \hspace{1cm} (4.1)

to first order in the angle $\theta$ here and also $\phi$, as we presume that $\theta, \phi \ll 1$. We consider an optical angular frequency $\omega$ that corresponds to a free-space wavelength of $2\pi c/\omega = 1.064 \times 10^{-6}$ m, which lies in the near infrared to which many molecules are indeed essentially transparent \[50, 51, 53, 55, 56, 58–61, 65, 67\]. We choose $\theta$, and hence, the wavenumber $\kappa = 2\omega \theta/c$, to yield helicity fringes of wavelength $2\pi/\kappa = 1 \times 10^{-5}$ m, which is also in line with experimental demonstrations \[99, 100\]. As an example, we consider hexahelicene, a chiral molecule with $M = 5.45 \times 10^{-25}$ kg: see figure 1 \[7–9\]. Using an empirical result obtained from a measurement of specific rotation \[7–9\], together with an appropriate theoretical angular frequency scaling \[7, 103\], we estimate hexahelicene’s trace to be $3G' = \pm 1 \times 10^{-34}$ m kg$^{-1}$ s$^3$ A$^2$; the plus and minus signs referring to the left-handed and right-handed enantiomers of the molecule. We consider an amplitude $E_0$ that corresponds to a notional intensity of $\epsilon_0 c E_0^2 = 1 \times 10^{15}$ kg s$^{-3}$, the latter being approximately one order of magnitude smaller than that typically employed \[50, 51, 53, 56, 58–61, 65, 67\]. This may help to reduce the possible effects of polarization-dependent alignment \[65, 66\] that threaten to complicate our picture and also allows us, to consider $t = 1 \times 10^{-6}$ s, which is approximately two orders of magnitude larger than usual \[50, 51, 53, 55, 56, 58–61, 65, 67\]: the probabilities of certain processes such as multi-photon ionization that promise to damage the molecule, thus limiting the maximum interaction time, scale in a highly nonlinear fashion with
Figure 5. The principle of operation of our chiral diffraction grating. (a) A chiral molecule such as the right-handed enantiomer of hexahelicene (see figure 1) is diffracted by a collection of helicity fringes. (b) An achiral molecule such as buckminsterfullerene (C\textsubscript{60}) does not ‘sense’ these fringes and hence, is not diffracted. Not to scale.

Even for our optimistic estimate, φ is rather ‘small’. Nevertheless, we hope that such deflections may be detectable in careful experiments.

It is possible, of course, to conceive of other novel possibilities offered for chiral molecules in the regime of Newtonian molecular optics by \( U_h \) and its contribution to \( \langle F \rangle \). At present, however, we turn our attention to a more delicate but sensitive regime, namely that of de Broglie molecular optics.

5. de Broglie molecular optics: chiral diffraction grating

In contrast to Newtonian molecular optics, de Broglie molecular optics is concerned with the manipulation of the centre-of-mass motion of a molecule in the delicate but sensitive regime where the motion cannot be viewed classically but rather should be viewed quantum mechanically [32]. The dipole potential energy \( U_w \) seen in (2.21) has also been utilized successfully in this regime in various experiments [57, 62–64, 105]. It seems natural, therefore, to enquire as to the novel possibilities offered for our molecule in the regime of de Broglie molecular optics by the discriminatory potential energy \( U_h \) seen in (2.23).

We recognize, for example, the possibility of using an optical field akin to the one presented in section 3 to diffract the molecule by virtue of its chirality. Specifically, we imagine employing a collection of helicity fringes as an optical phase grating to which the molecule is sensitive by virtue of its non-vanishing trace \( 3G' \neq 0 \). As a similar achiral molecule can only support a vanishing trace \( 3G' = 0 \) [13, 15, 22], it will not ‘sense’ these helicity fringes and thus, will not exhibit such diffraction: see figure 5. A device of this nature may constitute an incisive probe...
for chiral molecules in that the diffraction patterns it produces encode information regarding the molecules’ chiral geometry. We refer to our device simply as a chiral diffraction grating.

Let us now consider the results of some simple calculations pertaining to our chiral diffraction grating. We suppose that the molecule, of mass $M$, resides in the optical field presented in section 3 and describe it as a point particle behaving in accord with the Schrödinger equation under the influence of the potential energies $U_w$ and $U_n$ seen in (3.5) and (3.6). We suppose, moreover, that the molecule occupies, at some initial time $t = 0$, a linear momentum eigenstate with eigenvalue $MV_z\hat{\mathbf{z}}$, where $V_z$ is a speed. Considering an interaction time $0 < t \ll 2Mc^2/\hbar\omega^2$ significantly shorter than the inverse of the single-photon recoil angular frequency, say, we employ the Raman–Nath approximation and find, following a slight variant of a standard calculation [106], that the molecule evolves into a superposition of linear momentum eigenstates with eigenvalues $n\hbar \kappa \hat{x} + MV_z\hat{z}$, where $n \in \{0, \pm 1, \ldots \}$ and the probabilities $p_n = p_n(t)$ associated with these eigenvalues are

$$p_n = J_n^2 \left( G' E_0^2 t / \hbar c \right), \quad (5.1)$$

to first order in the angle $\theta \ll 1$ here, with $\hbar$ the reduced Planck constant and $J_n$ the Bessel function of the first kind of order $n$. In reality, we may associate $t$ with a notional width $d$ of the optical field as $t = d/V_z$. The Raman–Nath approximation then corresponds to a ‘thin’ [32, 106] chiral diffraction grating and the relative intensities of the diffraction orders observable in the far-field [57, 105], for example, are governed by the $p_n$. It will be noticed that the $p_n$ depend upon the magnitude of $3G'$ but not the sign. They are, therefore, equal for the enantiomers of the molecule. Consider now, as in section 4, an optical angular frequency $\omega$ that corresponds to a free-space wavelength of $2\pi c/\omega = 1.064 \times 10^{-6} \text{ m}$ and hexahelicene, for which we estimate $3G' = \pm 1 \times 10^{-34} \text{ m kg}^{-1} \text{ s}^3 \text{ A}^2$, as will be recalled. In line with an analogous experiment in which the diffraction of fullerenes due to their interaction with a traditional optical standing wave was observed, we consider $V_z = 1 \times 10^2 \text{ m s}^{-1}$ and $d = 5 \times 10^{-5} \text{ m}$ [57, 105], corresponding to $t = d/V_z = 5 \times 10^{-7} \text{ s}$. With $3G'$ and $t$ fixed, the $p_n$ are found to depend upon the amplitude $E_0$ and hence, the notional intensity $\epsilon_0 c E_0^2$ in a highly sensitive manner: see figure 6.

To illustrate the sensitivity of the chiral diffraction grating and its associated diffraction patterns to the chiral geometry of the molecule, we employ an analytical expression for hexahelicene’s trace $3G'$, obtained elsewhere using a dynamic coupling model [7, 107, 108]. As above, we consider $2\pi c/\omega = 1.064 \times 10^{-6} \text{ m}$ and $t = 5 \times 10^{-7} \text{ s}$. We fix $\epsilon_0 c E_0^2 = 2.5 \times 10^{13} \text{ kg s}^{-3}$, however, and vary the normalized pitch $-1 \leq \gamma \leq 1$ of the molecule in a hypothetical manner, examining the corresponding changes in the $p_n$. As the $p_n$ are identical for the enantiomers of the molecule, we need only consider the magnitude of $\gamma$. The limiting values $|\gamma| = 1$ and $|\gamma| = 0$ correspond to the usual helical shape adopted by hexahelicene, depicted in figure 1, and to a ‘flattened’ version of the molecule which is achiral. Thus, for $|\gamma| = 1$ our chiral diffraction grating gives rise to the diffraction pattern expected of hexahelicene in reality whereas for $|\gamma| = 0$, no diffraction pattern is found. Between these limiting cases, the $p_n$ vary drastically in responses to ‘small’ changes in $|\gamma|$: see figure 7.

For the enantiomers of the molecule, the chiral diffraction grating takes obvious advantage of the non-vanishing and equal magnitudes of $3G'$ but not of the opposite signs of $3G'$. It should be viewed, therefore, as something of a chirality detector, rather than a chirality

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9 The difference in appearance of the last panel of figure 6 and the first panel of figure 7 is due to the fact that they were derived from empirical and theoretical values of $3G'$ that themselves differ slightly.
Figure 6. Plots of the probabilities $p_n$ seen in (5.1), for $n = 0, \pm 1, \pm 2, \pm 3, \pm 4$, an interaction time of $t = 5 \times 10^{-7}$ s, a trace of $3G' = \pm 1 \times 10^{-34} \text{ m kg}^{-1} \text{s}^3 \text{A}^2$ and various values of the notional intensity $\epsilon_0 cE_0^2$.

Figure 7. Plots of the probabilities $p_n$ seen in (5.1), for $n = 0, \pm 1, \pm 2, \pm 3, \pm 4$, an interaction time of $t = 5 \times 10^{-7}$ s, a notional intensity of $\epsilon_0 cE_0^2 = 2.5 \times 10^{13} \text{ kg s}^{-3}$ and various hypothetical magnitudes of the normalized pitch $\gamma$ of the molecule, the corresponding shapes of which are depicted in each panel. The trace $3G'$ has been calculated here using a dynamic coupling model [7, 107, 108]. Note: for a given magnitude of $\gamma$, either enantiomer of the molecule gives rise to the $p_n$ shown.

discriminator. We can envisage, however, employing a two-stage device comprised of a chiral Stern–Gerlach deflector followed by a chiral diffraction grating. The absolute location of the resulting diffraction pattern would then differ for the enantiomers of the molecule whilst the
shape of the resulting diffraction pattern would encode information about their chiral geometry, as above.

It is possible, of course, to conceive of other novel possibilities offered for chiral molecules in the regime of de Broglie molecular optics by $U_{\hbar}$. We will return to these ideas elsewhere.

6. Discussion

We have suggested that the centre-of-mass motion of a chiral molecule is, under appropriate circumstances, sensitive to gradients in the helicity of an optical field. As we have not made any critical assumptions regarding the energy-level structure of the molecule, our findings may be applicable to a wide range of species in a wealth of different contexts. It should be noted, however, that molecular polarizabilities, upon which our approach is based, are state dependent [7]. This may give rise to interesting subtleties and additional possibilities for manipulation. We have imagined the molecule to be tumbling freely in the optical field, thus neglecting the possibility of alignment effects and treating the molecule, heuristically, in an isotropic manner. In reality, the molecule might initially occupy a suitable thermal mixed state of ‘high’ temperature that spans many rotational levels, for example. At ‘low’ temperatures and/or ‘high’ optical intensities, however, polarization-dependent alignment effects in certain optical fields may be important [65, 66], giving rise to further subtleties and possibilities for manipulation.

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References

[1] Lord Kelvin 1894 The molecular tactics of a crystal J. Oxford Univ. Jr. Sci. Club 18 3–57
[2] Bentley R 2010 Chiral: a confusing etymology Chirality 22 1–2
[3] Lough W J and Wainer I W 2002 Chirality in Natural and Applied Science (Cornwall: Blackwell)
[4] Lee T D and Yang C N 1956 Question of parity conservation in weak interactions Phys. Rev. 104 254–8
[5] Wu C S, Ambler E, Hayward R W, Hoppes D D and Hudson R P 1957 Experimental test of parity conservation in beta decay Phys. Rev. 105 1413–5
[6] Kondepudi D K and Durand D J 2001 Chiral asymmetry in spiral galaxies? Chirality 13 351–56
[7] Barron L D 2004 Molecular Light Scattering and Optical Activity (Cambridge: Cambridge University Press)
[8] Newman M S, Lutz W B and Lednicer D 1955 A new reagent for resolution by complex formation the resolution of phenanthro [3, 4-c] phenanthrene J. Am. Chem. Soc. 77 3420–1
[9] Newman M S and Lednicer D 1956 The synthesis and resolution of hexahelicene J. Am. Chem. Soc. 78 4765–70
[10] Bonner W A 1995 Chirality and life Origins Life Evol. B 25 175–90
[11] Patterson D, Schnell M and Doyle J M 2013 Enantiomer-specific detection of chiral molecules via microwave spectroscopy Nature 497 475–8
[12] Nafie L A 2013 Handedness detected by microwaves Nature 497 446–8
[13] Craig D P and Thirunamachandran T 1998 Molecular Quantum Electrodynamics: An Introduction to Radiation Molecule Interactions (New York: Dover)
[14] Mason S F 1982 *Molecular Optical Activity and the Chiral Discriminations* (Cambridge: Cambridge University Press)
[15] Salam A 2010 *Molecular Quantum Electrodynamics* (Hoboken, NJ: Wiley)
[16] Li Y, Bruder C and Sun C P 2007 Generalized Stern–Gerlach effect for chiral molecules *Phys. Rev. Lett.* 99 0130403
[17] Spivak B and Andreev A V 2009 Photoinduced separation of chiral isomers in a classical buffer gas *Phys. Rev. Lett.* 102 063004
[18] Xuan L and Shapiro M 2010 Spatial separation of enantiomers by coherent optical means *J. Chem. Phys.* 132 041101
[19] Xuan L and Shapiro M 2010 Theory of the spatial separation of racemic mixtures of chiral molecules *J. Chem. Phys.* 132 194315
[20] Eilam A and Shapiro M 2013 Spatial separation of chiral molecules *Phys. Rev. Lett.* 110 213004
[21] Canaguier-Durand A, Hutchison J A, Genet C and Ebbesen T W 2013 Mechanical separation of chiral dipoles by chiral light arXiv:1306.3708v1
[22] Atkins P and Friedman R 2011 *Molecular Quantum Mechanics* (Oxford: Oxford University Press)
[23] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1989 *Photons and Atoms: Introduction to Quantum Electrodynamics* (New York: Wiley)
[24] Jackson J D 1999 *Classical Electrodynamics* (New York: Wiley)
[25] Griffiths D J 2008 *Introduction to Electrodynamics* (Upper Saddle River, NJ: Pearson Education International)
[26] Cameron R P, Barnett S M and Yao A M 2013 Optical helicity of interfering waves *J. Mod. Opt.* doi:10.1080/09500340.2013.829874 (arXiv:1308.1308v1)
[27] Barnett S M and Loudon R 2006 On the electromagnetic force on a dielectric medium *J. Phys. B: At. Mol. Opt. Phys.* 39 3671–84
[28] Hinds E and Barnett S M 2009 Momentum exchange between light and a single atom: Abraham or Minkowski? *Phys. Rev. Lett.* 102 050403
[29] Barnett S M 2010 Resolution of the Abraham–Minkowski dilemma *Phys. Rev. Lett.* 104 070401
[30] Barnett S M and Loudon R 2010 The enigma of optical momentum in a medium *Phil. Trans. R. Soc. A* 368 927–39
[31] Bonin K D and Kresin V V 1997 *Electric-Dipole Polarizabilities of Atoms, Molecules and Clusters* (Singapore: World Scientific)
[32] Metcalf H J 1999 *Laser Cooling and Trapping* (New York: Springer)
[33] Seideman T 1999 New means of spatially manipulating molecules with light *J. Chem. Phys.* 111 4397–405
[34] Friedrich B and Herschbach D 1995 Alignment and trapping of molecules in intense laser fields *Phys. Rev. Lett.* 74 4623–6
[35] Friedrich B and Herschbach D 1995 Polarization of molecules induced by intense nonresonant laser fields *J. Phys. Chem.* 99 15686–93
[36] Seideman T 1997 Manipulating external degrees of freedom with intense light: laser focussing and trapping of molecules *J. Chem. Phys.* 106 2881–92
[37] Seideman T 1997 Molecular optics in an intense laser field: a route to nanoscale material design *Phys. Rev. A* 56 R17–20
[38] Seideman T 1997 Shaping molecular beams with intense light *J. Chem. Phys.* 107 10420–9
[39] Seideman T and Kharchenko V 1998 Two-dimensional scattering of slow molecules by laser beams *J. Chem. Phys.* 108 6272–81
[40] Yen Z-C and Seideman T 1999 Photomaneuvering of external molecular modes: A time-dependent self-consistent-field approach *J. Chem. Phys.* 111 4113–20
[41] Friedrich B 2000 Slowing of supersonically cooled atoms and molecules by time-varying nonresonant induced dipole forces *Phys. Rev. A* 61 025403
[42] Ryyty P and Kaivola M 2000 Pulsed standing-wave mirror for neutral atoms and molecules *Phys. Rev. Lett.* 84 5074–7

15
[43] Barker P F and Shneider M N 2001 Optical microlinear accelerator for molecules and atoms Phys. Rev. A 64 033408
[44] Barker P F and Shneider M N 2002 Slowing molecules by optical microlinear deceleration Phys. Rev. A 66 065402
[45] Gordon R J, Zhu L, Schroeder W A and Seideman T 2003 Nanolithography using molecular optics J. Appl. Phys. 94 669–76
[46] Dong G, Lu W and Barker P F 2003 Collisionless Boltzmann equation with an external periodic traveling force: analytical solution and application to molecular optics Phys. Rev. E 68 016607
[47] Dong G, Lu W and Barker P F 2004 Decelerating and bunching molecules with pulsed traveling optical lattices Phys. Rev. A 69 013409
[48] Dong G, Edvadsson S, Lu W and Barker P F 2005 Super-Gaussian mirror for high-field-seeking molecules Phys. Rev. A 72 031605
[49] Barker P F, Purcell S M and Shneider M N 2008 Spectra of molecular gases trapped in deep optical lattices Phys. Rev. A 77 063409
[50] Stapelfeldt H, Sakai H, Constant E and Corkum P B 1997 Deflection of neutral molecules using the nonresonant dipole force Phys. Rev. Lett. 79 2787–90
[51] Sakai H, Tarasevitch A, Danilov J, Stapelfeldt H, Yip R W, Ellert C, Constant E and Corkum P B 1998 Optical deflection of molecules Phys. Rev. A 57 2794–801
[52] Sakai H, Safvan C P, Larsen J J, Hilligsoe K M, Hald K and Stapelfeldt H 1999 Controlling the alignment of neutral molecules by a strong laser field J. Chem. Phys. 110 10235–8
[53] Zhao B S et al 2000 Molecular lens of the nonresonant dipole force Phys. Rev. Lett. 85 2705–8
[54] Larsen J J, Hald K, Bjerre N and Stapelfeldt H 2000 Three dimensional alignment of molecules using elliptically polarized laser fields Phys. Rev. Lett. 85 2470–3
[55] Ballard A, Bonin K and Louderback J 2000 Absolute measurement of the optical polarizability of C60 J. Chem. Phys. 113 5732–5
[56] Chung H S, Zhao B S, Lee S H, Hwang S, Cho K, Shim S-H, Lim S-M, Kang W K and Chung D S 2001 Molecular lens applied to benzene and carbon disulfide molecular beams J. Chem. Phys. 114 8293–302
[57] Nairz O, Brezger B, Arndt M and Zeilinger A 2001 Diffraction of complex molecules by structures made of light Phys. Rev. Lett. 87 160401
[58] Zhao B S, Lee S H, Chung H S, Hwang S, Kang W K, Friedrich B and Chung D S 2003 Separation of a benzene and nitric oxide mixture by a molecule prism J. Chem. Phys. 119 8905–9
[59] Fulton R, Bishop A I and Barker P F 2004 Optical Stark decelerator for molecules Phys. Rev. Lett. 93 243004
[60] Fulton R, Bishop A I, Shneider M N and Barker P F 2006 Controlling the motion of cold molecules with deep periodic optical potentials Nature Phys. 2 465–8
[61] Fulton R, Bishop A I, Shneider M N and Barker P F 2006 Optical stark deceleration of nitric oxide and benzene molecules using optical lattices J. Phys. B: At. Mol. Opt. Phys. 39 S1097–109
[62] Gerlich S et al 2007 A Kapitza–Dirac–Talbot–Lau interferometer for highly polarizable molecules Nature Phys. 3 711–5
[63] Hackermüller L, Hornberger K, Gerlich S, Gring M, Ulbricht M and Arndt M 2007 Optical polarizabilities of large molecules measured in near-field interferometry Appl. Phys. B 89 469–73
[64] Gerlich S, Gring M, Ulbricht H, Hornberger K, Tüxen J, Mayor M and Arndt M 2008 Matter-wave metrology as a complementary tool for mass spectrometry Angew. Chem. Int. Edn Engl. 47 6195–8
[65] Purcell S M and Barker P F 2009 Tailoring the optical dipole force for molecules by field-induced alignment Phys. Rev. Lett. 103 153001
[66] Ortigoso J and Rodríguez M 2009 Molecular optics: controlling the dipole force Nature Photon. 3 685–6
[67] Bishop A I, Wang L and Barker P F 2010 Creating cold stationary molecular gases by optical stark deceleration New. J. Phys. 12 073028
[68] Bateman H 1915 The Mathematical Analysis of Electrical and Optical Wave-Motion on the Basis of Maxwell’s Equations (Cambridge: Cambridge University Press)
[69] Cameron R P 2014 On the ‘second potential’ in electrodynamics J. Opt. 16 015708
[70] Candlin D J 1965 Analysis of the new conservation law in electromagnetic theory Il Nuovo Cimento 27 4106–11
[71] Cameron R P, Barnett S M and Yao A M 2012 Optical helicity, optical spin and related quantities in electromagnetic theory New. J. Phys. 14 053050
[72] Barnett S M, Cameron R P and Yao A M 2012 Duplex symmetry and its relation to the conservation of optical helicity Phys. Rev. A 86 013845
[73] Cameron R P and Barnett S M 2012 Electric-magnetic symmetry and Noether’s theorem New. J. Phys. 14 123019
[74] Bliokh K Y, Bekshaev A Y and Nori F 2012 Dual electromagnetism: helicity, spin, momentum and angular momentum New J. Phys. 15 033026
[75] Heaviside O 1892 On the forces, stresses and fluxes of energy in the electromagnetic field Phil. Trans. R. Soc. Lond. A 183 423–80
[76] Larmor J 1897 Dynamical theory of the electric and luminiferous medium III Phil. Trans. R. Soc. Lond. A 190 205–300
[77] Calkin M G 1965 An invariance property of the free electromagnetic field Am. J. Phys. 33 958–60
[78] Barron L D 1986 True and false chirality and parity violation Chem. Phys. Lett. 123 423–7
[79] Barron L D 1986 True and false chirality and absolute asymmetric synthesis J. Am. Chem. Soc. 108 5539–42
[80] Barron L D 2012 From cosmic chirality to protein structure: Lord Kelvin’s legacy Chirality 24 879–93
[81] Barron L D 2012 Cosmic chirality both true and false Chirality 24 957–8
[82] Coles M M and Andrews D L 2013 Photonic measures of helicity: optical vortices and circularly polarized reflection Opt. Lett. 38 869–71
[83] Lipkin D M 1964 Existence of a new conservation law in electromagnetic theory J. Math. Phys. 5 696–700
[84] Kibble T W B 1965 Conservation laws for free fields J. Math. Phys. 6 1022–6
[85] Tang Y and Cohen A E 2010 Optical chirality and its interaction with matter Phys. Rev. Lett. 104 163901
[86] Hendry E, Carpy T, Johnston J, Popland M, Mikhailovskiy R V, Lapthorn A J, Kelly S M, Barron L D, Gadegaard N and Kadowala M 2010 Ultrasensitive detection and characterization of biomolecules using superchiral fields Nature Nanotechnol. 5 783–7
[87] Bliokh K Y and Nori F 2011 Characterizing optical chirality Phys. Rev. A 83 021803
[88] Tang Y and Cohen A E 2011 Enhanced enantioselectivity in excitation of chiral molecules by superchiral light Science 332 333–6
[89] Yang N and Cohen A E 2011 Local geometry of electromagnetic fields and its role in multipole transitions J. Phys. Chem. B 115 5304–11
[90] Smart A G 2011 A mirror gives light an extra twist Phys. Today 64 16–7
[91] Hendry E, Mikhailovskiy R V, Barron L D, Kadodwala M and Davis T J 2012 Chiral electromagnetic fields generated by arrays of nanoslits Nano Lett. 12 3640–4
[92] Coles M M and Andrews D L 2012 Chirality and angular momentum in optical radiation Phys. Rev. A 85 063810
[93] Andrews D L and Coles M M 2012 Measures of chirality and angular momentum in the electromagnetic field Opt. Lett. 37 3009–11
[94] Schäferling M, Dregely D, Hentschel M and Giessen H 2012 Tailoring enhanced optical chirality: design principles for chiral plasmonic nanostructures Phys. Rev. X 2 031010
[95] Rosales-Guzmán C, Volke-Sepulveda K and Torres J P 2012 Light with enhanced optical chirality Opt. Lett. 37 3486–8
[96] Choi J S and Cho M 2012 Limitations of a superchiral field Phys. Rev. A 86 063834
[97] Davis T J and Hendry E 2013 Superchiral electromagnetic fields created by surface plasmons in nonchiral metallica nanostructures Phys. Rev. B 87 085405
[98] Jerrard H G 1949 The formation of fringes in a Babinet compensator J. Opt. Soc. Am. 39 1031–5
[99] Mohanty S K, Rao K D and Gupta P K 2005 Optical trap with spatially varying polarization: application in controlled orientation of birefringent microscopic particle(s) Appl. Phys. B 80 631–4
[100] Cipparrone G, Ricardez-Vargas I, Pagliusi P and Provenzano C 2010 Polarization gradient: exploring an original route for optical trapping and manipulation Opt. Express 18 6008–13
[101] Zambrini R and Barnett S M 2007 Angular momentum of multimode and polarization patterns Opt. Express 15 15214–27
[102] Bernstein J 2010 The Stern Gerlach experiment arXiv:1007.2435v1
[103] Polavarapu P L and Zhao C 1998 A comparison of ab initio optical rotations obtained with static and dynamic methods Chem. Phys. Lett. 296 105–10
[104] Deachapunya S, Fagan P J, Major A G, Reiger E, Ritsch H, Stefanov A, Ulbricht H and Arndt M 2008 Slow beams of massive molecules Eur. Phys. J. D 46 307–13
[105] Arndt M and Hornberger K 2009 Quantum interferometry with complex molecules arXiv:0903.1614v1
[106] Gupta S, Leanhardt A E, Cronin A D and Pritchard D E 2001 Coherent manipulation of atoms with standing light waves C.R. Acad. Sci. 2 479–95
[107] Fitts D D and Kirkwood J G 1955 The theoretical optical rotation of phenanthro [3, 4-c] phenanthrene J. Am. Chem. Soc. 77 4940–1
[108] Barron L D 1975 Theoretical optical rotation of orientated hexahelicene J. Chem. Soc. Farad. Trans. 2 71 293–300