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Optical Chirality and Its Interaction with Matter

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We introduce a measure of the local density of chirality of the electromagnetic field. This *optical chirality* determines the asymmetry in the rates of excitation between a small chiral molecule and its mirror image, and applies to molecules in electromagnetic fields with arbitrary spatial dependence. A continuity equation for optical chirality in the presence of material currents describes the flow of chirality, in a manner analogous to the Poynting theorem for electromagnetic energy. ''Superchiral'' solutions to Maxwell's equations show larger chiral asymmetry, in some regions of space, than is found in circularly polarized plane waves.

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A chiral object is a three-dimensional body, such as a human hand, whose mirror image may not be superimposed on the original. Objects of opposite chirality, called enantiomers, are identical in most regards: all scalar physical properties (e.g., density, molecular weight, enthalpy of formation, electronic and vibrational frequencies) are identical. Only in their interactions with other chiral objects do opposite enantiomers become distinguishable.

Circularly polarized light (CPL) is a chiral object. A chiral molecule has different absorption cross sections when illuminated with left or right CPL, an effect called circular dichroism (CD) [1]. The fractional difference in absorption is measured by the dissymmetry factor g. For most small molecules $g < 10^{-3}$ at visible wavelengths [2], a consequence of the small size of molecules relative to the helical pitch of CPL. In the language of multipolar electrodynamics [3,4], CD does not occur within the point electric dipole approximation, but requires expansion to first order in $ka \sim 10^{-3}$, where k is the wave vector of the light and a is the size of the molecule. Intense fields with complex *temporal* profiles may achieve coherent control that enhances chiroptical asymmetry in excitation of some processes (for a representative example, see [5]). With recent progress in plasmonics [6] and metamaterials [7], it is interesting to consider fields with complex *spatial* profiles, and, in particular, whether fields exist with greater chiral asymmetry than that of CPL.

For a non-plane-wave electromagnetic (EM) field that varies smoothly over a distance of molecular dimensions, one expects the degree of dissymmetry to depend on local properties of the field. Energy, momentum, and angular momentum are the three bilinear densities typically associated with an EM field. These quantities are, respectively, a scalar, a vector, and a pseudovector. Yet chiral interactions require a time-even pseudoscalar, and no such density is in use. Lipkin introduced such a quantity [8]:

$$C \equiv \frac{\epsilon_0}{2}\mathbf{E}\cdot\nabla\times\mathbf{E} + \frac{1}{2\mu_0}\mathbf{B}\cdot\nabla\times\mathbf{B}, \qquad (1)$$

where ϵ_0 and μ_0 are the permittivity and permeability of free space, respectively, and $\mathbf{E}$ and $\mathbf{B}$ are the time-dependent electric and magnetic fields. In a chiral field, the field lines wrap around a central axis, but also have a component parallel to that axis. The quantity C, which we call the *optical chirality*, embodies this geometrical picture. Lipkin and others after him dismissed this quantity as having no physical significance [9,10].

Here we demonstrate that C determines the degree of chiral asymmetry in the rate of excitation of a small chiral molecule. The response of a molecule to an EM perturbation may be calculated at various levels of theory [3,11] or obtained from experiment. For the present purpose a response function description suffices: the internal dynamics of the molecule are wrapped up in dynamic response tensors [1,12]. We restrict our attention to isotropic samples, for which the response tensors may be replaced by scalars. The restriction to isotropic samples is necessary because in oriented samples even achiral molecules may show circular dichroism [13].

A chiral molecule subjected to a monochromatic EM field generates an electric dipole moment $\mathbf{p}$ and a magnetic dipole moment $\mathbf{m}$ given by [1,11,14]

$$\tilde{\mathbf{p}} = \tilde{\alpha}\,\tilde{\mathbf{E}} - i\tilde{G}\,\tilde{\mathbf{B}}, \qquad \tilde{\mathbf{m}} = \tilde{\chi}\,\tilde{\mathbf{B}} + i\tilde{G}\,\tilde{\mathbf{E}}. \qquad (2)$$

Quantities with a tilde are complex, e.g., $\tilde{\alpha} = \alpha' + i\alpha''$. $\tilde{\alpha}$ is the electric polarizability, $\tilde{\chi}$ the magnetic susceptibility, and $\tilde{G}$ the isotropic mixed electric-magnetic dipole polarizability. $\mathbf{E}$ and $\mathbf{B}$ are the local fields at the molecule, which may need to be calculated numerically using the constitutive relations of the surrounding medium and appropriate boundary conditions. In Eq. (2), one should take the real part of each side to obtain physical quantities. Electric quadrupole transitions contribute in the same order as magnetic dipole, but we neglect them here because the quadrupolar contribution to the differential absorption averages to zero in isotropic samples [4].

In the most general monochromatic EM field, the electric and magnetic fields each describe an ellipse, with arbitrary relative phase and orientation. We consider a pair of such fields which are interchanged by application of parity:

$$\tilde{\mathbf{E}}(t) = \pm\tilde{\mathbf{E}}_0 e^{-i\omega t}, \qquad \tilde{\mathbf{B}}(t) = \tilde{\mathbf{B}}_0 e^{-i\omega t}, \tag{3}$$

where again the real parts of $\tilde{\mathbf{E}}(t)$ and $\tilde{\mathbf{B}}(t)$, denoted $\mathbf{E}$ and $\mathbf{B}$, describe the physical quantities. In Eq. (3), $\tilde{\mathbf{E}}_0$ and $\tilde{\mathbf{B}}_0$ are arbitrary complex vectors. $\mathbf{E}$ is odd under parity while $\mathbf{B}$ is even.

The rate of excitation of the molecule is [12]

$$A^{\pm} = \langle \mathbf{E}\cdot\dot{\mathbf{p}} + \mathbf{B}\cdot\dot{\mathbf{m}}\rangle = \frac{\omega}{2}\,\mathrm{Im}(\tilde{\mathbf{E}}^*\cdot\tilde{\mathbf{p}} + \tilde{\mathbf{B}}^*\cdot\tilde{\mathbf{m}}), \tag{4}$$

where the brackets indicate an average over time. Expanding the rate of excitation using Eq. (2) we have

$$A^{\pm} = \frac{\omega}{2}(\alpha''|\tilde{\mathbf{E}}|^2 + \chi''|\tilde{\mathbf{B}}|^2) \pm G''\omega\,\mathrm{Im}(\tilde{\mathbf{E}}^*\cdot\tilde{\mathbf{B}}). \tag{5}$$

The term involving χ is negligibly small for most molecules, and so we henceforth neglect it. We apply the identity $\omega\,\mathrm{Im}(\tilde{\mathbf{E}}^*\cdot\tilde{\mathbf{B}}) = \dot{\mathbf{B}}\cdot\mathbf{E} - \dot{\mathbf{E}}\cdot\mathbf{B}$ to the term containing G''. Applying Maxwell's equations in free space, we find $A^{\pm} = \frac{2}{\epsilon_0}(\omega U_e\alpha'' \mp CG'')$, where $U_e = \frac{\epsilon_0}{4}|\tilde{\mathbf{E}}|^2$ is the time-average electric energy density and C is as defined in Eq. (1).

For a monochromatic CPL plane wave, the dissymmetry factor is defined $g \equiv 2(A^+ - A^-)/(A^+ + A^-)$, where $A^{\pm}$ is the absorption rate in left (+) or right (−) CPL. We now generalize the definition of g to include any pair of EM fields interchanged by parity, whereupon we find

$$g = -\left(\frac{G''}{\alpha''}\right)\left(\frac{2C}{\omega U_e}\right). \tag{6}$$

Equation (6) is the fundamental result of this Letter. It shows that the chiral asymmetry in the rate of excitation of a small molecule is proportional to the product of the chirality of the matter and the chirality of the EM field. An alternate derivation of Eq. (6) based on time-dependent perturbation theory is given in the supplementary material [15].

Conventional CD is a special case of our general theory. When the EM field is CPL, the optical chirality is $C = \pm 2U_e\omega/c$, where c is the speed of light and positive chirality corresponds to left CPL. In this case Eq. (6) reduces to the textbook result, $g_{\mathrm{CPL}} = -4G''/c\alpha''$ [1], which appears to depend only on molecular parameters.

Material currents may act as a source or sink of optical chirality. This process is governed by a continuity equation. Taking the time derivative of Eq. (1) and applying Maxwell's equations yields (for a derivation see the supplementary material [15]):

$$\frac{\partial C}{\partial t} + \frac{1}{\mu_0}\nabla\cdot\mathbf{F} = -\frac{1}{2}(\mathbf{j}\cdot\nabla\times\mathbf{E} + \mathbf{E}\cdot\nabla\times\mathbf{j}), \tag{7}$$

where the quantity $\mathbf{F} \equiv \{\mathbf{E}\times(\nabla\times\mathbf{B}) - \mathbf{B}\times(\nabla\times\mathbf{E})\}/2$ represents the flux of chirality.

Equation (7) has the same structure as the Poynting theorem [14,16] for flux of EM energy: $\partial U/\partial t + (\nabla\cdot\mathbf{S})/\mu_0 = -\mathbf{j}\cdot\mathbf{E}$, where the EM energy density is $U = \frac{1}{2}(\epsilon_0\mathbf{E}\cdot\mathbf{E} + \frac{1}{\mu_0}\mathbf{B}\cdot\mathbf{B})$, the Poynting vector is $\mathbf{E}\times\mathbf{B}$, and the quantity $\mathbf{j}\cdot\mathbf{E}$ describes how material currents act as a source or sink of EM energy. The similarity of Eq. (7) to the Poynting theorem illustrates a parallel between optical chirality and optical intensity. Both quantities are quadratic in the fields, so scaling all fields by a constant value does not change the ratio of chirality to intensity. However, these two quantities have opposite symmetry under parity.

Do Maxwell's equations permit solutions with chiral asymmetry greater than that found in CPL plane waves, i.e., in which $|C/U_e| > 2\omega/c$ in some region of space? Here we show by explicit construction that the answer is yes. Enhanced chiral asymmetry is achieved at the nodes of a specially constructed optical standing wave. Small molecules localized to these regions are predicted to show enhanced chiral asymmetry in their rate of excitation.

The standing wave is constructed from two counterpropagating plane waves of CPL, of opposite handedness, equal frequency, and slightly different intensity. Let E_1 be the electric field amplitude of the left CPL beam, propagating from right to left, and E_2 be the electric field amplitude of the right CPL beam, propagating from left to right. We assume that E_1 is slightly greater than E_2 (Fig. 1).

The interference of the two counterpropagating beams leads to a standing wave, with energy density in the electric field:

$$U_e(z) = \frac{\epsilon_0}{2}[E_1^2 + E_2^2 - 2E_1E_2\cos(2kz)]. \tag{8}$$

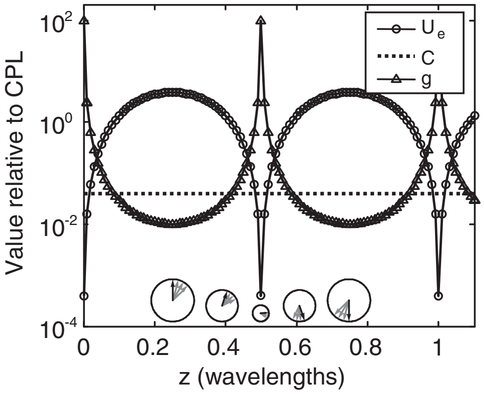

FIG. 1. Enhanced chiral asymmetry in superchiral light. The intensity (circles) is modulated in a standing wave, while the optical chirality (dashed line) is not. The ratio C/U_e, which determines the enantioselectivity (triangles), becomes large near a node in the standing wave. For this example, $E_2 = 0.98E_1$, and each quantity is plotted relative to its value for a single CPL plane wave. The diagram at the bottom shows the time trajectory of the electric field at several points along the standing wave. The black arrows indicate $\mathbf{E}(t)$, and the gray arrows indicate $\mathbf{E}$ at earlier times.

The minimum energy density at the nodes is $U_{e,\min} = \epsilon_0(E_1 - E_2)^2/2$. Meanwhile the chirality of the combined field does not contain any interference between the two beams [this can be shown by applying the definition of chirality to the field $\mathbf{E}_1(z,t) + \mathbf{E}_2(z,t)$]. We find $C(z) = \omega\epsilon_0(E_1^2 - E_2^2)/c$, independent of position. The maximum value of g is

$$g_{\max} = \left(\frac{-4G''}{c\alpha''}\right)\left(\frac{E_1 + E_2}{E_1 - E_2}\right). \tag{9}$$

The definition of g requires $|g| < 2$. This condition is maintained as E_2 approaches E_1 by achiral magnetic dipole transitions, proportional to $\chi''|\tilde{\mathbf{B}}|^2$, which we have thus far neglected.

The enhanced chiral asymmetry at the nodes of a superchiral standing wave arises from the suppression of the electric dipole-allowed transitions, rather than from an enhancement of the chirally sensitive electric dipole-magnetic dipole interference transitions. As E_2 approaches E_1 the electric energy density at a node, $U_{e,\min}$, and the optical chirality C approach zero. But $U_{e,\min}$ approaches zero faster than C, so the ratio $C/U_{e,\min}$ grows.

The configuration of fields leading to a superchiral standing wave is remarkably simple to generate, at least in concept. Reflection of a left CPL plane wave at normal incidence off an imperfect mirror leads to a right CPL plane wave of the same frequency and fixed relative phase, with slightly lower amplitude, propagating in the opposite direction: precisely the conditions to set up a superchiral standing wave. A mirror with reflectivity $R = (E_2/E_1)^2$ yields

$$g_{\max} = \left(\frac{-4G''}{c\alpha''}\right)\left(\frac{1 + \sqrt{R}}{1 - \sqrt{R}}\right) = g_{\mathrm{CPL}}\frac{1 + \sqrt{R}}{1 - \sqrt{R}}. \tag{10}$$

To observe enantioselective photoexcitation in a superchiral field, one must localize chiral molecules to a very thin film. For the example of Fig. 1, the regions in which $g/g_{\mathrm{CPL}} > 1$ have a thickness of 0.032λ, corresponding to 11 nm at $\lambda = 355$ nm. We consider a thin film of randomly oriented chiral fluorescent molecules, e.g., dissolved in a polymer matrix. For a reasonable concentration (100 μM) and extinction coefficient (50 000 $\mathrm{cm}^{-1}\,\mathrm{M}^{-1}$), the film will have negligible effect on the incident field (absorbance $= 5 \times 10^{-6}$). It is unrealistic to detect absorption in such an optically thin sample, but fluorescence provides a highly sensitive measure of the rate of excitation. Fluorescence detected circular dichroism can, in principle, be observed on single molecules [17], though claims that this has been achieved have not been substantiated [18]. For the present purposes, one may signal average over an area millimeters wide, containing $>10^6$ molecules. A planar mirror is coated with a transparent staircase nanostructure, with step heights corresponding to a small fraction of a wavelength (Fig. 2). The steps are coated with the chiral film. The device is illuminated at normal incidence alternately with right CPL and left CPL, and the difference in fluorescence intensity is recorded. Molecules stationed near a node in the standing wave are predicted to show enhanced chiral asymmetry. A silver mirror with $R = 92\%$ leads to a 48-fold enhancement in $g_{\max}$, while a mirror with $R = 99\%$ leads to a nearly 400-fold enhancement.

There have been many efforts to use CPL to induce an enantiomeric excess in photochemical reactions [19]. Because of the smallness of g, these efforts typically achieve very small enantiomeric excess. If such a reaction were run within a superchiral node, the enantiomeric excess would be dramatically enhanced. However, the small volumes with enhanced g in the present geometry are likely to limit the immediate practical application of this phenomenon.

In the supplementary material [15] we consider standing waves composed of plane waves with other polarization states. We show that circular polarization is neither necessary nor sufficient for optical chirality, contrary to widespread assumption.

The present theory is limited to chiroptical effects arising from an interference between electric dipole and magnetic dipole transitions, and to EM fields sufficiently weak that the material response remains linear in the fields. Interesting chiroptical phenomena occur outside these bounds.

Harris and co-workers showed that there is no single measure of chirality appropriate to all material bodies: for any measure, one can construct a chiral body for which the measure is zero [20]. Thus, electric dipole-magnetic dipole interferences may not be the dominant contributors to a body's chiroptical response; higher multipole moments

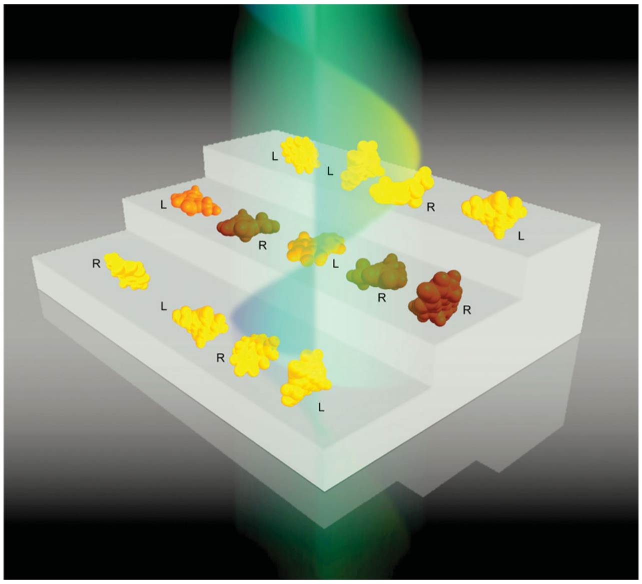

FIG. 2 (color). Proposed experiment to probe superchiral light. Molecules are confined to thin films at a range of heights above a reflective surface. When illuminated with CPL, molecules at the nodal planes of the standing wave are predicted to show enhanced chiral asymmetry.

may be necessary. This situation arises when the size of the body is comparable to the wavelength of light, such as with chiral polymers or cholesteric liquid crystals. An infinite set of chiral parameters has been suggested to describe the geometry of a chiral body [21], and so there exists an infinite set of parameters to describe its chiroptical response.

Similarly, there cannot be a single measure of electromagnetic chirality appropriate to all EM fields. There exist chiral fields for which C as defined in Eq. (1) is zero. Indeed, the field of any static, chiral configuration of point charges is chiral, yet by Eq. (1), $C = 0$. This claim is proved by noting that $\nabla \times \mathbf{E} = -\partial \mathbf{B}/\partial t$ but $\mathbf{B} = 0$ for a configuration of static point charges. Yet chiral fields with $C = 0$ may undergo chirally selective interactions. The optical chirality of Eq. (1) may be part of a hierarchy of bilinear chiral measures that involve higher spatial derivatives of the electric and magnetic fields [22]. We speculate that all linear chiral light-matter interactions can be described by sums of products of material chiralities and time-even pseudoscalar optical chiralities.

In the context of nonlinear optics, time-even pseudoscalar measures of EM chirality can be constructed from third and higher powers of the electric and magnetic fields, and are distinct from C. For instance, magnetochiral dichroism is proportional to the product of a magnetic field and two electric fields [1], and chiral sum frequency generation is proportional to the product of three electric fields [23].

In spite of the restriction to weak fields that vary gradually over molecular dimensions, the measure of EM chirality defined in Eq. (1) may find application in a range of circumstances. The superchiral fields discussed above are a mathematically simple illustration of optical chirality, but nanostructures and photonic crystals may also generate fields with locally enhanced chirality. The present theory provides a means to evaluate the rate of excitation of a small chiral molecule immersed in such a field, where the field may be calculated analytically or numerically. Chiroptically selective nanostructures may find applications as biosensors or as chiral photochemical catalysts.

Measures of chirality of the form $\mathbf{A} \cdot \nabla \times \mathbf{A}$ have been introduced for a variety of physical transverse vector fields $\mathbf{A}$. Woltjer showed that, under suitable conditions, $\int \mathbf{A} \cdot \nabla \times \mathbf{A} d^3 r$ gives a measure of the knottedness of the field lines of the quantity $\nabla \times \mathbf{A}$ [24]. Topological measures of chirality have been applied to plasma physics and astrophysics [24,25], fluid dynamics [26], the Frank free energy in liquid crystals [27], and Chern-Simons topological field theory [28]. Application of these formulas to EM vector potentials, however, led to expressions that were not gauge invariant [29,30]. By defining the EM chirality in terms of the fields rather than the potentials we avoid the problem of gauge dependence.

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[1] L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, Cambridge, England, 2004).

[2] Y. Inoue and V. Ramamurthy, *Chiral Photochemistry* (Marcel Dekker, New York, 2004).

[3] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).

[4] D. P. Craig and T. Thirunamachandran, *Molecular Quantum Electrodynamics* (Courier Dover, New York, 1998).

[5] A. Salam and W. J. Meath, Chem. Phys. **228**, 115 (1998).

[6] E. Ozbay, Science **311**, 189 (2006).

[7] J. B. Pendry, Science **306**, 1353 (2004).

[8] D. Lipkin, J. Math. Phys. (N.Y.) **5**, 696 (1964).

[9] T. W. B. Kibble, J. Math. Phys. (N.Y.) **6**, 1022 (1965).

[10] M. Przanowski, B. Rajca, and J. Tosiek, Acta Phys. Pol. B **25**, 1065 (1994).

[11] A. Salam, *Molecular Quantum Electrodynamics: Long-Range Intermolecular Interactions* (Wiley, New York, 2009).

[12] R. A. Harris, J. Chem. Phys. **43**, 959 (1965).

[13] C. Isborn, K. Claborn, and B. Kahr, J. Phys. Chem. A **111**, 7800 (2007).

[14] D. P. Craig and T. Thirunamachandran, Theor. Chem. Acc. **102**, 112 (1999).

[15] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevLett.104.163901 for a derivation of Eq. (6) via perturbation theory and a discussion of optical chirality of standing waves.

[16] J. Poynting, Phil. Trans. R. Soc. London **175**, 343 (1884).

[17] R. Hassey, E. Swain, N. Hammer, D. Venkataraman, and M. Barnes, Science **314**, 1437 (2006).

[18] Y. Tang and A. Cohen, J. Phys. Chem. A **113**, 6213 (2009).

[19] A. G. Griesbeck and U. J. Meierhenrich, Angew. Chem., Int. Ed. **41**, 3147 (2002).

[20] A. B. Harris, R. D. Kamien, and T. C. Lubensky, Rev. Mod. Phys. **71**, 1745 (1999).

[21] A. B. Harris, R. Kamien, and T. Lubensky, Phys. Rev. Lett. **78**, 1476 (1997).

[22] S. Anco and J. Pohjanpelto, Acta Appl. Math. **69**, 285 (2001).

[23] P. Fischer and F. Hache, Chirality **17**, 421 (2005).

[24] L. Woltjer, Proc. Natl. Acad. Sci. U.S.A. **44**, 489 (1958).

[25] S. Kandaswamy and A. Brandenburg, Astrophys. J. **648**, L71 (2006).

[26] H. Moffatt, J. Fluid Mech. **35**, 117 (1969).

[27] F. Frank, Discuss. Faraday Soc. **25**, 19 (1958).

[28] A. Zee, *Quantum Field Theory in a Nutshell* (Orient Longman, Princeton, 2005).

[29] A. Ranada, Eur. J. Phys. **13**, 70 (1992).

[30] J. Trueba and A. Ranada, Eur. J. Phys. **17**, 141 (1996).