Chiral Light–Chiral Matter Interactions: an Optical Force Perspective

Cyriaque Genet

ACS Photonics

pubs.acs.org/journal/apchd5

Perspective

Chiral Light−Chiral Matter Interactions: an Optical Force Perspective

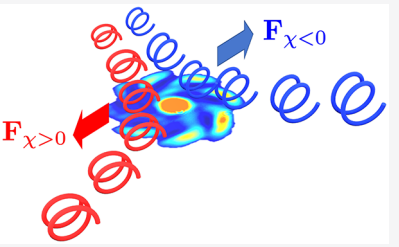
Cyriaque Genet*

Cite This: https://doi.org/10.1021/acsphotonics.1c01130

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Optical forces are involved in many physical processes and are used routinely in the laboratory for manipulating and cooling matter, from the micro down to the quantum scales. It has been realized recently that new forms of optical forces can emerge when a chiral system is immersed within a chiral light field. These new forces involve not only the chirality of the system on which they exert their mechanical action, but the chirality itself of the optical field that generate them. As such, they have fascinating properties, the crucial one being that they are enantioselective. We will highlight recent and important advances in this newborn field of research, where the interactions and exchanges between theory and experiments are particularly strong. The key advances selected in this Perspective are representative of the vitality of the current research activity. These advances clearly point toward future designs for all-optical chiral separation strategies of high potential. They also shape new means for controlling chiral systems, such as atoms and molecules, at the quantum level. The viewpoint adopted in this Perspective overall aims at showing how chiral optical forces shed new light on chiral light−chiral matter interactions.



KEYWORDS: *chirality, nano-optics, optical forces and torques, dipolar regime, chiral discrimination, chiral dispersion forces*

Chirality and optics have a long joint history that "crystallized" in the course of the 19th century, when the knot between polarization and chirality was first tied. This historical sequence is well-known and well documented.[1] In the first decade of that century, E.-L. Malus studied the phenomena of reflection and refraction by forging the concept of light polarization. Malus' discoveries and concepts immediately attracted L. Arago's attention, who demonstrated in 1811 that properly cleaved quartz plates are capable of rotating the plane of polarization, a capacity coined as the rotatory power.[2] In 1822, A. Fresnel discovered the circular polarization of light.[3] It is, however, J. Herschel, practically in the same years, following the work of both J.-B. Biot on the molecular rotatory action and R.-J. Haüy on crystal hemihedry, that related rotatory power to the spatial organization of hemihedric facettes between two forms of the quartz crystal. This crucial observation connected the optical manifestations of rotatory power to a geometric enantiomorphism of a crystal and paved the way to stereochemistry.[4,5]

Forces and optics are similarly intertwined since the advent of modern physics, as seen for example in the famous 1619 explanation of Kepler that the Sun light is mechanically responsible for the specific orientations of the comet tails. Along with the Newtonian corpuscular theory of light, the 18th century saw the development of many experimental debates related to the mechanical pressure inevitable in the corpuscular viewpoint.[6] These discussions were formally given consistency by the electromagnetic theory of light, and the predictions of 1873 Maxwell's Treatise on Electricity and Magnetism that electromagnetic waves can exert pressure on a medium forms one important discussion.[7,8] This prediction was immediately put to test, and in 1901, P. N. Lebedev demonstrated the existence of the radiation pressure.[9,10] This experiment, soon followed by famous others, like the Nichols and Hull one,[11,12] was a tour-de-force, measuring pN radiation pressures with an impressive experimental accuracy at the percent level on torsional pendula.[13]

The field of nano-optics brought back the concept of optical force to the spotlight with confined and controllable electromagnetic excitations that can yield enhanced momentum transfers, both linear and angular, at the level of nanometer-sized objects.[14] This renewed interest led to envisioning new dynamical coupling mechanisms at the nanoscale with a great variety of schemes.[15] Recently, the concept of chirality has permeated the field of optical forces with the discovery of new forces that are chiral in nature and enantioselective in effect. This Perspective focuses on presenting these new chiral optical forces as they now form an emerging research topic. Remarkably, this topic summons different areas of physics and physical chemistry for pushing further our fundamental understanding of chirality and for exploiting the enantioselective nature of these forces, a nature that gives its backbone to the current intense research activity that we will illustrate with representative examples.

Received: July 27, 2021
Revised: December 21, 2021
Accepted: December 28, 2021

As it will be discussed in this Perspective, these forces have shed new light on an old problem, chiral separation, which is of primary importance in many sectors of activity, ranging from analytical chemistry, biology, pharmaceutics, and so on. Chiral optical forces have today the potential to provide entirely new strategies for chiral separation that only involve all-optical means. It is evident that the future of the field is to exploit these chiral optical forces at the molecular scales, in reliable, efficient, and high-throughput architectures, capable of changing the existing technologies, such as chiral column chromatography. Not yet ready for real-world applications, the recent advances highlighted in the Perspective are, however, definitely promising in tackling the challenge.

Beyond applications, chiral optical forces are also the playground for a rare and exceptionally vivid exchange between fundamental optics, molecular physics, optomechanics, and quantum physics. Better understanding chiral optical forces implies dwelling into chiral optics and molecular chirality together, in such ways as to harness chirality as a new means for manipulating matter down to the quantum level. The interest in chirality in the quantum realm is opening fascinating perspectives that are currently explored by many, with new communities and integrated research programs emerging. The purpose of this Perspective is to expose the reasons behind this excitement with a viewpoint that we hope to be as fair as possible to the ever growing literature on chiral optical force fields.

CHIRALITY AND FORCES

The theoretical proposal made in 1996 by Kucirka and Shekhtman is probably the first to show the possibility to induce a force through the coupling of the chirality of matter with the helicity of light.[16] This work details how a gradient optical force can depend on the handedness of a molecular enantiomer inside a circularly polarized standing wave, as schematized in Figure 1. By emphasizing that an "elastic interaction of a chiral molecular beam with a circularly polarized laser wave naturally results in a difference in enantiomers speeds", the authors proposed an all-optical route for the deracemization of an initial racemic mixture of chiral molecules, thereby pioneering our topic. This founding article has, unfortunately, but involuntarily, remained unnoticed by the recent work (including ours) on which the field has grown since.

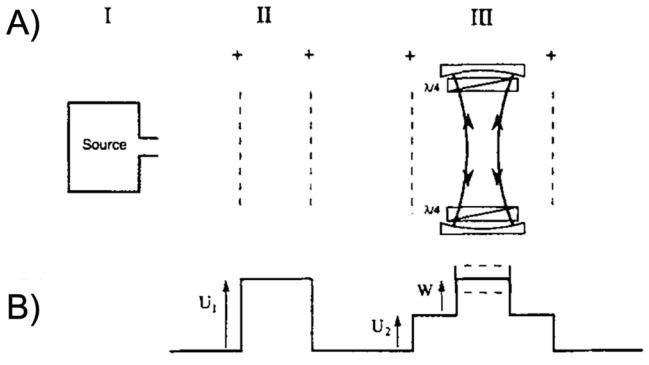


Figure 1. Chiral separation scheme proposed by Kucirka and Shekhtman in ref 16, implementing the first idea of optical chiral forces. (A) A thermal beam of molecular ions is sourced and collimated in region I, passed through two capacitors in regions II and III that fix precisely the electric potentials displayed in (B). A resonant cavity is placed inside capacitor III with quater wave-plates forming a circularly polarized standing wave. Inside this standing wave, it is shown that the chiral molecular ions constituting the beam will feel a chiral optical potential $W(\mathbf{r})$ whose height is changed for right and left handed ions. This is indicated in (B) in dashed lines. As a consequence, an enantiodependent gradient force $\mathbf{F} = -\nabla W(\mathbf{r})$ is acting on the beam and modulates the speed of the molecules as a function of their enantiomeric forms. Figure adapted with permission from ref 16. Copyright 1996 Elsevier.

More than a decade later, in the same context of molecular beams, Y. Li et al. took another perspective by showing how laser-induced gauge-effective potentials can lead to a splitting in the center-of-mass motion between each enantiomer constituting a beam of oriented molecules.[17,18] Further exploiting the fact that Rabi frequencies that quantify the interaction between the electric dipole of the chiral molecule and the electric field of the laser differ in sign for each enantiomer, it is also possible to spatially separate chiral molecules using coherent optical fields.[19,20] For instance, in ref 21 it is demonstrated that homo- versus heterochiral dimers can be optically sorted by pumping homochiral dimers into a dark state, protected from any light-induced potential, and heterochiral dimers into a bright state where the center-of-mass motion is deflected.

Another source of inspiration came from the first experimental work reported by G. Cipparrone et al. in 2011 where a chiral optical force was observed by trapping micron-sized chiral cholesteric beads in stable or unstable trap potentials.[22] The chiral character of the forces involved in this work proceeded from the chiroptical properties of the beads that can be described as a circular Bragg reflector that reflects or transmits left or right circularly polarized beam, respectively. This differential effect is accompanied by a force balance inside the optical trap that depends on the helicity of the trapping beam. Interestingly, the circular Bragg reflection mechanism found on such a cholesteric system was studied in the context of radiation pressure by B.M. Ross and A. Lakhtakia in 2008 using chiral sculptured thin films, showing how the light pressure exerted on such "chiral mirrors" depends both on the handedness of the incident light and of the mirror.[23] The helicity-preserving reflective properties of chiral Bragg mirrors, in opposition to a conventional mirror that reverses the helicity of the incident light, corresponds to an angular momentum transfer from the light to the mirror (or the bead) that has been well observed and analyzed on optically trapped chiral cholesteric beads[24−26] and later used to sort such chiral cholesteric microdroplets, as we will discuss further down.

It is also interesting to note that Cipparrone's work came just after a theory paper by Guzatov and Klimov where the pressure exerted by a circularly polarized plane wave on a large chiral spherical particle is studied.[27] In this important theory work, the particle is made of a chiral isotropic medium and the radiation pressure is evaluated by the Maxwell stress tensor built on the incident and scattered fields, the latter calculated within the Mie theory. This work was the first to emphasize the relevance of a Mie scattering approach for describing how circularly polarized light can modulate the radiation pressure exerted on a chiral particle in comparison with the achiral situation.

DIPOLAR OPTICAL FORCES

We choose for this Perspective to shift the focus slightly off these large chiral objects and rather analyze how these intriguing chiral optical forces manifest themselves in the dipolar framework, involving harmonic electromagnetic fields. This choice for simplicity will enable physical interpretations of each terms engaged in the chiral coupling between the matter and field parts

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

that lead to the emergence of these new forces. As discussed below, this interpretation turns crucial when aiming at developing all-optical chiral separation strategies at the molecular scales.

This choice also reveals how an optical force approach, simply starting from the Lorenz law, can most directly give access to subtle issues currently discussed in fundamental optics. Finally, one other attracting asset of the dipolar framework is the ease at which it lends itself to envision further developments, in particular, in the chiral quantum realm.

We thus open the discussion with a harmonic electromagnetic field $(\mathcal{E}, \mathcal{H})$ of angular frequency ω exerting a mechanical action on an electric dipole $\mathcal{P}$ immersed in a medium of permittivity ε_f and permeability μ_f that takes the form of a force according to the classical Lorentz law $\mathbf{F} = (\mathcal{P}\cdot\nabla)\mathcal{E} + \mu_f\dot{\mathcal{P}} \times \mathcal{H}$ and of a torque $\mathbf{\Gamma} = \mathcal{P} \times \mathcal{E}$.[28,29] The time-averaged optical force has a remarkable closed-form expression $\langle \mathbf{F} \rangle_T = \varepsilon_f \mathrm{Re}[\alpha \mathbf{f}_0]/2$, where α is the complex polarizability of the dipolar moment and $\mathbf{f}_0$ is a vector field well-known since the early times of cold atom physics,[29] although rediscovered more recently in nano-optics.[30] In the simplest case of a linearly polarized field of amplitude $\rho(\mathbf{r})$ and phase $\phi(\mathbf{r})$, where the complex electric field is given by a scalar component $E(\mathbf{r}) = \rho(\mathbf{r})e^{i\phi(\mathbf{r})}$, this vector field writes as $\mathbf{f}_0 = \rho\nabla\rho - i\rho^2\nabla\phi$ that immediately leads to decompose the force into reactive and dissipative components. The reactive component is proportional to $\mathrm{Re}[\mathbf{f}_0]$ and corresponds to the well-known gradient optical force (for instance, the one involved in optical traps[31]). The conservative character of this force, thus associated with an electric dipolar potential energy, has been exploited for controlling the motion of atoms, and molecules, in the context of cold matter[32] and matter-wave physics.[33]

The dissipative component, given by $\mathrm{Im}[\mathbf{f}_0]$ is proportional to the phase gradient, well-known to be associated with radiation pressure.[36] For the present discussion, it is important to discuss the general polarization case associated with inhomogeneous light fields, where each component of the electric field $E_0^j = \rho^j e^{i\phi^j}$ has its own amplitude ρ^j and phase ϕ^j. While one can still write $\mathrm{Re}[\mathbf{f}_0]$ as an amplitude gradient, $\mathrm{Im}[\mathbf{f}_0] = -\sum_j (\rho^j)^2\nabla\phi^j$ becomes a weighted average of each component's phase gradient. As demonstrated in refs 28, 37, and 38, this generalized phase gradient term can be expressed as the orbital part of the Poynting vector $\mathbf{\Pi}_O = \mathbf{\Pi} - \nabla \times \mathbf{\Phi}_E/2\omega\mu_f$, which is given by the full Poynting vector $\mathbf{\Pi}$ minus a contribution proportional to the curl of the electric polarization ellipticity $\mathbf{\Phi}_E$ that corresponds to the spin part of the Poynting vector.[39] The dissipative, radiation pressure, component of the optical force thus writes as $\mathbf{F}_r^{\mathrm{diss}} = \omega\varepsilon_f\mu_f\mathrm{Im}[\alpha]\mathbf{\Pi}_O$. The electric ellipticity is itself proportional to the spin density $\mathbf{S}$ of the light field with $\mathbf{\Phi}_E = \langle \| \mathcal{E} \|^2 \rangle_T \mathbf{S}$.

This result might sound surprising given the usual association between radiation pressure and the full Poynting vector. It has raised debates within the nano-optics community where some have preferred to identify the spin curl term to an additional contribution to radiation pressure.[40−42] But reserving only the orbital part of the Poynting vector to linear momentum exchanges has a clear physical meaning. This appears when evaluating the optical torque under the same illumination conditions, where $\mathbf{\Gamma}(\mathbf{r}) = \varepsilon_f\mathrm{Im}[\alpha]\mathbf{\Phi}_E(\mathbf{r})$ links the spin density of the light field to angular momentum exchanges. In other words, these expressions show how mechanical energy is transferred by the incident light field through dissipation, $\mathrm{Im}[\alpha]$, into two different channels: a dissipative force component (radiation pressure) induced by the orbital energy flux and a torque applied to the dipole related to the spin angular momentum density of the light field. It has been clearly discussed in ref 43 how these physical expressions involve gauge invariant canonical linear and angular momentum densities.

These expressions for the electric dipole can be readily extended to the magnetic dipolar case, exploiting the "electric−magnetic democracy", using M. Berry's words.[37,44] One simply defines the magnetic dipole $\mathbf{m} = \beta\mathbf{H}$ from the complex magnetic polarizability β, and derive, simply from the magnetic part of the Lorentz law $(\mathcal{M}\cdot\nabla)\mathcal{H} + \varepsilon_f\dot{\mathcal{M}} \times \mathcal{E}$, the time-averaged force exerted by the magnetic field on the magnetic dipole as $\mathrm{Re}[\beta\mathbf{g}_0]/2$, where the vector field $\mathbf{g}_0$ is exactly the magnetic counterpart of $\mathbf{f}_0$.

CHIRAL OPTICAL FORCES

The dipolar description of a small chiral object, such as a chiral nanoparticle or a chiral molecule, corresponds to a coupled system of induced electric and magnetic dipole moments

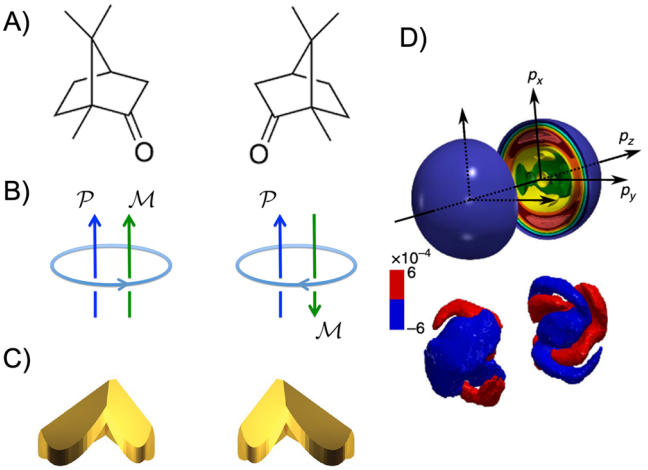


Figure 2. (A) Two molecular enantiomers (like R- (left hand side) and S- (right hand side) camphor here) can be represented by coupled electric and magnetic dipoles, as schematized in (B). This dipolar system will similarly describe the scattering properies of small chiral nanostructures, like the chiral nanopyramids shown in (C) that were optically trapped and analyzed in situ in ref 58. The combination of linear vs circular motion of charges engaged in a chiral molecular ground-to-excited state transition (see Box 1) has been observed in real-time using ultrafast photoelectron circular dichroism on photoionized chiral camphor molecules.[59] Reprinted with permission from ref 59. Copyright 2018 Springer Nature; https://creativecommons.org/licenses/by/4.0/.

schematized in Figure 2. In the harmonic and linear regimes, the system writes as

$$\begin{aligned} \mathbf{p} &= \varepsilon_f\alpha\mathbf{E} + i\chi\sqrt{\varepsilon_f\mu_f}\,\mathbf{H} \\ \mathbf{m} &= -i\chi\sqrt{\varepsilon_f/\mu_f}\,\mathbf{E} + \beta\mathbf{H}, \end{aligned} \tag{1}$$

assuming again for simplicity isotropic responses, so that the polarizabilities (α, β, χ) remain complex scalars. The polarizability χ is the mixed electric−magnetic dipole polarizability specific to chirality.[45] It is associated with the absence of any center of inversion and of any mirror symmetry for the dipolar

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

system, as expected for a chiral molecule. Its sign determines the enantiomeric form associated with the dipolar system (see Box 1).

Box 1. Chiral Dipole

The chiroptical response, such as circular dichroism (CD), associated with a ground (g)-to-excited (e) states molecular transition, involves both electric and magnetic dipole transitions.[34] Fundamentally, the CD of a molecular transition is measured by the optical rotatory strength $R_{ge} = \mathrm{Im}[\mathbf{d}_{ge}\cdot\mathbf{m}_{eg}]$ defined by the electric $\mathbf{d}_{ge}$ and magnetic $\mathbf{m}_{eg}$ dipole moment matrix elements.[35] As expected, R_{ge} changes sign under spatial inversion. From a physical point of view, the electric dipole transition is associated with a linear displacement of charges going from the ground to the excited states, whereas the magnetic dipole transition in contrast is associated with a circular motion of charges induced in the g-to-e transition. This stems from the fact that the magnetic dipole moment is determined from the angular momentum operator. Such a combination of charge motions, linear along one axis and circular around that same axis, corresponds precisely to the electric−magnetic dipolar system used in the force law for modeling the chiral nature of matter coupled to the light field. As such, therefore, the chiral dipole system defined in eq 1 responds to the requirement of modeling the helical movement of charges implicit in the measurement of molecular chiroptical responses.

Equipped with such a chiral dipolar response, we go back to the Lorentz force law, combining electric, magnetic, and mixed contributions. It is remarkable that, in the harmonic framework, this law offers a complete separation of terms

$$\langle \mathbf{F}\rangle_T = \frac{1}{2}\mathrm{Re}\left[\varepsilon_f\alpha\mathbf{f}_0 + \beta\mathbf{g}_0 + \frac{\chi}{\omega\sqrt{\varepsilon_f\mu_f}}\mathbf{h}_0\right] \tag{2}$$

where each electric, magnetic and chiral polarizabilities are connected with one $\mathbf{f}_0$, $\mathbf{g}_0$, or $\mathbf{h}_0$ vector field.[46] Next to the achiral ($\mathbf{f}_0$, $\mathbf{g}_0$) optical force contributions, one new term arises that engages the chiral polarizability χ of the dipole to the new vector field $\mathbf{h}_0$. This derivation leads to the definition of an optical force that is obviously depending on the sign of the chiral polarizability, that is, on the enantiomeric form of the dipole. As initially stressed in refs 46 and 47, this derivation, despite its simplicity, is accompanied by rich physical discussions.

It is important to analyze precisely the structure of this new chiral force through a decomposition into reactive and dissipative components, as we analyzed in detail in ref 46. The reactive component

$$\mathbf{F}_\chi^{\mathrm{reac}}(\mathbf{r}) = \mathrm{Re}[\chi]\frac{\nabla K(\mathbf{r})}{\omega\sqrt{\varepsilon_f\mu_f}} \tag{3}$$

gives a conservative force that derives from a truly chiral potential $K(\mathbf{r}) = \omega\varepsilon_f\mu_f\mathrm{Im}[\mathbf{E}(\mathbf{r})\cdot\mathbf{H}^*(\mathbf{r})]/2$. The surprise came when realizing that this potential is actually a well-defined quantity in chiral optics: the optical chirality density. This quantity is known in fundamental optics since 1964 as the 00-zilch density introduced by D.M. Lipkin.[48] It was brought back to light by Y. Tang and A. E. Cohen that showed how this density can quantify, locally, the chirality of a field and contribute to enhance the detection of molecular circular dichroism.[49] This prediction had a strong impact, and led to a genuine renewal of studies in optical chirality, both from very fundamental perspectives[50−53] and more experimental ones.[54−57] The connection between $K(\mathbf{r})$ and the optical chirality density is straightforward here only because we work with harmonic electromagnetic fields. But this does not hide the absolutely remarkable fact that a chiral force signal is shaped by the mere combination of the gradient of this chiral density with the real part of the dipolar chiroptical response.

A similar and complementary combination can be identified on the dissipative, nonconservative, chiral force component

$$\mathbf{F}_\chi^{\mathrm{diss}}(\mathbf{r}) = \sqrt{\varepsilon_f\mu_f}\,\mathrm{Im}[\chi](2\mathbf{\Phi}(\mathbf{r}) - \nabla\times\mathbf{\Pi}(\mathbf{r})) \tag{4}$$

built from the product between $\mathrm{Im}[\chi]$ of the chiral dipole and the electromagnetic quantity $\mathbf{\Phi} = \omega(\varepsilon_f\mathbf{\Phi}_E + \mu_f\mathbf{\Phi}_H)/2$ that corresponds to a chiral flux. This flux is built, in the harmonic regime, on the electric and magnetic polarization ellipticities and, just like the density of chirality, is time independent. The structure of the chiral dissipative force component is analogous to the achiral radiation pressure with a spin−orbit separation of the optical chirality flux $\mathbf{\Phi} = \mathbf{\Phi}_O + \mathbf{\Phi}_S$, where $\mathbf{\Phi}_O = -\mathrm{Im}[\boldsymbol{h}_0]/4$ and $\mathbf{\Phi}_S = \nabla\times\mathbf{\Pi}/2$, in agreement with the definition of the chiral momentum density presented in ref 50.

In the harmonic regime, chirality density and flux are time-independent local quantities, respectively, proportional to the helicity density and helicity flux density, itself built on polarization ellipticities and proportional to the spin density of the light field.[51,60,61] More generally, the chirality flux is related to the optical chirality density by a conservation law that has been the source of an important literature, discussing in particular the physical meaning of such a conservation law in comparison with the continuity equation for the electromagnetic energy density.[50,62−64] Charge current density source terms that can be added to the chiral conservation law yield a (pseudoscalar) coupling between the electric field and the matter current density that can be viewed as a loss rate of optical chirality density. This has been exploited by L. V. Poulikakos et al.[62] in proposing a conservation law of chirality that quantifies the necessary breaking, in the scattered field, of the balance between the left and right circular polarizations upon the linear polarized excitation of a lossy, dispersive chiral object. The operational formulation of this law therefore gives the possibility to measure the scattered chirality flux directly by analyzing the polarization of the scattered far field.[65] This relation has been central for developing enantiomeric recognition protocols at the single chiral nano-object level performed in situ an optical trap.[58] Such work contributes to the current effort for detecting and measuring optical activity at the level of single nano-objects.[66−69]

The force approach therefore connect quantities of the electromagnetic field characterizing chirality with the chiral response of matter, as other approaches do, for instance, scattering ones.[70,71] But it is a strong asset of the dipolar framework presented above to make this connection straightforward (see Box 2). It is indeed remarkable to see the full optical force decomposed into distinct, noninterfering, achiral, and chiral contributions. This implies from the force perspective a remarkable separation between the achiral response of the dipolar system coupled to the achiral part of the interacting field, and the chiral response of the dipole engaging only the chirality of the electromagnetic field. Finally, as R. P. Cameron and colleagues did,[47] we would like to emphasize the generality of

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

Box 2. Recoil and Multipoles

It is fair to stress that the dipolar approach is not free from ambiguities. The problem starts with the possibility to add, besides the Lorentz force law, a contribution from the self-interaction of the dipole.[41] This contribution corresponds to a recoil optical force involving both the electric and magnetic dipole moments through the interfering term $\boldsymbol{p} \times \boldsymbol{m}^*$.[72,73] Resorting to the self-interaction of the dipole is important when the dipole is considered as a true physical system, because it ensures energy and momentum conservation in relation with the optical theorem.[74] However, the term becomes questionable when the dipolar model is used for describing a small nanoparticle of radius R, with polarizabilities scaling as R^3. This can be seen with a rigorous multipolar evaluation of the optical force using the generalized chiral Mie theory that has been developed by different groups.[27,70,75−78] To leading-order R^3, both the dipolar and multipolar force calculations give the same result, validating that the strict dipolar approach corresponds to the first order expansion of the force acting on a nanoparticle at the small-size limit. But the next-to-leading-order term given by the multipolar result scales as R^5, coming from the electric and magnetic quadrupolar terms, whereas the self-interaction term contributes with R^6. Therefore, by missing the dominant quadrupolar contributions, the recoil force added to the dipolar force does not improve the accuracy in the evaluation of the force in the small sphere limit.[79] This shows why the multipolar approach, free from such next-to-leading-order issues, should guide any quantitative evaluation of force signals in the perspective of high-precision theory-experiment comparison. It remains that the strict dipolar Rayleigh regime gives the most simple access to a physical interpretation of the various force components.

the dipolar approach that defines chiral optical forces free from any description of a specific energy level structure of a given chiral molecule. This clearly contrasts with the alternative approaches cited above.

Measuring these new chiral optical forces has not been, and is not, an obvious task. Figures 3 and 4 gather few relevant schemes that measure the forces by analyzing their influence on the motion of the chiral enantiomers, either through the monitoring of single, ballisitic trajectories for the larger chiral objects, like in ref 80, or through the statistical analysis of the diffusing motion of ensemble of chiral smaller objects, like in ref 81. Atomic force microscopy is also one important method proposed, using atomic force microscopes with chirally structured cantilevers that have demonstrated their potential for measuring chiral optical forces at the nanoscale.[82] In between these techniques, recent proposals involve optical tweezers as promising setups for reaching the appropriate resolution level needed for measuring chiral optical force fields.[58,77,83−85]

CHIRAL TORQUES AND CROSS MOMENTUM TRANSFERS

We now turn to another fascinating aspect most clearly revealed by looking at the full torque $\boldsymbol{\Gamma} = \mathcal{P} \times \mathcal{E} + \mathcal{M} \times \mathcal{H}$. Just like the force, the time-averaged torque exerted on a chiral dipole by a harmonic chiral light field splits into distinct achiral and chiral components $\langle \boldsymbol{\Gamma} \rangle = \langle \boldsymbol{\Gamma}_{\alpha,\beta} \rangle + \langle \boldsymbol{\Gamma}_{\chi} \rangle$. While the achiral torques described above are determined by the field ellipticities $\boldsymbol{\Phi}_E$ and $\boldsymbol{\Phi}_H$, the chiral torque

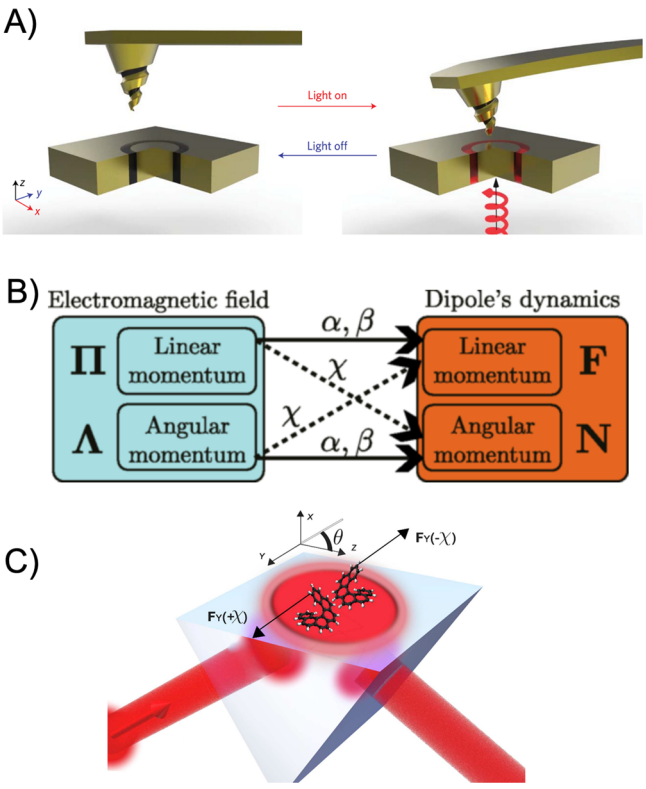


Figure 3. (A) Atomic force microscopy (AFM) has been used for measuring chiral optical forces. As shown in ref 82, a chiral AFM cantilever can act as a chiral dipole that, when immersed within the chiral near field of a plasmonic coaxial nanoaperture,[103] responds to induced chiral optical forces. Adapted with permission from ref 82. Copyright 2017 Springer Nature. (B) This table shows direct and crossed momentum transfers that can be at play on a chiral dipole. The nonchiral component α, β of the dissipative force/torque couples the linear/angular momentum of the light to the linear/angular momentum of the particle, while the chiral component χ of the dissipative force and of the torque cross-couples linear to angular momenta in both directions.[76] Adapted with permission from ref 76. Copyright 2015 American Physical Society. (C) An evanescent field irradiating a chiral molecule can produce lateral chiral forces with opposite directions along the surface of the prism for opposite enantiomers, as discussed in ref 104. Adapted with permission from ref 104. Copyright 2015 National Academy of Sciences of the United States of America.

$$\langle \boldsymbol{\Gamma}_{\chi} \rangle = 2\mathrm{Im}[\chi]\boldsymbol{\Pi}/c \tag{5}$$

involves the (time-averaged) full Poynting vector of the irradiating light field, thereby rehabilitating it as taking part in the definition of a genuine observable, when achiral force and torque had it truncated to its orbital or spin parts only.[28,86]

Physically, the involvement of the full Poynting vector means that a torque can be induced on a chiral object independently from the chirality of the light field. This is the analog of the simple physical situation of a rotating helix immersed in a laminar flow. Torques therefore couple the achiral dipolar response to the chiral content of the field and the chiral dipolar response with the achiral content of the field. This is in striking contrast with the way forces engage achiral and chiral parts of the light−matter interaction. This exchanged symmetry found on torques explains the rotational motions observed by the transfer of spin angular momentum to achiral absorbing particles under circularly polarized light illumination,[87−90] or to chiral birefringent particles using achiral linearly polarized light,[91,92]

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

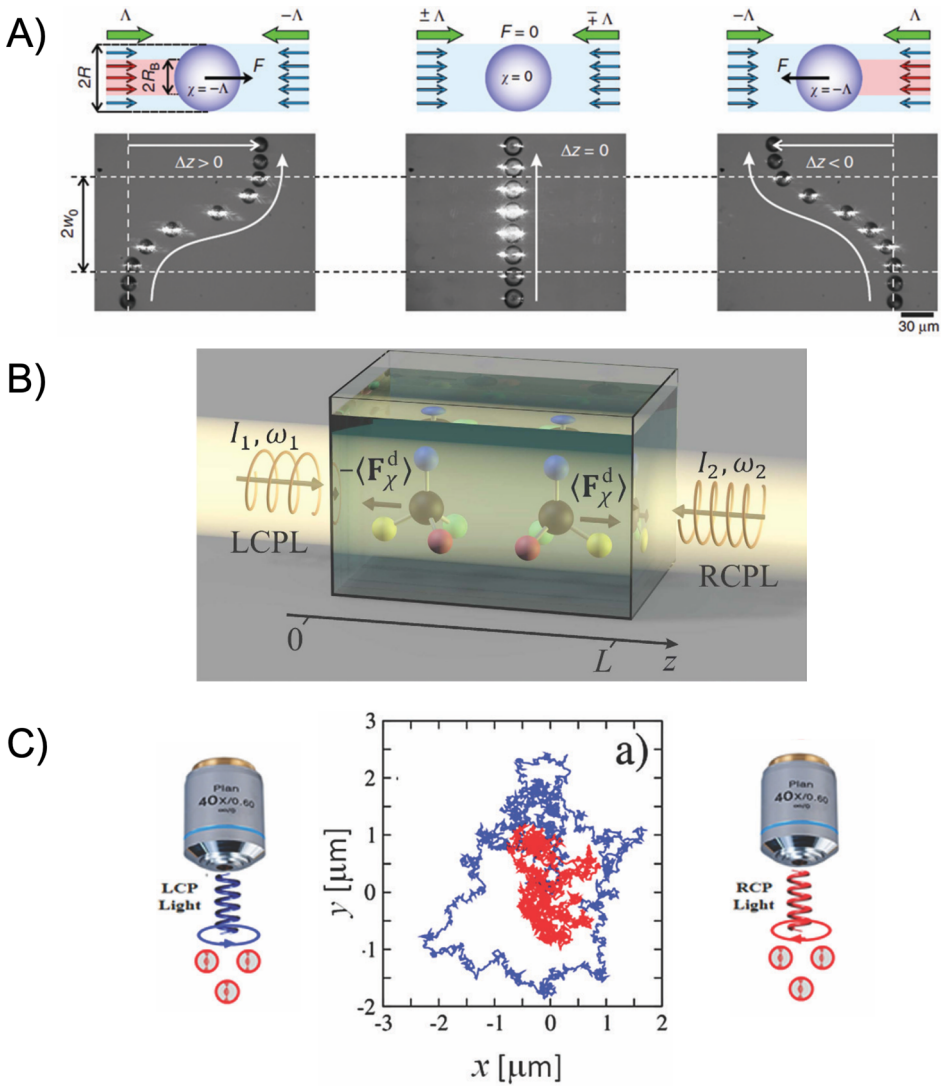


Figure 4. (A) In ref 80, microsized cholesteric particles are deflected to the right or left depending on their chirality and the polarization of the light by combining laminar flow with chiral optical forces. The case $\chi = 0$ corresponds to a nonchiral particle, and $\chi = \pm 1$ to right/left-handed chiral particles. Adapted with permission from ref 80. Copyright 2014 Springer Nature. (B) The scheme in ref 81 is designed to separate molecular enantiomers in the superposition volume of two counterpropagating laser beams of opposite helicity. The different frequencies of each beam lead to differential absorption rates of enantiomers and, thus, to their spatial separation. Reprinted with permission from ref 81. Copyright 2016 Springer Nature; https://creativecommons.org/licenses/by/4.0/. (C) As an example of the discriminative action of chiral optical forces within confined optical volumes, ref 117 studies the Brownian trajectories of a right-handed particle optically trapped by a circularly polarized laser trapping beam focused through an objective. Depending on the left/right circular polarization, the right-handed particle explores a different volume within the trap. Reprinted with permission from ref 117. Copyright 2020 Royal Society of Chemistry; https://creativecommons.org/licenses/by/3.0/.

as Beth first identified in his historical experiment on light angular momentum transfers through suspended quarter-wave plates.[93]

Taken altogether, the dipolar expressions of the achiral and chiral forces and torques reveal how the mechanical actions exerted by the light field illuminating the dipole are connected to specific light−matter momentum transfers. It is seen that the dissipative part of the achiral optical force is associated with a transfer of (orbital) linear momentum of light to linear momentum of the dipole, when the achiral torque has its optical source in a transfer of (spin) angular momentum of light to angular momentum of the dipole. Achiral and dissipative, these linear-to-linear and angular-to-angular transfers involve the imaginary parts of the α, β polarizabilities.

In striking contrast, chiral dynamical effects cross-couple light-dipole linear and angular momenta through the chiral polarizability χ. On the one hand, the expression of the chiral torque reveals that the linear momentum of light, carried by the Poynting vector, is coupled to the dipole angular momentum in the chiral torque, eq 5. The chiral dissipative force, eq 4, on the other hand, contributing to the linear momentum of the chiral dipole stems from the angular momentum of light described by the electric and magnetic ellipticities that form the optical flux of chirality $\mathbf{\Phi}$ in the harmonic regime. The crossed momentum transfers that involve the chiral polarizability χ are sketched in Figure 3.

By their separation, achiral and chiral dynamical terms can be balanced by the competition between direct momentum transfers, and crossed momentum transfers assisted by the chiral polarizability only. This competition implies the possibility to regulate the achiral and chiral dynamical action on the chiral dipole by the relative strengths of the chiral χ and

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

achiral polarizabilities α, β, at fixed energy density of the illuminating light field. The freedom given on the sign of the chiral force by the choice of one enantiomer or the other (changing the sign of χ) gives way to actually fix the sign of the resulting (achiral + chiral) optical forces and torques, as soon as $\mathrm{Im}[\chi]$ dominates over $\mathrm{Im}[\alpha, \beta]$. This possibility gives a direct route toward so-called pulling forces and left-handed torques, as discussed in ref 76, 94, and 95. This chiral route meets here recent efforts aimed at realizing negative (pulling) optical forces and left-handed torques as new means for optical micro- and nanomanipulations.[96−102]

The pulling force effect corresponds to the displacement of the illuminated particle in a direction opposite to the propagation direction of the incident light beam, measured by the direction of the field linear momentum. In the context of chirality, this reversal of the direction of the force with respect to the direction of the beam is induced by the crossed transfer from optical angular momentum to linear momentum of the dipole. It can be clearly discussed in the most simple case of a chiral dipole illuminated by a circularly polarized plane wave of intensity I_0 propagating along the $\hat{\mathbf{z}}$ direction, where $\mathbf{F}_{\alpha}^{\mathrm{diss}} = \omega\varepsilon_f\mu_f I_0 \mathrm{Im}[\alpha]\hat{\mathbf{z}}$ and $\mathbf{F}_{\chi}^{\mathrm{diss}} = 2\omega\varepsilon_f\mu_f I_0 \mathrm{Im}[\chi]\hat{\mathbf{z}}$ add up to the total optical force exerted on the dipole. As detailed above, the dissipative achiral component comes from the linear momentum of the plane wave and the dissipative chiral force from the spin angular momentum. If the achiral force is always in the positive direction of the (orbital part of the) Poynting vector since $\mathrm{Im}[\alpha] > 0$ for all passive materials, there is no restriction on the direction of the chiral force with respect to the direction of the spin angular momentum since the sign of χ can be reversed simply by exchanging the enantiomeric form of the chiral particle. Therefore, if the crossed momentum transfer induced by χ is strong enough, a negative chiral force can overcome the positive achiral force and, in such conditions, can lead to a pulling total force. Of course, for this to happen, $\mathrm{Im}[\chi]$ must be large enough so that $\mathrm{Im}[\alpha + 2\chi] < 0$. The second kind of negative mechanical effect, the left-handed torque, proceeds from the same mechanism. The chiral torque can become so "left-handed" for a sufficiently strong chiral particle that it can compensate the achiral "right-handed" torque and eventually reverse the sign of the total torque.[76]

No standard chiral molecule can yield such strong $\mathrm{Im}[\chi]$ contributions and the possibilities for observing pulling forces and left-handed torques demand specific and optimally chiral system to be designed. In this context, chiral metal-molecular hybrids have recently revealed extraordinary strong chiral signatures. For instance, DNA−Au nanoparticle hybrids, three-dimensional chiral metallic/plasmonic colloids, to give a few examples, constitute relevant candidates considering their exceptionally high effective chiral polarizabilities.[105−110] Such possibilities for unusual, crossed momentum transfers rooted on chiral coupling constitute new mechanisms that can be explored in order to yield all-optical dynamic phenomena. They are closely related to what has been observed for achiral systems,[99,101,111] but they have yet to be experimentally explored and exploited in the context of chirality. Obviously, momentum transfers mediated by chirality can be engineered with more complex systems and more complex fields, such as highly focused beams, vortex beams carrying orbital angular momentum, and so on.[71,112,113]

ALL-OPTICAL CHIRAL DISCRIMINATION

The possibility to sort out racemic mixtures made of equal amounts of right- and left-handed enantiomers depending on their chirality (a process named "chiral separation" or "chiral resolution") using enantioselective chiral optical forces that act on opposite directions for opposite enantiomers currently fuels a strong theoretical and experimental research activity. The potential impact of such an all-optical sorting strategy is evident when considered at molecular scales where noninvasive, large scale, and high throughput alternative methods to the ones existing could be proposed in the context of analytical chemistry and pharmaceutical industry.[115] Following the classification of L. D. Barron,[116] the genuine discriminative action of the chiral optical forces can be rooted in the true chiral nature of the chiral coupling that determines the chiral force field with the optical chirality density and flux respectively time-even pseudoscalar and pseudovector quantities.

The first all-optical chiral sorter was demonstrated by G. Tkatchenko and E. Brasselet in 2014.[80] In close relation with the dipolar scheme proposed in ref 46, two counterpropagating circularly polarized light beams with opposite helicities were shown to shift along their colinear propagation direction a chiral (cholesteric) microsized particle traversing their spatial extension. As shown in Figure 4, the direction of the shift was demonstrated to be fixed by the enantiomeric form of the microparticle in relation with the circular polarization of the beams, when the trajectories of achiral (nematic) particles remained unperturbed by the counterpropagating beams.

From the viewpoint of chiral separation, the target is to go from this microscale down to the molecular scale. It represents a formidable challenge that motivates many proposals, as discussed below. The main issue one is confronted with at molecular scale is Brownian diffusion induced by the inevitable thermal fluctuations. The challenge is thus to design experiments capable of measuring the motional effect induced by the chiral optical force on molecular enantiomers over thermal diffusion. Although difficult to precisely estimate without knowing the strength of the chiral polarizability χ (real and imaginary parts) to be associated with the chiral molecule (see Box 3), it is clear that chiral optical forces are weak forces, not exceeding the fN level. In the down-scaling scenario, therefore, experiments will have to involve high resolution measurement strategies.[84]

A similar sorting strategy involving chiral radiation pressure was implemented experimentally recently.[81] The strategy consists in having the two counterpropagating waves of opposite helicity at different frequencies (noninterfering), thus, absorbed at different rates by a chiral nanoparticle placed in this light field. As shown, the nanoparticle experiences a net average optical force which is absolutely discriminatory, attributed to $\mathrm{Im}[\chi]$ of the chiral nanoparticle. In this work too, the limitations set by Brownian diffusion on the separation capacity of such chiral discriminatory scheme extrapolated at the molecular level are identified.

Thus, moving from fluids to vacuum with molecular beams is a particularly appealing approach for reducing the thermal limit set by Brownian diffusion. Along this line, one most promising sorting scheme was proposed by R. P. Cameron and colleagues in 2014 using the reactive component of the chiral optical force. The idea is to form a grating of optical chirality density with adjustable periodicity by superposing two linearly polarized light beams making a small angle between them. The modulation of

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

Box 3. Pasteur Medium

Small chiral spherical particles can be modeled as made of a bi-isotropic chiral medium, a so-called "Pasteur medium",[114] defined by an electric permittivity $\varepsilon_m(\omega)$, a magnetic permeability $\mu_m(\omega)$ and a chirality parameter $\kappa_m(\omega)$, all three dimensionless, dispersive, scalars. This chirality parameter corresponds to the difference in the effective refractive index between left- and right-handed circularly polarized waves determined from the constitutive Pasteur relations between the displacement and magnetic fields and the electric and magnetization fields propagating through the chiral medium.[76] Such relations together with the dipolar definition given above lead, in the quasistatic limit, to the definition of the dipolar polarizabilities (α, β, χ) on which the force and torque expressions are built from the macroscopic bulk susceptibilities (ε_m, μ_m, κ_m) according to

$$\alpha = 4\pi R^3 \frac{(\varepsilon_m - \varepsilon_f)(\mu_m + 2\mu_f) - \kappa_m^2}{(\varepsilon_m + 2\varepsilon_f)(\mu_m + 2\mu_f) - \kappa_m^2} \quad (6)$$

$$\beta = 4\pi R^3 \frac{(\varepsilon_m + 2\varepsilon_f)(\mu_m - \mu_f) - \kappa_m^2}{(\varepsilon_m + 2\varepsilon_f)(\mu_m + 2\mu_f) - \kappa_m^2} \quad (7)$$

$$\chi = 12\pi R^3 \frac{\kappa_m}{(\varepsilon_m + 2\varepsilon_f)(\mu_m + 2\mu_f) - \kappa_m^2} \quad (8)$$

where ε_f and μ_f are the permittivity and permeability of the fluid (assuming that both are purely real) that the chiral nanosphere is immersed into. This connection (that reduces to the usual Clausius−Mossotti relations for $\kappa_m = 0$) refines the relation between χ and the standard chiroptical observables of optical rotatory dispersion (ORD) associated with $\mathrm{Re}[\kappa_m]$ and circular dichroism (CD) with $\mathrm{Im}[\kappa_m]$. The structure of eq 8 shows that both ORD and CD are mixed in the denominator of the definition of χ, with $\mathrm{Re}[\chi]$ and $\mathrm{Im}[\chi]$ determining, respectively, the optical chiral reactive and dissipative forces. Therefore, a chiral system that display either ORD or CD can lead to both reactive and dissipative chiral force signals. The second important consequence of this model is the volumic nature of χ showing a reduction of the chiral polarizability with size as R^3.

the chirality density yields a nonzero reactive chiral force field that points in opposite direction for molecular enantiomers.[47] This scheme turns out to act as a "chiral Stern-Gerlach deflector".[118]

All-optical chiral sorting strategies have also been designed in optical trapping configurations where the enantiomeric balance can be locally broken inside the trapping potential. An early proposal aims at concentrating, within the trapping volume of an optical tweezer, and by the assistance of the optical chiral reactive force, one enantiomeric specie of a racemic solution of chiral molecules by using a circularly polarized laser as the trapping beam.[119] At sufficiently high laser intensities, different local concentrations of the two enantiomers are predicted,[120] although the feasibility of this idea has led to interesting discussions and debates.[121,122] These authors also include in their description of the chiral discriminatory effect the fact that chiral molecules are nonspherical and that their interaction with the circularly polarized trapping beam will induce orientational effects, confirming their views on a possible migration difference between the two enantiomers in and out the intense field regions inside the trap. Such trapping configurations have been further explored theoretically within the Mie formalism,[77] accounting very precisely for the influence of the high numerical aperture of the trapping beam on the chiral optical force field exerted on the optically trapped chiral particle.[85]

While evaluating the dynamics of single chiral nanoparticle optically trapped in such conditions under high focus, P. A. Maia Neto and colleagues have probed the sensitivity to chirality of rotational movements detected by off-axis displacements of the trapped chiral nanoparticle. With a rotation angle dependent on the handedness of the nanoparticles, they have proposed an alternative mechanism for all-optical chiral resolution combined with chiral recognition all together within the optical trap.[78] These important ideas pave the way to implement genuine chiral resolution using rotational degrees of freedom, in a continuation of previous proposals and experiments where the helicity of the optical trapping beam is exploited for selectively trapping chiral microparticle.[25,123] Setting up a dual beam approach functioning on this helicity-dependent trapping, it is shown that chiral microparticles can be stabilized or expelled from the trapping volume depending on the sign product of their handedness and the helicity of the light field, giving again another all-optical possibility for chiral resolution.[25]

The potentialities for all-optical sorting have been further explored in confined volume at the level of atomic force microscopy tips,[82,112,124] nanostructured devices, such as plasmonic coaxial apertures[103] or plasmonic asymmetric nanoapertures.[125] Plasmonic coaxial structures under circularly polarized illumination behave as genuine plasmonic tweezers at the level of which a strong chiral reactive force can be induced, benefiting from the strong inhomogeneity of the plasmonic field.[82,126] Such induced chiral reactive forces have opposite signs for opposite enantiomers, so that the total force field exerted on the chiral molecules deposited on top of such a coaxial nanostructure will trap in a deep potential one enantiomer and repel the opposite one with a potential barrier. Such enantiomer-aperture elements are particularly promising in that they can be easily integrated for high throughput architectures yet to be exploited for asymmetric chemical syntheses or for chiral resolution.

For sorting purposes, chiral lateral forces have also been considered, acting on a chiral nanoparticle placed on a substrate at the surface of which an interference optical field with complex polarization states is created.[15] On such an interface, chiral optical forces are induced in a direction perpendicular to the direction of the illumination light and thus exert a lateral action in opposite directions depending on the handedness of the enantiomer. This clear sorting action was first described by C. T. Chan and coauthors.[57] It is rooted on the possibility for the chiral particle to interact with its scattered field that, reflected by the interface, carries a longitudinal polarization component, that is, along the direction of propagation. This component determines a transverse spin density that directly corresponds to a lateral force acting on the chiral particle. Such transverse features of spin densities at interfaces, and more particularly for evanescent waves, are at the heart of a recent and vast literature, as very well reviewed in refs 127 and 128, for instance. Combining these discussions, one can then describe the sorting action of chiral lateral forces in evanescent fields,[104] plasmonic fields,[79,129] with potentially very rich dynamical landscapes.[130] The description of chiral lateral forces has also been extended to the multipolar regime.[79]

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

In this regime, new effects emerge that cannot be seen when merely considering a chiral dipole. In particular, lateral forces are offering a perfect template for exploring the strong and intriguing correlations between multipolar effects and chiral coupling. This has led to the description of lateral force enhancements induced by multipolar response of chiral nanocylinders, for example,[131] or even more spectacularly of sign inversion of the lateral force when changing the size of the chiral particle, as demonstrated in refs 79 and 132. Such a sign reversal is clearly reminiscent of the multipolar effects on angular-to-linear crossed momentum transfers mediated by chirality, as discussed above in the context of and left-handed torques and pulling forces. Such crossed momentum transfers have recently been exploited for chiral sorting purposes, with the remarkable outcome that enantioselectivity is ensured for chiral microspheres of arbitrarily small chiral parameters.[95] This work exemplifies how such multipole-chiral force correlations can have important consequences in the perspective of chiral discriminatory protocols.

As stressed above, the scale reduction needed for targeting the molecular level is necessarily accompanied by the increasing influence of Brownian diffusion and its potential detrimental influence in a chiral resolution process. But the coupling to thermal fluctuations of a chiral nano-object on which chiral optical forces are exerted actually opens new potentialities looking at the role played by chirality in the viewpoint of stochastic thermodynamics.[134] Viewing the Brownian chiral dipole as being immersed within a chiral optical environment indeed leads to identifying various thermodynamical manifestations of the optical forces that literally emerge from the chiral coupling between the chiral diffusing probe and the chiral optical environment. Turning this way chiral (internal) degrees of freedom into true thermodynamic parameters draws interesting analogies with long lasting issues in the field of chirality.[135] In close analogy with asymmetric synthesis performed under circularly polarized light[136] or chiral liquid crystals nuclear magnetic resonance and chiral chromatography,[137] the framework of chiral optical forces gives a unique capacity to access explicitly the thermodynamic costs and consequences of enantiospecific and chirally discriminative processes. This new vision uncovers unexpected but fertile paths that should now be explored following Pasteur's views of "asymmetric forces" involved in any systematic coupling mechanism able to lift the degeneracy in the free energy between opposite enantiomers, and thereby in the asymmetry observed in biochemistry.[138] This constitutes a vast program yet to be opened, with new opportunities in the context of chiral sensing, recognition, and chiral separation at the nanoscale (see Box 4).

Box 4. Cryptochirality

Equation 8 also reveals that the chiral susceptibility κ_m not only defines the chiral polarizability χ but is also involved in the purely electric and magnetic polarizabilities. This implies that the achiral optical forces and torques that do not depend on χ still involve the chiral properties of the illuminating object through κ_m if present. This involvement is quadratic in κ_m, confirming that the enantioselectivity is the genuine asset of the chiral optical forces and torques. This also implies that the notion of an achiral mechanical action of the light field on a particle is to be understood as the invariance of the force and torque signals for two opposite enantiomers, rather than linked to the (more stringent) definition of a force field defined in the strict $\kappa_m \to 0$ limit. This exactly corresponds to a cryptochiral case where the "substance" model is chiral but the actual "operation" performed on the system remains achiral: "the chirality is thus subliminal", as put by K. Mislow and P. Bickart.[133] It is precisely the fact that the directions of the chiral optical force and torque depend on the sign of χ, in other words on the enantiomeric form of the illuminated dipole, that yields the most important feature of the optomechanical manifestation of chirality and that determines the whole applicative potential of such new forces in the context of enantioseparation.

QUANTUM CHIRAL FORCES

Probing the mechanical action of chiral optical forces using chiral molecular quantum interferometers has also been proposed.[118] In the regime of de Broglie molecular optics where the center-of-mass motion of a molecule cannot be viewed classically anymore, but rather described in terms of de Broglie waves, state-of-the-art techniques already developed for large molecule quantum interferometry are available.[33,139,140] The ideas of R. P. Cameron and colleagues consist in diffracting the de Broglie waves associated with chiral molecules sent through an optical grating of chiral helicity fringes, see Figure 5. Besides the fact that such a grating spatially separates the enantiomers of a chiral molecule (a so-called "chiral beam splitter"), it also yields a high sensitivity toward chirality (an achiral molecule is not diffracted), allowing to measure the intrinsic chiral response of the molecule by recording the entire diffraction patterns produced. Both conservative and dissipative diffraction regimes have been discussed,[141] and the work has recently been expanded to include the influence of molecular rotational states.[142] This chiral matter-wave interferometry also allows preparing molecules in a superposition of enantiomer states, from which interferometric sensing and measurements of enantiodependent chiral optical forces can be expected with unprecedented accuracy, as detailed in ref 143. These work clearly emphasize how molecular interferometry constitutes one firm promise for investigating in full depth the signatures and features of chiral optical forces.

At the single atom level, chiral optical forces have also been recently identified.[145] Here, the light field is an evanescent waveguided mode in a nano-optical fiber. The chirality of the light field is associated with the longitudinal component of the electric field that oscillates in phase quadrature with respect to its radial component, and the chirality of the atom is determined by the rotation of its dipolar moment in the meridional plane of polarization.[146] Chiral forces proceed from a spin−orbit coupling mechanism that imposes a directional dependence on the radiative coupling between the spin polarized atomic dipole and the near-resonant evanescent guided mode with respect to its propagation direction. This directionality corresponds to a breaking of the mirror symmetry in the radiative rates and its consequence is a modification of the recoil balance in spontaneous emission in the two directions. This eventually leads to a chiral force that acts on the atom along the selected direction propagation of the guided mode. It is important to stress that this mechanism based on optical spin−orbit interaction is at the core of chiral quantum optics, a recent extension of quantum optics where mirror symmetry broken directional couplings have proven their potential for a new generation of integrated quantum platforms where nonreciprocal protocols and gates can be designed and implemented.[147] Certainly, the link between chiral quantum optical forces and chiral quantum optics is drawing promising

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

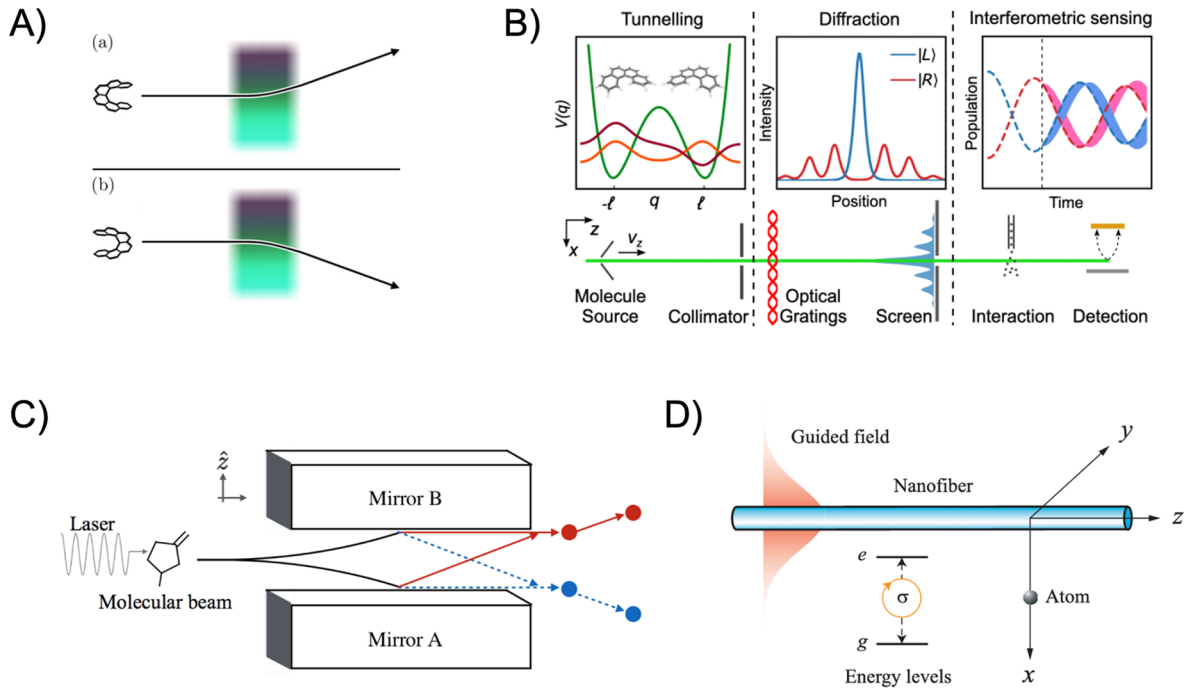


Figure 5. (A) The chiral Stern-Gerlach deflector proposed in ref 47 involves a single optical helicity fringe that induces on a chiral molecule passing through it a chiral optical force directed upward or downward depending on the enantiomeric form of the molecule. The consequence is a change in the center-of-mass motion of the molecule. Adapted with permission from ref 47. Copyright 2014 Institute of Physics IOP Science. (B) Quantum superpositions of enantiomers can be prepared by diffracting a molecular beam sent through a similar optical helicity grating inducing a handedness-dependent phase shift. Through their transit, chiral molecules tunnel continuously between their two enantiomeric forms, giving the possibility to generate superpositions of enantiomers by a careful adjustment of the grating phases, as discussed in ref 143. Such superpositions can be measured and exploited using state-of-the-art interferometric sensing methods developed in the context of matter-wave interferometry.[33] Reprinted with permission from ref 143. Copyright 2021 American Physical Society; https://creativecommons.org/licenses/by/4.0/. (C) The concept of chiral Stern-Gerlach separator has been extended in ref 144 to involve quantum vacuum fluctuations. Here, a molecular beam of chiral molecules passes through a planar cavity made of chiral mirrors. A chiral dependence of the Casimir-Polder potentials deflects differently enantiomers of opposite handedness, resulting in the spatial separation of the enantiomers. Adapted with permission from ref 144. Copyright 2019 American Physical Society. (D) Following the proposal of ref 145, a spin polarized atomic transition, represented here by a two-level atom with a dipole rotating in the meridional plane of polarization placed just below an optical fiber, will experience differential spontenous emission rates along the two possible propagation directions of the guided light along the fiber. This corresponds to a directional dependence of the Rabi frequency that leads to a mirror symmetry breaking of the atomic center-of-mass motion, that is, to the emergence of a chiral force induced by the guided light on the atom. Reprinted with permission from ref 145. Copyright 2018 American Physical Society; https://creativecommons.org/licenses/by/4.0/.

routes, with possibilities to transfer strongly directional photonic spin−orbit coupled degrees of freedom to atomic center-of-mass motions, including superposition states. This strong directionality has been recognized as particularly relevant in the context of atomic lattices, quantum atomic interferometers, and for the design of new chiral quantum information protocols based on Rydberg-atom-nanofiber interfaces.[148,149]

While real fields have been involved up to this stage of the Perspective when describing chiral optical forces, S. Y. Buhmann and colleagues have very recently involved fluctuating fields for studying the enantiodependent dispersion interaction between a chiral Rydberg atom and a nearby chiral mirror, coming up with analogous predictions regarding the chiral discriminatory nature of optical forces.[150] Studying chiral dispersion Casimir-Polder forces between a chiral microscopic object (a molecule) and a chiral macroscopic object (a chiral mirror plate), these authors have shown that the van der Waals interaction between two chiral molecules can be largely enhanced when mediated by a chiral surface.[151] Opposite regimes of interaction, attractive vs repulsive chiral interactions, have been identified as a function of the plate's positions and have been shown, most remarkably, to be discriminatory with respect to enantiomers of different handedness. This has led to a scheme involving a molecular beam, passing through a planar Fabry−Perot cavity made of chiral mirrors for separating molecular enantiomers, as sketched in Figure 5. The scheme exploits parity violation in the Casimir-Polder interaction potential between chiral mirrors and chiral molecules that results in the spatial separation of the chiral mixture composing the initially racemic molecular beam sent through the cavity. This idea and scheme add a quantum flavor to the concept of the Stern-Gerlach chiral deflector presented above.[144,152]

Obviously, extensions of the concept of chiral optical forces to the realm of quantum fluctuating fields has immediate connections with Casimir physics. Reminiscent of the van der Waals interaction that can become repulsive between two molecules that display chiral polarizabilities,[153] the Casimir force exerted by the quantum vacuum fluctuations between two chiral metamaterial mirrors can be largely reduced through the chiroptical response of each mirror.[154] This setup brings forward interesting issues at the crossroad between thermodynamic passivity, causality and Casimir repulsion.[155] Repulsion is also found if the intracavity volume is filled with an optically active, chiral medium.[156] In such a case, the different phase velocities for the left- versus right-circular vacuum photons break the reflection symmetry at the mirror surfaces and opens the

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

possibility for repulsion between the mirrors. Such a chiral Casimir force turns out to be strongly repulsive and, as such, give a particularly appealing example of a quantum levitating system.[157−161]

That chirality eventually takes a lead role in such topics like chiral molecular matter-wave interferometry, quantum sensing, or Casimir quantum levitation draws fascinating perspective for probing, in the quantum realm, the pervasive character of the concept of chirality. Such original ideas and the new directions they offer are currently put to experimental tests withing large collaborative structures, such as the ones set up at the Quantum Optics and Laser Science group at Imperial College, London, involving universities of Strathclyde, Sorbonne-Paris-Nord, or at the Collaborative Research Center 1319 ELCH at the University of Kassel, to name a couple.

CONCLUSION

The choice taken in this Perspective to start with classical chiral optical forces has driven us a long way, unfolding many different aspects of chirality in a complex and rich research field, starting from the initial surprise of finding enantioselective optical forces that only engage the chirality of the object with the chirality of the field. Now, this enantioselective nature encoded in chiral discriminating signals is one of the main drive of the current excitement. It opens radically new strategies for chiral resolution that might become in the near future solid alternatives to the existing ones used for enantiomer separations, such as liquid column chromatography. Through its rapid development and progress, other aspects of chirality have entered the field and have enriched existing contexts, ranging from molecular physics, optomechanics, stochastic thermodynamics, and quantum physics. As for any other fertile topic, chiral optical forces have opened many new perspectives and revitalized long-standing discussions on the actual role played by chirality in fundamental physical phenomena. The complicity between optical force chirality and molecular chirality fertilizes many ideas and potentialities of this very active field of research. It is obviously fueled by the formidable challenge that represent all-optical chiral discrimination at the molecular realm, with potentially a huge impact in the context of analytical chemistry. For that purpose, the large collaborations mentioned above and their associated platforms shape the right interdisciplinary landscapes for pushing forward the study of chiral light−chiral matter interactions along the exciting trends presented here and the new ones to come.

AUTHOR INFORMATION

Corresponding Author

Cyriaque Genet − *Université de Strasbourg, CNRS, Institut de Science et d'Ingénierie Supramoléculaires, UMR 7006, 67000 Strasbourg, France;* orcid.org/0000-0003-0672-7406; Email: genet@unistra.fr

Complete contact information is available at: https://pubs.acs.org/10.1021/acsphotonics.1c01130

Funding

This work of the Interdisciplinary Thematic Institute QMat, as part of the ITI 2021 2028 program of the University of Strasbourg, CNRS and Inserm, was supported by IdEx Unistra (ANR 10 IDEX 0002), by SFRI STRAT'US project (ANR 20 SFRI 0012), by the Labex NIE (ANR-11-LABX-0058 NIE) and CSC (ANR-10-LABX-0026 CSC) Projects, and by the University of Strasbourg Institute for Advanced Study (USIAS; ANR-10-IDEX-0002-02) under the framework of the French Investments for the Future Program.

Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

The author thanks Antoine Canaguier-Durand, Gabriel Schnoering, Samuel Albert, Luìs Pires, Yoseline Rosales-Cabara, Lisa V. Poulikakos, David J. Norris, Thomas Hermans, James A. Hutchison, Eloise Devaux, and Thomas W. Ebbesen for discussions, support, and active participation in the research on chiral optical forces and chirality performed in the Institut de Science et d'Ingénierie Supramoléculaires, a mixed unit of the University of Strasbourg and the CNRS.

REFERENCES

(1) Brosseau, C. *Polarization and Coherence Optics: Historical Perspective, Status, and Future Directions*; Progress in Optics; Elsevier, 2010; Vol. *54*; Chapter 3, pp 149−208.
(2) Kahr, B. Polarization in France. *Chirality* **2018**, *30*, 351−368.
(3) Leclercq, F. Arago, Biot, and Fresnel Elucidate Circular Polarization. *Rev. Hist. Sci.* **2013**, *66*, 395−416.
(4) Collet, A.; Crassous, J.; Dutasta, J.-P.; Guy, L. *Molécules Chirales*; EDP Sciences, 2021.
(5) Busch, K. W., Busch, M. A., Eds. In *Chiral Analysis*; Elsevier: Amsterdam, 2006.
(6) Worrall, J. The pressure of light: The strange case of the vacillating 'crucial experiment. *Stud. Hist. Philos. Sci. A* **1982**, *13*, 133−171.
(7) Maxwell, J. C. *A Treatise on Electricity and Magnetism*; Dover Publications, 1954.
(8) Longair, M. S.; Longair, M. S. *Theoretical Concepts in Physics: an Alternative View of Theoretical Reasoning in Physics*; Cambridge University Press, 2003.
(9) Masalov, A. V. In *Quantum Photonics: Pioneering Advances and Emerging Applications*; Boyd, R. W., Lukishova, S. G., Zadkov, V. N., Eds.; Springer International Publishing, 2019; pp 425−453.
(10) Lebedev, P. N. Die Druckkrafte des Lichtes. *Annalen der Physik (Leipzig)* **1901**, *6*, 433.
(11) Nichols, E. F.; Hull, G. F. A Preliminary Communication on the Pressure of Heat and Light Radiation. *Phys. Rev. (Series I)* **1901**, *13*, 307−320.
(12) Garmire, E. In *Quantum Photonics: Pioneering Advances and Emerging Applications*; Boyd, R. W., Lukishova, S. G., Zadkov, V. N., Eds.; Springer International Publishing, 2019; pp 455−479.
(13) Gillies, G. T.; Ritter, R. C. Torsion balances, torsion pendulums, and related devices. *Rev. Sci. Instrum.* **1993**, *64*, 283−309.
(14) Zayats, A. V.; Richards, D. *Nano-Optics and Near-Field Optical Microscopy*; Artech House, 2009.
(15) Qiu, C.-W.; Palima, D.; Novitsky, A.; Gao, D.; Ding, W.; Zhukovsky, S. V.; Gluckstad, J. Engineering light-matter interaction for emerging optical manipulation applications. *Nanophotonics* **2014**, *3*, 181−201.
(16) Kucirka, J.; Shekhtman, A. G. On the deracemization of a chiral molecular beam by interaction with circularly polarized light. *Phys. Lett. A* **1996**, *221*, 273−276.
(17) Li, Y.; Bruder, C.; Sun, C. P. Generalized Stern-Gerlach Effect for Chiral Molecules. *Phys. Rev. Lett.* **2007**, *99*, 130403.
(18) Jacob, A.; Hornberger, K. Effect of molecular rotation on enantioseparation. *J. Chem. Phys.* **2012**, *137*, 044313.
(19) Li, X.; Shapiro, M. Theory of the optical spatial separation of racemic mixtures of chiral molecules. *J. Chem. Phys.* **2010**, *132*, 194315.
(20) Jia, W. Z.; Wei, L. F. Probing molecular chirality by coherent optical absorption spectra. *Phys. Rev. A* **2011**, *84*, 053849.
(21) Eilam, A.; Shapiro, M. Spatial Separation of Dimers of Chiral Molecules. *Phys. Rev. Lett.* **2013**, *110*, 213004.

(22) Cipparrone, G.; Mazzulla, A.; Pane, A.; Hernandez, R. J.; Bartolino, R. Chiral Self-Assembled Solid Microspheres: A Novel Multifunctional Microphotonic Device. *Adv. Mater.* **2011**, *23*, 5773−5778.
(23) Ross, B. M.; Lakhtakia, A. Light pressure on chiral sculptured thin films and the circular Bragg phenomenon. *Optik* **2008**, *119*, 7−12.
(24) Tkachenko, G.; Brasselet, E. Spin Controlled Optical Radiation Pressure. *Phys. Rev. Lett.* **2013**, *111*, 033605.
(25) Donato, M.; Hernandez, J.; Mazzulla, A.; Provenzano, C.; Saija, R.; Sayed, R.; Vasi, S.; Magazzù, A.; Pagliusi, P.; Bartolino, R.; et al. Polarization-dependent optomechanics mediated by chiral microresonators. *Nat. Commun.* **2014**, *5*, 1−7.
(26) Brzobohatý, O.; Hernández, R. J.; Simpson, S.; Mazzulla, A.; Cipparrone, G.; Zemánek, P. Chiral particles in the dual-beam optical trap. *Opt. Express* **2016**, *24*, 26382−26391.
(27) Guzatov, D. V.; Klimov, V. V. Chiral particles in a circularly polarised light field: new effects and applications. *Quantum Electron* **2011**, *41*, 526.
(28) Canaguier-Durand, A.; Cuche, A.; Genet, C.; Ebbesen, T. W. Force and torque on an electric dipole by spinning light fields. *Phys. Rev. A* **2013**, *88*, 033831.
(29) Stenholm, S. The semiclassical theory of laser cooling. *Rev. Mod. Phys.* **1986**, *58*, 699−739.
(30) Chaumet, P. C.; Nieto-Vesperinas, M. Time-averaged total force on a dipolar sphere in an electromagnetic field. *Opt. Lett.* **2000**, *25*, 1065−1067.
(31) Ashkin, A. Optical trapping and manipulation of neutral particles using lasers. *Proc. Natl. Acad. Sci. U. S. A.* **1997**, *94*, 4853−4860.
(32) Fulton, R.; Bishop, A. I.; Shneider, M. N.; Barker, P. F. Controlling the motion of cold molecules with deep periodic optical potentials. *Nat. Phys.* **2006**, *2*, 465−468.
(33) Hornberger, K.; Gerlich, S.; Haslinger, P.; Nimmrichter, S.; Arndt, M. Colloquium: Quantum interference of clusters and molecules. *Rev. Mod. Phys.* **2012**, *84*, 157−173.
(34) Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics: An Introduction to Radiation−Molecule Interactions*; Dover, Inc., 1998.
(35) Berova, N.; Nakanishi, K.; Woody, R. W. *Circular Dichroism: Principles and Applications*; John Wiley & Sons, 2000.
(36) Cohen-Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. *Atom−Photon Interactions: Basic Processes and Applications*; Wiley-VCH, 2010.
(37) Berry, M. V. Optical currents. *J. Opt. A: Pure Appl. Opt.* **2009**, *11*, 094001.
(38) Ruffner, D. B.; Grier, D. G. Comment on "Scattering Forces from the Curl of the Spin Angular Momentum of a Light Field. *Phys. Rev. Lett.* **2013**, *111*, 059301.
(39) Bialynicki-Birula, I.; Bialynicka-Birula, Z. Canonical separation of angular momentum of light into its orbital and spin parts. *J. Opt.* **2011**, *13*, 064014.
(40) Albaladejo, S.; Marqués, M. I.; Laroche, M.; Sáenz, J. J. Scattering Forces from the Curl of the Spin Angular Momentum of a Light Field. *Phys. Rev. Lett.* **2009**, *102*, 113602.
(41) Nieto-Vesperinas, M.; Sáenz, J. J.; Gómez-Medina, R.; Chantada, L. Optical forces on small magnetodielectric particles. *Opt. Express* **2010**, *18*, 11428−11443.
(42) Marqués, M. I.; Saénz, J. J. Scattering forces and electromagnetic momentum density in crossed circularly polarized standing waves. *Opt. Lett.* **2012**, *37*, 2787−2789.
(43) Leader, E. The photon angular momentum controversy: Resolution of a conflict between laser optics and particle physics. *Phys. Lett. B* **2016**, *756*, 303−308.
(44) Aiello, A.; Berry, M. V. Note on the helicity decomposition of spin and orbital optical currents. *J. Opt.* **2015**, *17*, 062001.
(45) Barron, L. D. *Molecular Light Scattering and Optical Activity*, 2nd ed.; Cambridge University Press, 2004.
(46) Canaguier-Durand, A.; Hutchison, J. A.; Genet, C.; Ebbesen, T. W. Mechanical separation of chiral dipoles by chiral light. *New J. Phys.* **2013**, *15*, 123037.
(47) Cameron, R. P.; Barnett, S. M.; Yao, A. M. Discriminatory optical force for chiral molecules. *New J. Phys.* **2014**, *16*, 013020.
(48) Lipkin, D. M. Existence of a New Conservation Law in Electromagnetic Theory. *J. Math. Phys.* **1964**, *5*, 696−700.
(49) Tang, Y.; Cohen, A. E. Optical Chirality and Its Interaction with Matter. *Phys. Rev. Lett.* **2010**, *104*, 163901.
(50) Bliokh, K. Y.; Nori, F. Characterizing optical chirality. *Phys. Rev. A* **2011**, *83*, 021803.
(51) Cameron, R. P.; Barnett, S. M.; Yao, A. M. Optical helicity, optical spin and related quantities in electromagnetic theory. *New J. Phys.* **2012**, *14*, 053050.
(52) Coles, M. M.; Andrews, D. L. Chirality and angular momentum in optical radiation. *Phys. Rev. A* **2012**, *85*, 063810.
(53) Yoo, S.; Park, Q.-H. Chiral Light-Matter Interaction in Optical Resonators. *Phys. Rev. Lett.* **2015**, *114*, 203003.
(54) Hendry, E.; Carpy, T.; Johnston, J.; Popland, M.; Mikhaylovskiy, R.; Lapthorn, A.; Kelly, S.; Barron, L.; Gadegaard, N.; Kadodwala, M. Ultrasensitive detection and characterization of biomolecules using superchiral fields. *Nat. Nanotechnol.* **2010**, *5*, 783−787.
(55) Tang, Y.; Cohen, A. E. Enhanced Enantioselectivity in Excitation of Chiral Molecules by Superchiral Light. *Science* **2011**, *332*, 333−336.
(56) Choi, J. S.; Cho, M. Limitations of a superchiral field. *Phys. Rev. A* **2012**, *86*, 063834.
(57) Wang, S.; Chan, C. Lateral optical force on chiral particles near a surface. *Nat. Commun.* **2014**, *5*, 1−8.
(58) Schnoering, G.; Poulikakos, L. V.; Rosales-Cabara, Y.; Canaguier-Durand, A.; Norris, D. J.; Genet, C. Three-Dimensional Enantiomeric Recognition of Optically Trapped Single Chiral Nanoparticles. *Phys. Rev. Lett.* **2018**, *121*, 023902.
(59) Comby, A.; Bloch, E.; Bond, C.; Descamps, D.; Miles, J.; Petit, S.; Rozen, S.; Greenwood, J.; Blanchet, V.; Mairesse, Y. Real-time determination of enantiomeric and isomeric content using photoelectron elliptical dichroism. *Nat. Commun.* **2018**, *9*, 1−14.
(60) Barnett, S. M.; Cameron, R. P.; Yao, A. M. Duplex symmetry and its relation to the conservation of optical helicity. *Phys. Rev. A* **2012**, *86*, 013845.
(61) Cameron, R. P.; Barnett, S. M.; Yao, A. M. Optical helicity of interfering waves. *J. Mod. Opt.* **2014**, *61*, 25−31.
(62) Poulikakos, L. V.; Gutsche, P.; McPeak, K. M.; Burger, S.; Niegemann, J.; Hafner, C.; Norris, D. J. Optical chirality flux as a useful far-field probe of chiral near fields. *ACS Photonics* **2016**, *3*, 1619−1625.
(63) Nienhuis, G. Conservation laws and symmetry transformations of the electromagnetic field with sources. *Phys. Rev. A* **2016**, *93*, 023840.
(64) Crimin, F.; Mackinnon, N.; Götte, J. B.; Barnett, S. M. On the conservation of helicity in a chiral medium. *Journal of Optics* **2019**, *21*, 094003.
(65) Poulikakos, L. V.; Dionne, J. A.; García-Etxarri, A. Optical helicity and optical chirality in free space and in the presence of matter. *Symmetry* **2019**, *11*, 1113.
(66) Vinegrad, E.; Vestler, D.; Ben-Moshe, A.; Barnea, A. R.; Markovich, G.; Cheshnovsky, O. Circular dichroism of single particles. *ACS Photon* **2018**, *5*, 2151−2159.
(67) Spaeth, P.; Adhikari, S.; Le, L.; Jollans, T.; Pud, S.; Albrecht, W.; Bauer, T.; Caldarola, M.; Kuipers, L.; Orrit, M. Circular dichroism measurement of single metal nanoparticles using photothermal imaging. *Nano Lett.* **2019**, *19*, 8934−8940.
(68) Sachs, J.; Günther, J.-P.; Mark, A. G.; Fischer, P. Chiroptical spectroscopy of a freely diffusing single nanoparticle. *Nat. Commun.* **2020**, *11*, 1−7.
(69) Oki, O.; Kulkarni, C.; Yamagishi, H.; Meskers, S. C. J.; Lin, Z.-H.; Huang, J.-S.; Meijer, E. W.; Yamamoto, Y. Robust Angular Anisotropy of Circularly Polarized Luminescence from a Single Twisted-Bipolar Polymeric Microsphere. *J. Am. Chem. Soc.* **2021**, *143*, 8772−8779.
(70) Bohren, C. F. Light scattering by an optically active sphere. *Chem. Phys. Lett.* **1974**, *29*, 458−462.
(71) Fernandez-Corbaton, I.; Rockstuhl, C. Unified theory to describe and engineer conservation laws in light-matter interactions. *Phys. Rev. A* **2017**, *95*, 053829.

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

(72) Bekshaev, A. Y. Subwavelength particles in an inhomogeneous light field: optical forces associated with the spin and orbital energy flows. *J. Opt.* **2013**, *15*, 044004.
(73) Bliokh, K. Y.; Bekshaev, A. Y.; Nori, F. Extraordinary momentum and spin in evanescent waves. *Nat. Commun.* **2014**, *5*, 1−8.
(74) Nieto-Vesperinas, M. Optical torque on small bi-isotropic particles. *Opt. Lett.* **2015**, *40*, 3021−3024.
(75) Wu, Z.-S.; Shang, Q.-C.; Li, Z.-J. Calculation of electromagnetic scattering by a large chiral sphere. *Appl. Opt.* **2012**, *51*, 6661−6668.
(76) Canaguier-Durand, A.; Genet, C. Chiral route to pulling optical forces and left-handed optical torques. *Phys. Rev. A* **2015**, *92*, 043823.
(77) Patti, F.; Saija, R.; Denti, P.; Pellegrini, G.; Biagioni, P.; Iatì, M. A.; Maragò, O. M. Chiral optical tweezers for optically active particles in the T-matrix formalism. *Sci. Rep.* **2019**, *9*, 1−10.
(78) Ali, R.; Pinheiro, F. A.; Dutra, R. S.; Rosa, F. S. S.; Maia Neto, P. A. Probing the optical chiral response of single nanoparticles with optical tweezers. *J. Opt. Soc. Am. B* **2020**, *37*, 2796−2803.
(79) Canaguier-Durand, A.; Genet, C. Plasmonic lateral forces on chiral spheres. *J. Opt.* **2016**, *18*, 015007.
(80) Tkachenko, G.; Brasselet, E. Optofluidic sorting of material chirality by chiral light. *Nat. Commun.* **2014**, *5*, 1−7.
(81) Rukhlenko, I. D.; Tepliakov, N. V.; Baimuratov, A. S.; Andronaki, S. A.; Gun'ko, Y. K.; Baranov, A. V.; Fedorov, A. V. Completely chiral optical force for enantioseparation. *Sci. Rep.* **2016**, *6*, 1−8.
(82) Zhao, Y.; Saleh, A. A.; Van De Haar, M. A.; Baum, B.; Briggs, J. A.; Lay, A.; Reyes-Becerra, O. A.; Dionne, J. A. Nanoscopic control and quantification of enantioselective optical forces. *Nat. Nanotechnol.* **2017**, *12*, 1055−1059.
(83) Liu, L.; Kheifets, S.; Ginis, V.; Capasso, F. Subfemtonewton Force Spectroscopy at the Thermal Limit in Liquids. *Phys. Rev. Lett.* **2016**, *116*, 228001.
(84) Li, M.; Sentissi, O.; Azzini, S.; Schnoering, G.; Canaguier-Durand, A.; Genet, C. Subfemtonewton force fields measured with ergodic Brownian ensembles. *Phys. Rev. A* **2019**, *100*, 063816.
(85) Ali, R.; Pinheiro, F. A.; Dutra, R. S.; Rosa, F. S. S.; Maia Neto, P. A. Enantioselective manipulation of single chiral nanoparticles using optical tweezers. *Nanoscale* **2020**, *12*, 5031−5037.
(86) Bliokh, K. Y.; Kivshar, Y. S.; Nori, F. Magnetoelectric Effects in Local Light-Matter Interactions. *Phys. Rev. Lett.* **2014**, *113*, 033601.
(87) Friese, M. E. J.; Enger, J.; Rubinsztein-Dunlop, H.; Heckenberg, N. R. Optical angular-momentum transfer to trapped absorbing particles. *Phys. Rev. A* **1996**, *54*, 1593−1596.
(88) O'Neil, A. T.; MacVicar, I.; Allen, L.; Padgett, M. J. Intrinsic and Extrinsic Nature of the Orbital Angular Momentum of a Light Beam. *Phys. Rev. Lett.* **2002**, *88*, 053601.
(89) Garcés-Chávez, V.; Volke-Sepulveda, K.; Chávez-Cerda, S.; Sibbett, W.; Dholakia, K. Transfer of orbital angular momentum to an optically trapped low-index particle. *Phys. Rev. A* **2002**, *66*, 063402.
(90) Lehmuskero, A.; Ogier, R.; Gschneidtner, T.; Johansson, P.; Käll, M. Ultrafast spinning of gold nanoparticles in water using circularly polarized light. *Nano Lett.* **2013**, *13*, 3129−3134.
(91) Higurashi, E.; Ohguchi, O.; Tamamura, T.; Ukita, H.; Sawada, R. Optically induced rotation of dissymmetrically shaped fluorinated polyimide micro-objects in optical traps. *J. Appl. Phys.* **1997**, *82*, 2773−2779.
(92) Friese, M. E.; Nieminen, T. A.; Heckenberg, N. R.; Rubinsztein-Dunlop, H. Optical alignment and spinning of laser-trapped microscopic particles. *Nature* **1998**, *394*, 348−350.
(93) Beth, R. A. Mechanical Detection and Measurement of the Angular Momentum of Light. *Phys. Rev.* **1936**, *50*, 115−125.
(94) Ding, K.; Ng, J.; Zhou, L.; Chan, C. T. Realization of optical pulling forces using chirality. *Phys. Rev. A* **2014**, *89*, 063825.
(95) Ali, R.; Dutra, R. S.; Pinheiro, F. A.; Maia Neto, P. A. Enantioselection and chiral sorting of single microspheres using optical pulling forces. *Opt. Lett.* **2021**, *46*, 1640−1643.
(96) Chen, J.; Ng, J.; Lin, Z.; Chan, C. Optical pulling force. *Nat. Photonics* **2011**, *5*, 531−534.
(97) Saenz, J. J. Laser tractor beams. *Nat. Photonics* **2011**, *5*, 514−515.
(98) Sukhov, S.; Dogariu, A. Negative Nonconservative Forces: Optical "Tractor Beams" for Arbitrary Objects. *Phys. Rev. Lett.* **2011**, *107*, 203602.
(99) Hakobyan, D.; Brasselet, E. Left-handed optical radiation torque. *Nat. Photonics* **2014**, *8*, 610−614.
(100) Magallanes, H.; Brasselet, E. Macroscopic direct observation of optical spin-dependent lateral forces and left-handed torques. *Nat. Photonics* **2018**, *12*, 461−464.
(101) Diniz, K.; Dutra, R. S.; Pires, L. B.; Viana, N. B.; Nussenzveig, H. M.; Maia Neto, P. A. Negative optical torque on a microsphere in optical tweezers. *Opt. Express* **2019**, *27*, 5905−5917.
(102) Li, H.; Cao, Y.; Shi, B.; Zhu, T.; Geng, Y.; Feng, R.; Wang, L.; Sun, F.; Shi, Y.; Miri, M. A.; Nieto-Vesperinas, M.; Qiu, C.-W.; Ding, W. Momentum-Topology-Induced Optical Pulling Force. *Phys. Rev. Lett.* **2020**, *124*, 143901.
(103) Saleh, A. A. E.; Dionne, J. A. Toward Efficient Optical Trapping of Sub-10-nm Particles with Coaxial Plasmonic Apertures. *Nano Lett.* **2012**, *12*, 5581−5586.
(104) Hayat, A.; Mueller, J. P. B.; Capasso, F. Lateral chirality-sorting optical forces. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 13190−13194.
(105) Yan, W.; Xu, L.; Xu, C.; Ma, W.; Kuang, H.; Wang, L.; Kotov, N. A. Self-Assembly of Chiral Nanoparticle Pyramids with Strong R/S Optical Activity. *J. Am. Chem. Soc.* **2012**, *134*, 15114−15121.
(106) Ma, W.; Kuang, H.; Wang, L.; Xu, L.; Chang, W.-S.; Zhang, H.; Sun, M.; Zhu, Y.; Zhao, Y.; Liu, L.; et al. Chiral plasmonics of self-assembled nanorod dimers. *Sci. Rep.* **2013**, *3*, 1−6.
(107) McPeak, K. M.; van Engers, C. D.; Blome, M.; Park, J. H.; Burger, S.; Gosálvez, M. A.; Faridi, A.; Ries, Y. R.; Sahu, A.; Norris, D. J. Complex Chiral Colloids and Surfaces via High-Index Off-Cut Silicon. *Nano Lett.* **2014**, *14*, 2934−2940.
(108) Shen, X.; Zhan, P.; Kuzyk, A.; Liu, Q.; Asenjo-Garcia, A.; Zhang, H.; García de Abajo, F. J.; Govorov, A.; Ding, B.; Liu, N. 3D plasmonic chiral colloids. *Nanoscale* **2014**, *6*, 2077−2081.
(109) McPeak, K. M.; van Engers, C. D.; Bianchi, S.; Rossinelli, A.; Poulikakos, L. V.; Bernard, L.; Herrmann, S.; Kim, D. K.; Burger, S.; Blome, M.; Jayanti, S. V.; Norris, D. J. Ultraviolet Plasmonic Chirality from Colloidal Aluminum Nanoparticles Exhibiting Charge-Selective Protein Detection. *Adv. Mater.* **2015**, *27*, 6244−6250.
(110) González-Rubio, G.; Mosquera, J.; Kumar, V.; Pedrazo-Tardajos, A.; Llombart, P.; Solís, D. M.; Lobato, I.; Noya, E. G.; Guerrero-Martínez, A.; Taboada, J. M.; Obelleiro, F.; MacDowell, L. G.; Bals, S.; Liz-Marzán, L. M. Micelle-directed chiral seeded growth on anisotropic gold nanocrystals. *Science* **2020**, *368*, 1472−1477.
(111) Dogariu, A.; Sukhov, S.; Sáenz, J. Optically induced 'negative forces. *Nat. Photonics* **2013**, *7*, 24−27.
(112) Kamandi, M.; Albooyeh, M.; Veysi, M.; Rajaei, M.; Zeng, J.; Wickramasinghe, H. K.; Capolino, F. Unscrambling Structured Chirality with Structured Light at the Nanoscale Using Photoinduced Force. *ACS Photon* **2018**, *5*, 4360−4370.
(113) Ayuso, D.; Ordonez, A. F.; Decleva, P.; Ivanov, M.; Smirnova, O. Enantio-sensitive unidirectional light bending. *Nat. Commun.* **2021**, *12*, 1−9.
(114) Lindell, I.; Sihvola, A.; Tretyakov, S.; Viitanen, A. J. *Electromagnetic Waves in Chiral and Bi-Isotropic Media*; Artech House, 1994.
(115) Marichez, V.; Tassoni, A.; Cameron, R. P.; Barnett, S. M.; Eichhorn, R.; Genet, C.; Hermans, T. M. Mechanical chiral resolution. *Soft Mat* **2019**, *15*, 4593−4608.
(116) Barron, L. D. True and false chirality and absolute enantioselection. *Rend. Fis. Acc. Lincei* **2013**, *24*, 179−189.
(117) Hernández, R. J.; Sevilla, F. J.; Mazzulla, A.; Pagliusi, P.; Pellizzi, N.; Cipparrone, G. Collective motion of chiral Brownian particles controlled by a circularly-polarized laser beam. *Soft Matter* **2020**, *16*, 7704−7714.
(118) Cameron, R. P.; Yao, A. M.; Barnett, S. M. Diffraction Gratings for Chiral Molecules and Their Applications. *J. Phys. Chem. A* **2014**, *118*, 3472−3478.
(119) Bradshaw, D. S.; Andrews, D. L. Chiral discrimination in optical trapping and manipulation. *New J. Phys.* **2014**, *16*, 103021.

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX

(120) Bradshaw, D. S.; Andrews, D. L. Laser optical separation of chiral molecules. *Opt. Lett.* **2015**, *40*, 677−680.
(121) Bradshaw, D. S.; Coles, M. M.; Andrews, D. L. Challenges concerning the discriminatory optical force for chiral molecules. *arXiv e-prints arXiv:1507.04231* **2015**, na.
(122) Cameron, R. P.; Barnett, S. M.; Yao, A. M. Response to recent works on the discriminatory optical force for chiral molecules. *arXiv e-prints arXiv:1506.07423* **2015**, na.
(123) Tkachenko, G.; Brasselet, E. Helicity-dependent three-dimensional optical trapping of chiral microparticles. *Nat. Commun.* **2014**, *5*, 1−8.
(124) Kamandi, M.; Albooyeh, M.; Guclu, C.; Veysi, M.; Zeng, J.; Wickramasinghe, K.; Capolino, F. Enantiospecific Detection of Chiral Nanosamples Using Photoinduced Force. *Phys. Rev. Applied* **2017**, *8*, 064010.
(125) Champi, H. A. A.; Bustamante, R. H.; Salcedo, W. J. Optical enantioseparation of chiral molecules using asymmetric plasmonic nanoapertures. *Opt. Mater. Express* **2019**, *9*, 1763−1775.
(126) Solomon, M. L.; Saleh, A. A. E.; Poulikakos, L. V.; Abendroth, J. M.; Tadesse, L. F.; Dionne, J. A. Nanophotonic Platforms for Chiral Sensing and Separation. *Acc. Chem. Res.* **2020**, *53*, 588−598.
(127) Bliokh, K. Y.; Nori, F. Transverse and longitudinal angular momenta of light. *Phys. Rep.* **2015**, *592*, 1−38. Transverse and longitudinal angular momenta of light.
(128) Bliokh, K. Y.; Rodríguez-Fortuño, F. J.; Nori, F.; Zayats, A. V. Spin−orbit interactions of light. *Nat. Photonics* **2015**, *9*, 796−808.
(129) Alizadeh, M. H.; Reinhard, B. M. Transverse Chiral Optical Forces by Chiral Surface Plasmon Polaritons. *ACS Photonics* **2015**, *2*, 1780−1788.
(130) Abujetas, D. R.; Marqués, M. I.; Sánchez-Gil, J. A. Modulated flipping torque, spin-induced radiation pressure, and chiral sorting exerted by guided light. *Opt. Express* **2021**, *29*, 16969−16979.
(131) Zhu, T.; Shi, Y.; Ding, W.; Tsai, D. P.; Cao, T.; Liu, A. Q.; Nieto-Vesperinas, M.; Sáenz, J. J.; Wu, P. C.; Qiu, C.-W. Extraordinary Multipole Modes and Ultra-Enhanced Optical Lateral Force by Chirality. *Phys. Rev. Lett.* **2020**, *125*, 043901.
(132) Shi, Y.; Zhu, T.; Zhang, T.; Mazzulla, A.; Tsai, D. P.; Ding, W.; Liu, A. Q.; Cipparrone, G.; Sáenz, J. J.; Qiu, C.-W. Chirality-assisted lateral momentum transfer for bidirectional enantioselective separation. *Light Sci. Appl.* **2020**, *9*, 1−12.
(133) Mislow, K.; Bickart, P. An Epistemological Note on Chirality. *Isr. J. Chem.* **1976**, *15*, 1−6.
(134) Sekimoto, K. *Stochastic Energetics*; Springer, 2010; Vol. *799*.
(135) Schnoering, G.; Albert, S.; Canaguier-Durand, A.; Genet, C. Chiral thermodynamics in tailored chiral optical environments. *Phys. Rev. X* **2021**, *11*, 041022.
(136) Kagan, H.; Moradpour, A.; Nicoud, J. F.; Balavoine, G.; Martin, R.; Cosyn, J. Photochemistry with circularly polarised light. II) Asymmetric synthesis of octa and nonahelicene. *Tetrahedron Lett.* **1971**, *12*, 2479−2482.
(137) Lesot, P.; Aroulanda, C.; Berdagué, P.; Meddour, A.; Merlet, D.; Farjon, J.; Giraud, N.; Lafon, O. Multinuclear NMR in polypeptide liquid crystals: Three fertile decades of methodological developments and analytical challenges. *Prog. Nucl. Magn. Reson. Spectrosc.* **2020**, *116*, 85−154.
(138) Pasteur, L. Recherches sur la dissymétrie moléculaire des produits organiques naturels. *Leçons professées à la Société Chimique de Paris le 20 janvier et le 3 février, in Oeuvres de Pasteur, Tome I, réunies par Pasteur Vallery-Radot* **1860**, 314−344.
(139) Arndt, M.; Nairz, O.; Vos-Andreae, J.; Keller, C.; Van der Zouw, G.; Zeilinger, A. Wave−particle duality of C 60 molecules. *Nature* **1999**, *401*, 680−682.
(140) Fein, Y. Y.; Geyer, P.; Zwick, P.; Kiałka, F.; Pedalino, S.; Mayor, M.; Gerlich, S.; Arndt, M. Quantum superposition of molecules beyond 25 kDa. *Nat. Phys.* **2019**, *15*, 1242−1245.
(141) Cameron, R. P.; Götte, J. B.; Barnett, S. M.; Cotter, J. P. Matter-wave grating distinguishing conservative and dissipative interactions. *Phys. Rev. A* **2016**, *94*, 013604.
(142) Cameron, R. P.; Götte, J. B.; Barnett, S. M. Chiral rotational spectroscopy. *Phys. Rev. A* **2016**, *94*, 032505.
(143) Stickler, B. A.; Diekmann, M.; Berger, R.; Wang, D. Enantiomer superpositions from matter-wave interference of chiral molecules. *Phys. Rev. X* **2021**, *11*, 031056.
(144) Suzuki, F.; Momose, T.; Buhmann, S. Y. Stern-Gerlach separator of chiral enantiomers based on the Casimir-Polder potential. *Phys. Rev. A* **2019**, *99*, 012513.
(145) Le Kien, F.; Hejazi, S. S. S.; Truong, V. G.; Nic Chormaic, S.; Busch, T. Chiral force of guided light on an atom. *Phys. Rev. A* **2018**, *97*, 063849.
(146) Le Kien, F.; Rauschenbeutel, A. Anisotropy in scattering of light from an atom into the guided modes of a nanofiber. *Phys. Rev. A* **2014**, *90*, 023805.
(147) Lodahl, P.; Mahmoodian, S.; Stobbe, S.; Rauschenbeutel, A.; Schneeweiss, P.; Volz, J.; Pichler, H.; Zoller, P. Chiral quantum optics. *Nature* **2017**, *541*, 473−480.
(148) Kien, F. L.; Kornovan, D. F.; Hejazi, S. S. S.; Truong, V. G.; Petrov, M. I.; Chormaic, S. N.; Busch, T. Force of light on a two-level atom near an ultrathin optical fiber. *New J. Phys.* **2018**, *20*, 093031.
(149) Stourm, E.; Lepers, M.; Robert, J.; Nic Chormaic, S.; Mølmer, K.; Brion, E. Spontaneous emission and energy shifts of a Rydberg rubidium atom close to an optical nanofiber. *Phys. Rev. A* **2020**, *101*, 052508.
(150) Buhmann, S. Y.; Giesen, S. M.; Diekmann, M.; Berger, R.; Aull, S.; Zahariev, P.; Debatin, M.; Singer, K. Quantum sensing protocol for motionally chiral Rydberg atoms. *New J. Phys.* **2021**, *23*, 083040.
(151) Barcellona, P.; Safari, H.; Salam, A.; Buhmann, S. Y. Enhanced Chiral Discriminatory van der Waals Interactions Mediated by Chiral Surfaces. *Phys. Rev. Lett.* **2017**, *118*, 193401.
(152) Safari, H.; Barcellona, P.; Buhmann, S. Y.; Salam, A. Medium-assisted van der Waals dispersion interactions involving chiral molecules. *New J. Phys.* **2020**, *22*, 053049.
(153) Craig, D. P.; Power, E. A.; Thirunamachandran, T. The interaction of optically active molecules. *Proc. R. Soc. A: Math. Phys. Sci.* **1970**, *6*, 211−214.
(154) Zhao, R.; Zhou, J.; Koschny, T.; Economou, E. N.; Soukoulis, C. M. Repulsive Casimir Force in Chiral Metamaterials. *Phys. Rev. Lett.* **2009**, *103*, 103602.
(155) Silveirinha, M. G.; Maslovski, S. I. Comment on "Repulsive Casimir Force in Chiral Metamaterials. *Phys. Rev. Lett.* **2010**, *105*, 189301.
(156) Jiang, Q.-D.; Wilczek, F. Chiral Casimir forces: Repulsive, enhanced, tunable. *Phys. Rev. B* **2019**, *99*, 125403.
(157) Milling, A.; Mulvaney, P.; Larson, I. Direct Measurement of Repulsive van der Waals Interactions Using an Atomic Force Microscope. *J. Colloid Interface Sci.* **1996**, *180*, 460−465.
(158) Munday, J. N.; Capasso, F.; Parsegian, V. A. Measured long-range repulsive Casimir−Lifshitz forces. *Nature* **2009**, *457*, 170−173.
(159) Liu, X.; Zhang, Z. M. Tunable Stable Levitation Based on Casimir Interaction between Nanostructures. *Phys. Rev. Applied* **2016**, *5*, 034004.
(160) Zhao, R.; Li, L.; Yang, S.; Bao, W.; Xia, Y.; Ashby, P.; Wang, Y.; Zhang, X. Stable Casimir equilibria and quantum trapping. *Science* **2019**, *364*, 984−987.
(161) Esteso, V.; Carretero-Palacios, S.; Míguez, H. Casimir−Lifshitz Force Based Optical Resonators. *J. Phys. Chem. Lett.* **2019**, *10*, 5856−5860.

https://doi.org/10.1021/acsphotonics.1c01130
ACS Photonics XXXX, XXX, XXX−XXX