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Toward Molecular Chiral Polaritons

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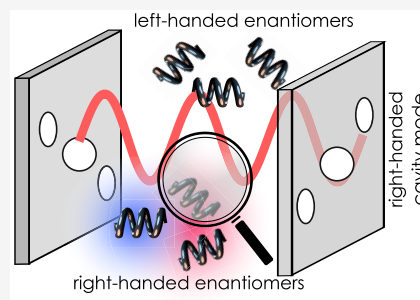
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ABSTRACT: Coupling between light and material excitations underlies a wide range of optical phenomena. Polaritons are eigenstates of a coupled system with a hybridized wave function. Owing to their hybrid composition, polaritons exhibit at the same time properties typical for photonic and electronic excitations, thus offering new ways for controlling electronic transport and even chemical kinetics. While most theoretical and experimental efforts have been focused on polaritons with electric-dipole coupling between light and matter, in chiral quantum emitters, electronic transitions are characterized by simultaneously nonzero electric and magnetic dipole moments. Thus, it is natural to wonder what kinds of novel effects chirality may enable in the realm of strong light–matter coupling. Right now, this field located at the intersection of nanophotonics, quantum optics, and chemistry is in its infancy. In this Perspective, we offer our view toward chiral polaritons. We review basic physical concepts underlying chirality of matter and electromagnetic field, discuss the main theoretical and experimental challenges that need to be solved, and consider novel effects that could be enabled by strong coupling between chiral light and matter.

KEYWORDS: strong coupling, polaritons, optical cavities, resonances, chirality, handedness, *ab initio* QED



1. INTRODUCTION

A system of a few interacting oscillators, either of classical or quantum nature, is a primitive mathematical model that describes the behavior of a wide spectrum of mechanical, thermodynamic, electromagnetic and other kinds of physical systems. Polaritons are eigenstates of the system when electromagnetic fields and matter couple strongly, i.e., when the coupling rate exceeds all the decay and decoherence rates in the system, and share a mixed light-matter characteristic.¹ In the optical domain, polaritonic states are often realized by means of coupling an optical cavity mode with excitonic or vibrational transitions in resonant media.^{2–4} Owing to this hybrid composition, polaritons show properties indicative of massless photonic and massive electronic/vibrational excitations simultaneously,⁵ thus offering new ways for controlling electronic transport and modifying chemical kinetics.^{6–12}

Most theoretical and experimental efforts in this field have been focused on coupling optical cavities with linearly- or circularly polarized electric dipole transitions of various quantum emitters (QEs). This is justified by the abundance of electronic and vibrational emitters whose interaction with light is dominated by the electric-dipole term of the Hamiltonian, while higher-order contributions, including the magnetic-dipole term, are often negligible. To put it another way, natural materials very weakly respond to magnetic fields oscillating with optical frequencies.^{13,14} Nevertheless, in certain specific cases, a non-negligible magnetic transition dipole moment can be of pivotal importance. Chiral media^{15,16} represent a practically relevant example.

A three-dimensional rigid body, which cannot be aligned with its mirror image by a series of rotations and translations, is referred to as chiral.¹⁷ Two mirrored versions of a chiral object are called left and right enantiomers, and usually qualitative differences between them are obvious. However, an attempt to define a unique quantitative measure of the geometric chirality easily leads to confusion: one can introduce different seemingly meaningful parameters which may vanish for different configurations and remain unrelated to the chiral physical phenomena.¹⁸ Much more fruitful is the practical approach, when one assesses the chirality of an object by its interactions with other chiral entities.

For example, acting on a chiral biological receptor, opposite enantiomers of the same molecule cause a different response, perceived as a different odor or taste.¹⁹ In pharmaceuticals, the opposite enantiomer of a drug molecule can be useless at best, but often it is insidiously toxic for the chiral human body.^{20,21} The majority of molecules involved in biological processes, such as neurotransmitters (norepinephrine, ephedrine, and others), are chiral. In this regard, there is a great demand from the pharmaceutical industry to develop effective methods of separating chiral enantiomers.

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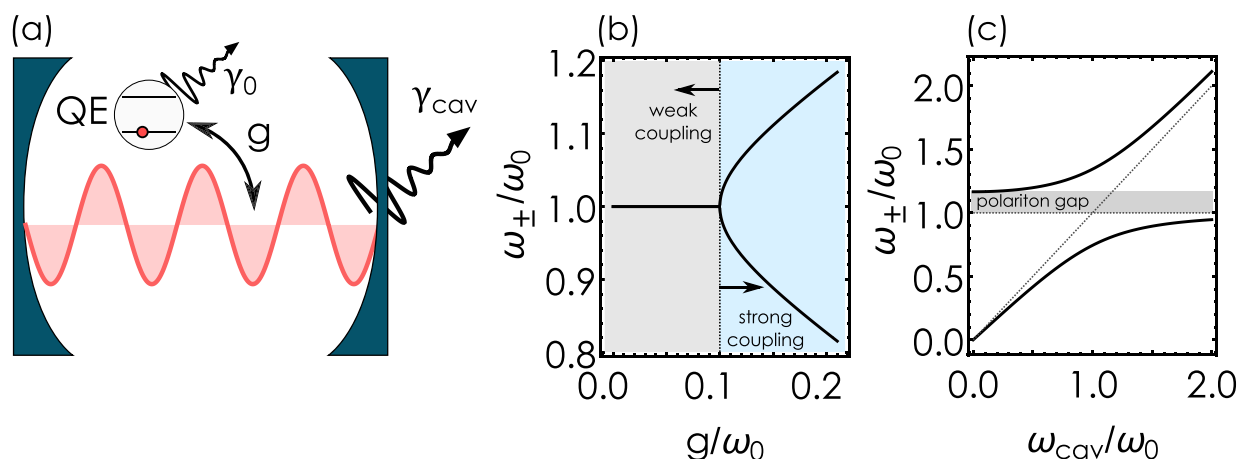


Figure 1. The basic picture of strong light–matter coupling. (a) Schematic illustration of an electronic transition of a two-level atom coupled to a single photonic mode of an optical cavity. (b) Eigenvalues of the coupled-mode Hamiltonian, eq 2, as a function of the coupling constant g for the zero-detuning case, $\omega_{\text{cav}} = \omega_0$. (c) The eigenvalues spectrum plotted as a function of the cavity frequency for a fixed coupling constant.

Chirality profoundly affects interactions of matter with electromagnetic radiation. As soon as a medium is composed of chiral constituents (such as molecules or meta-atoms), it acquires a magneto-electric response, which mixes \mathbf{E} and \mathbf{B} , and \mathbf{H} and \mathbf{D} , correspondingly.¹⁵ The study of the interaction between chiral light and matter has uncovered many fundamental effects, but, so far, has been limited to weak light–matter coupling, where the presence of the photonic field can be treated perturbatively. Some recent studies make an attempt to address the behavior of strongly coupled system where at least one of the constituents (either light or the material) is chiral.^{22–24} All this raises a question: which new phenomena should arise from the chirality of a QE, or of a cavity, or of both, when they become strongly coupled?

In this Perspective, we offer a conceptual view on the notion of chiral polaritonics. We review the essential physics underlying strong light–matter coupling, the chirality of matter and electromagnetic fields. We discuss the main theoretical and experimental challenges for chiral polaritonics and provide a perspective on its potential and future development. The interdisciplinary nature of the problem suggests that a joint effort of researches from classical electromagnetism, quantum optics, material science, and biology might be needed in order to establish chiral polaritonics as the versatile framework it promises to be.

2. STRONG LIGHT–MATTER COUPLING

Let us begin by briefly recounting theoretical apparatus describing the interaction of an optical emitter, such as an atom, a molecule, a lattice vibration, or an artificial harmonic meta-atom, with a single electromagnetic mode of an optical cavity. There are several frameworks to model such an interaction, and the choice of the particular model in each situation depends on the context. As long as anharmonic effects related to the saturability of two-level system(s) may be ignored, and as long as the coupling strength is not too high compared to resonant energies, the light–matter coupling can be conceptually modeled using the following coupled-mode Hamiltonian:^{2–4}

$$H = \begin{pmatrix} \omega_{\text{cav}} - i\gamma_{\text{cav}} & g \\ g^* & \omega_0 - i\gamma_0 \end{pmatrix} \quad (1)$$

where $\omega_0 - i\gamma_0$ and $\omega_{\text{cav}} - i\gamma_{\text{cav}}$ are the complex-valued eigenfrequencies characterizing the material and photonic oscillations, correspondingly,²⁵ and g is the coupling constant. For a single emitter coupled to a cavity, we have $g = g_0 = \mathcal{E}_{\text{vac}}\mu$, where \mathcal{E}_{vac} is the vacuum electric field of the cavity mode, and μ is the transition dipole moment of the emitter. If N identical emitters are coupled to the same cavity mode, the collective coupling constant reads $g = \sqrt{N}g_0$.⁴ The two eigenvalues of the Hamiltonian eq 1 read:

$$\omega_{\pm} = \frac{\omega_{\text{cav}} + \omega_0}{2} - i\frac{\gamma_{\text{cav}} + \gamma_0}{2} \pm \sqrt{|g|^2 + \frac{1}{4}(\omega_{\text{cav}} - \omega_0 - i(\gamma_{\text{cav}} - \gamma_0))^2} \quad (2)$$

Within this model of light–matter interaction, two different regimes may be realized.

Figure 1b shows the eigenvalues of Hamiltonian eq 1 as a function of the coupling constant g for the zero-detuning case, $\omega_{\text{cav}} = \omega_0$. Weak coupling regime occupies the left part of this diagram, where $g < |\gamma_{\text{cav}} - \gamma_0|/2$. In this regime the two eigenstates have equal real parts of their eigenenergies (although different imaginary parts). An excited QE undergoes exponential decay into the ground state at a rate γ , accompanied by spontaneous emission of a photon in the environment. The point $g = |\gamma_{\text{cav}} - \gamma_0|/2$ marks the transition to the strong coupling regime. Once the coupling constant exceeds the threshold value, the real parts of eigenenergies split into two branches separated by the so-called Rabi splitting. Correspondingly, wave functions of the two eigenstates become equal 50% mixes of photonic and material components, and are referred to as upper and lower polaritons. When plotted as a function of the cavity frequency for a fixed coupling constant, the energy spectrum displays the well-known picture of anticrossing between two polaritonic modes, Figure 1c.

When the coupling constant becomes comparable to the resonant energies of the system ($g > 0.1\omega$), the system enters the ultrastrong coupling (USC) regime in which all eigenstates become noticeably renormalized by the interaction.²⁶ At this point, the trivial coupled-mode Hamiltonian as well as the widely used rotating-wave approximation yield unphysical spectra and become inaccurate, thus the underlying theoretical foundation of QED has to be consulted. A simple and widely used model was derived by Hopfield.^{27,28} In coupled structures where the spatial coherence of the polariton is at the center, for

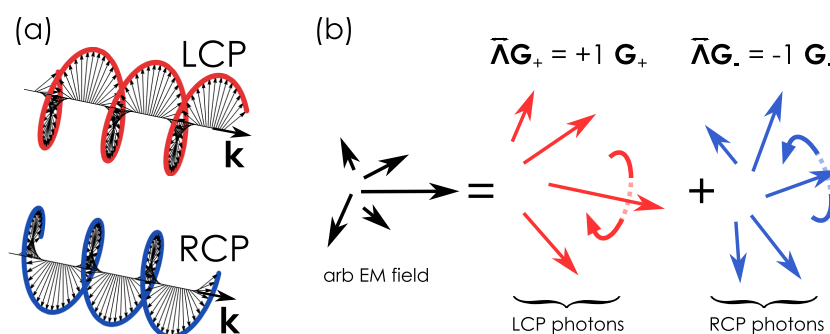


Figure 2. The basics of electromagnetic field chirality. (a) Illustration of the spatial structure of and RCP and LCP plane wave in free space. The arrows indicate spatial distribution of the instantaneous electric field vectors in space for a fixed time instance. (b) Schematic illustration of expansion of an arbitrary nonparaxial electromagnetic field into Riemann-Silberstein vectors. The red and blue arrows represent left-handed and right-handed components of the total field, which contain LCP (red) and RCP (blue) photons only, respectively, and become the eigenvectors of the helicity operator with eigenvalues ± 1 .

example, in systems exhibiting polariton condensation,^{5,29} other approaches might be used that capture the nonlocal and nonlinear properties of polaritons, such as the Gross–Pitaevskii equation.

The hybrid wave function of polaritons has far-reaching implications for the microscopic properties of the coupled system. In particular, the possibility of strong light–matter coupling to affect the rates of chemical reactions (ones involving the coupled material as a product or as a reactant) has been the subject of intense experimental^{6,7,9,11,30,31} and theoretical^{8,10,32–36} investigation in the past decade. Thus, it is natural to wonder whether bridging polaritons with chirality may break the symmetric yield of chiral products and enable other practically valuable effects.

3. FIELD AND MATTER CHIRALITY

3.1. Chirality of Light. In the following subsections we briefly overview the concepts of chiral light and chiral matter. Chirality of light is most easily approached through the notion of handedness. Left-handed (LCP) and a right-handed (RCP) circularly polarized plane waves represent primordial examples of chiral electromagnetic field, Figure 2a. LCP (RCP) wave in a transparent dielectric can be defined as a monochromatic plane wave with its magnetic field $\pi/2$ ahead (behind) the electric field everywhere in space:

$$Z\mathbf{H}_{\text{LCP}}(\mathbf{r}) = -i\mathbf{E}_{\text{LCP}}(\mathbf{r}), \quad Z\mathbf{H}_{\text{RCP}}(\mathbf{r}) = +i\mathbf{E}_{\text{RCP}}(\mathbf{r}) \quad (3)$$

where $Z = \sqrt{\mu\mu_0/\epsilon\epsilon_0}$ is the medium impedance. Considering an RCP (LCP) wave frozen in time yields a helix twisted clockwise (counterclockwise) in the propagation direction, Figure 3a. The handedness quality of a circularly polarized plane wave is preserved upon arbitrary rotation of the field in space, and also upon time reversal. However, this quality is flipped upon a mirror reflection, or an inversion. Thus, the handedness can be used as a basis for constructing a time-even pseudoscalar field.

To that end, consider the helicity operator $\vec{\Lambda} = \frac{1}{k} \begin{pmatrix} \nabla \times & 0 \\ 0 & \nabla \times \end{pmatrix}$ acting on the complex electric and magnetic field vectors $\Psi = (\mathbf{E}, Z\mathbf{H})^T$. One immediately realizes that LCP and RCP waves are eigenstates of this operator with eigenvalues $\lambda = +1$ and $\lambda = -1$, respectively.^{37,38} Correspondingly, any linear combination of LCP (RCP) plane waves is an eigenvector of $\vec{\Lambda}$. Calculating the local expected value of the helicity operator $\langle \Psi(\mathbf{r}) | \vec{\Lambda} | \Psi(\mathbf{r}) \rangle$

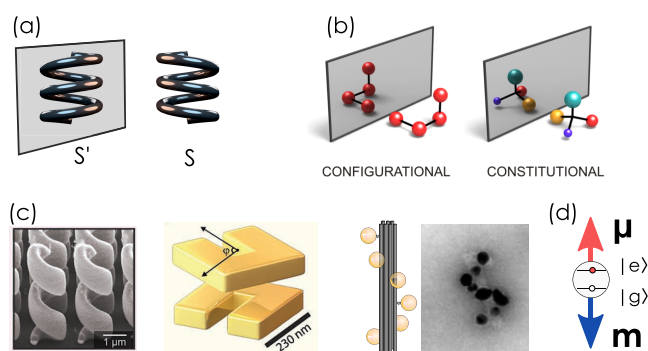


Figure 3. The basics of matter chirality. (a) Visual representation of a chiral object S and its mirrored enantiomer S' . The two objects are related by a mirror transformation and cannot be mapped into one another by a series of rotation and translations. (b) Configurational and constitutional chirality. Configurational chirality involves identical constituent elements arranged in a geometrically chiral shape. Constitutional chirality involves nonidentical elements arranged in an otherwise nonchiral shape. (c) Examples of chiral meta-atoms: metallic helices, twisted split-ring resonators, and DNA origami scaffolds. (d) Schematic illustration of a chiral source of electromagnetic field involving a pair of parallel electric and magnetic dipole transitions. Panel (b) was adapted with permission from ref 45. Copyright 2012 American Chemical Society. Parts of panel (c) were adapted with permission from refs 46 (Copyright 2009 RSC) and 47 (Copyright 2012 Nature).

and adjusting the prefactor, we obtain the chirality density, a local measure of handedness of a nonhomogeneous field:^{39,40}

$$C(\mathbf{r}, \omega) = \frac{\epsilon_0 \omega}{2} \text{Im}[\mathbf{E} \cdot \mathbf{B}^*] \quad (4)$$

This quantity characterizes the local geometry of light polarization, expressing the degree of “screwiness” of the electric and magnetic field lines.⁴¹ It can also be interpreted as the normalized difference between the number of left-handed and right-handed photons in a monochromatic field. On a side note, the presence of material dissipation strongly modifies the expression for chirality density.⁴²

To grasp how the chirality density is generally applicable to arbitrary monochromatic electromagnetic field distributions, one notices that a solution of Maxwell’s equations in a transparent medium can always be expanded into two components with well-defined handedness, called Riemann–Silberstein vectors:⁴³

$$\mathbf{G}_{\pm}(\mathbf{r}) = \frac{\mathbf{E}(\mathbf{r}) \pm iZ\mathbf{H}(\mathbf{r})}{\sqrt{2}} \quad (5)$$

Each of the two Riemann–Silberstein vectors is an eigenstate of the helicity operator, Figure 2b, meaning that it only contains fields of the corresponding handedness. According to our handedness convention, \mathbf{G}_+ (\mathbf{G}_-) represents the LH (RH) field component.

In the most general sense, a combination of electromagnetic fields is chiral if its mirror image cannot be aligned with itself by a series of rotations and translations. The local chirality density, eq 4, being perfect for characterizing plane waves, cannot exhaustively cover the structured light chirality. There are plenty of solutions of Maxwell's equations, such as chiral vortex beams, having $C = 0$ everywhere in space, yet being chiral.⁴⁴ It is unclear at the moment whether the chirality of spatial field distribution, also dubbed as Kelvin's chirality, can be quantified by an appropriate measure.

3.2. Chirality of Matter. Not only the electromagnetic field, but rigid geometrical bodies as well can be characterized with chirality. A geometrical body in three-dimensional space is said to be chiral if it cannot be superimposed upon its mirror image by rotations and translations, Figure 3a. Geometrical chirality has fundamental implications on the electromagnetic response of matter. Any medium composed of chiral microscopic elements, such as molecules or meta-atoms, acquires a magneto-electric response, wherein electric displacement \mathbf{D} becomes linked to \mathbf{H} , and magnetic induction \mathbf{B} becomes linked to \mathbf{E} . For a reciprocal bi-isotropic material, the constitutive relations take the following form:¹⁵

$$\begin{pmatrix} \mathbf{D} \\ \mathbf{B} \end{pmatrix} = \begin{pmatrix} \epsilon_0\epsilon(\omega) & + i\kappa(\omega)/c \\ -i\kappa(\omega)/c & \mu_0\mu(\omega) \end{pmatrix} \begin{pmatrix} \mathbf{E} \\ \mathbf{H} \end{pmatrix} \quad (6)$$

where ϵ and μ are the scalar relative permittivity and permeability, correspondingly, and $\kappa = \kappa' + i\kappa''$ is a complex dimensionless pseudoscalar Pasteur parameter of the coupling between the electric and magnetic fields. Generally, any of these quantities can be a tensor (pseudotensor), in which case the medium is called bianisotropic. In the case of a bi-isotropic medium with a pseudoscalar Pasteur parameter, its real part κ' introduces a difference in phase velocities of RCP and LCP plane waves, resulting in the optical rotation (OR) of linear polarization direction. The imaginary part κ'' gives rise to different absorption of RCP and LCP waves, which amounts to the circular dichroism (CD).

Prominent examples of naturally chiral compounds are different inorganic crystals such as quartz or cinnabar. Much more common is the chirality on the molecular scale of organic substances. Although the corresponding effects of bi-isotropy described by eq 6, as well as of a more sophisticated bianisotropy remain also typically weak, the valuable information encoded in OR and CD spectra motivates persistent improvement of the corresponding techniques of optical chirality diagnostics.⁴⁸

Profound chiral optical phenomena occur when the molecular chirality is given an opportunity to govern a bottom-up self-assembly of chiral superstructures. For a particular example, one can consider chiral nematic liquid crystals: cholesterics. Here the structural chirality of constituent organic molecules induces smooth twisting of the otherwise homogeneous nematic. Upon appropriate preparation and alignment, cholesterics form stable helical configurations with variable pitch.⁴⁹

Besides the variety of naturally occurring organic and inorganic substances, chirality can be engineered in nanostructures at the mesoscopic level.^{50–52} Truly fascinating prospects of boosting the chiral optics to its fundamental limits have opened with the advent of metamaterial concept, as the most sophisticated top-down nanotechnology approaches have been applied to produce designer meta-structures for versatile optical functionality.⁵³ Typically, their chirality stems from that of constituting elements: meta-atoms. The mirror symmetry of the latter can be broken in different ways. A meta-atom chirality may originate purely from the geometry of its construction, in which case, it is referred to as configurational chirality, Figure 3b. Alternatively, it may be determined by the mutual arrangement of specific different parts of an otherwise achiral structure, in which case it is referred to as constitutional chirality.

Examples of artificial chiral nanostructures include metallic helices,^{54,55} chiral arrangements of nonchiral meta-atoms,⁵⁶ and numerous bioinspired chiral plasmonic nanostructures build around DNA scaffolds,^{51,57,58} Figure 3d. It is truly remarkable how almost infinitesimally small biomolecules can impart chiral optical response to otherwise achiral plasmonic structures. The latter can amplify and effectively transfer subtle chiral fingerprints of biomolecules from the ultraviolet to the more convenient visible range.⁵⁹ Moreover, proteins can trigger the formation of chiral plasmonic complexes which then directly visualize the structural molecular chirality by the visible plasmonic CD.⁶⁰

Metasurfaces, periodic arrangements of chiral meta-atoms in planar arrays, have proven to perform extremely strong chiral light–matter interactions within the optical paths smaller and even much smaller than the wavelength.⁶¹ Moreover, the palette of available chiral optical phenomena greatly exceeds the capabilities of natural materials: a chiral metasurface is characterized by a set of scattering matrix elements $r_{\mu\nu}$ and $t_{\mu\nu}$ describing reflection and transmission of light from polarization state ν into polarization state μ . Depending on the metasurface design, some of these coefficients can vanish, while others become dominant. The metasurface point symmetry group plays the key role in the analysis of all such possibilities.

Chiral metasurfaces possessing a 3-fold or higher rotational symmetry around a vertical axis scatter normally incident light in a relatively simple fashion.^{62,63} The only relevant dichroic characteristic of such metasurfaces is the transmission CD, which describes the difference in transmittances of RCP and LCP waves:

$$\text{CD} = \frac{|t_{RR}|^2 - |t_{LL}|^2}{|t_{RR}|^2 + |t_{LL}|^2} \quad (7)$$

and OR, which describes the difference in phase delays. Qualitatively, such metasurfaces are similar to slabs of natural chiral Pasteur media.⁶⁴ The quantitative differences, however, are immense: the CD and OR delivered by metasurfaces can take any physically meaningful value including the extreme maxima and minima ($\text{CD} = \pm 1$ and $\text{OR} = \pm 90^\circ$) after the light travels only fractions of its wavelength.⁶⁵ Recent transition to all-dielectric platforms has enabled creating strongly chiral and transparent samples.^{66–68} Moreover, precisely engineering quasi-bound states in the continuum,⁶⁹ it is possible to realize the maximum chirality combining full transparency to waves of one circular polarization with full absorption of waves of the opposite circular polarization.⁷⁰

Merging chirality with broken rotational symmetry allows obtaining even more sophisticated polarization responses, which expand the multitude of chiral metasurface functionalities further.^{71–74} Carefully engineered arrays of silicon helices⁷⁵ or silicon bars of different height^{76,77} achieve lossless maximum chirality, when transparency to waves of one circular polarization is accompanied by a full reflection of the other.

CD, being an optical signature of geometric chirality, should not be confused with similar effects inherent to achiral objects. For example, metasurfaces having at most 2-fold rotational symmetry around a vertical axis can exhibit unequal RCP-to-LCP and LCP-to-RCP transmission described by the so-called circular conversion dichroism: $CCD = (|t_{RL}|^2 - |t_{LR}|^2) / (|t_{RL}|^2 + |t_{LR}|^2)$. Although the copolarized transmittances are bound to be equal for achiral structures, such metasurfaces may exhibit unequal total power transmission upon illumination with RCP and LCP waves: $|t_{RR}|^2 + |t_{LR}|^2 \neq |t_{LL}|^2 + |t_{RL}|^2$.⁷⁸ By adjusting the resonances of an achiral metasurface possessing an in-plane mirror symmetry, but lacking high-order ($n \geq 3$) rotational symmetries and out-of-plane mirror symmetries, one can design handedness-preserving chiral mirrors.^{79,80} Stacking such a mirror with its inverse produces a chiral cavity supporting modes of a particular handedness,⁸¹ which is a key building block of chiral polaritons.

One can also introduce the notion of a chiral source of electromagnetic field. A point chiral source is a combination of parallel electric $\boldsymbol{\mu}$ and magnetic \mathbf{m} point dipoles with a $\pm\pi/2$ phase difference, Figure 3d:

$$\mathbf{m} = -i\xi\boldsymbol{\mu} \quad (8)$$

where ξ is a real-valued parameter. $\xi = \pm 1$ defines an ideal LH (“+1”) and RH (“−1”) chiral source, respectively. When placed in vacuum, they emit only waves of the corresponding circular polarization in all directions.^{38,82} Contrary to one’s intuition, circularly polarized (also called spinning) electric dipoles do not represent chiral electromagnetic sources, as they (i) radiate circularly polarized waves of a particular handedness only in one direction, and (ii) possess mirror symmetry planes thus being achiral. A chiral source should necessarily involve both electric and magnetic dipole components, which directly follows from their different parity with respect to mirror reflections.⁸³ This simple argument rules out transition metal dichalcogenides with circularly polarized valley transitions,⁸⁴ as well as numerous magnetic media, including (anti)ferromagnetic materials supporting magnon-polaritons,⁸⁵ as potential platforms for chiral polaritons.

The notion of chiral sources naturally translates to quantum emitters (QEs). A chiral QE is one, whose transition between its ground and excited levels is quantified by a combination of collinear electric and magnetic dipole moments satisfying eq 8.⁸⁶ Under an external monochromatic field such a polarizable QE would exhibit unequal absorption and extinction cross sections associated with circular dichroism.⁴⁰ Chiral QEs are abundant in organic chemistry. Examples include numerous peptides,⁸⁷ proteins, α -helices,⁸⁸ and lanthanide complexes.⁸⁹ The data on transition dipole moments of chiral QEs is very sparse in the literature; Govorov et al. quote $|\boldsymbol{\mu}| \sim 10$ D and $|\mathbf{m}| \sim 0.04 \mu_B$ for chiral dye molecules,⁸⁸ where μ_B is Bohr’s magneton. Kubo et al. estimated $|\boldsymbol{\mu}| \sim 1$ D and $|\mathbf{m}| \sim 0.2 \mu_B$ for helicene molecules.⁹⁰ Overall, this places the matter chirality factor ξ at or below 10^{-3} for most organic molecules.⁹¹

In addition, the electric and magnetic transition dipole moments of realistic QEs are usually not aligned ideally as

required by eq 8, but possess a perpendicular component of the magnetic dipole moment $\mathbf{m} \perp \boldsymbol{\mu}$. This component can be associated with the so-called ω -type bianisotropic response of the medium.¹⁵

Knowledge of the transition dipole moments of a particular QE allows one to describe an ensemble of those in terms of macroscopic permittivity and Pasteur parameter, as in eq 6. Although often assumed nondispersive, the correct frequency dispersion of the Pasteur parameter (as well as its permittivity) will be crucial for the description of strong coupling between quantum emitters and electromagnetic field. As long as a single electronic transition of the QE is involved, the permittivity and the Pasteur parameter of a macroscopic ensemble of such EQs with volume density ρ can be described by the Lorentz model:⁹²

$$\varepsilon(\omega) = \varepsilon_\infty + f \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega}, \quad \kappa(\omega) = g \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (9)$$

where $\omega_p^2 = \rho e^2 / (3\varepsilon_0 m)$ is the plasma frequency of the transition (1/3 accounts for isotropic orientation of QEs), e and m are the electron mass and charge, respectively, $f = 2m\omega_0|\boldsymbol{\mu}|^2 / (e^2\hbar)$ and $g = 2m\omega_0\text{Im}[\boldsymbol{\mu} \cdot \mathbf{m}^*] / (e^2\hbar c)$ are the electric and magneto-electric oscillator strengths of the chiral transition, ω_0 and γ are the transition frequency and line width, respectively.

3.3. Relation to Spin and Orbital Angular Momentum of Light. In quantum electrodynamics, the fundamental role of chirality becomes clear already at the basic level of intrinsic symmetries of free space electromagnetic field.⁹³ For a particle with mass, such symmetry can be conveniently analyzed in its rest frame. As rest frames are generally nonexistent for photons, one has to consider the space transformations preserving the photon propagation direction. Circularly polarized plane waves are natural eigenstates of such coordinate transforms. The absence of the rest frame, on the other hand, does not allow for a proper introduction of a photon spin, which otherwise appears as an intrinsic angular momentum of a resting particle with mass. Considering photon parity with respect to the coordinate inversion, however, one recognizes the necessity to introduce a close analog of spin describing the intrinsic angular momentum of a photon—its spin angular momentum (SAM).

In terms of the classical electrodynamics, SAM of an electromagnetic field can be treated as a continuous field variable. From this standpoint, the SAM density is a vector quantity, which for a monochromatic electromagnetic field $\{\mathbf{E}(\mathbf{r}), \mathbf{H}(\mathbf{r})\}$ in free space reads as follows:⁹⁴

$$\mathbf{s} = \frac{1}{4\omega} \text{Im}[\varepsilon_0 \mathbf{E}^* \times \mathbf{E} + \mu_0 \mathbf{H}^* \times \mathbf{H}] \quad (10)$$

A trivial situation, wherein an electromagnetic field possesses SAM density, is presented by an RCP or LCP plane wave. In this case, the SAM density is parallel or antiparallel to the wave vector depending on the handedness of the wave.

Another far less obvious situation when an electromagnetic field features a SAM density is presented by evanescent plane waves. Consider a monochromatic transverse-magnetic evanescent wave propagating in free space along the x axis and attenuating exponentially in the z direction: $\mathbf{H} \propto \hat{\mathbf{y}} e^{ik_x x - \kappa_z z}$, $\mathbf{E} \propto (-i\kappa_z \hat{\mathbf{x}} + k_x \hat{\mathbf{z}}) e^{ik_x x - \kappa_z z}$, where the wave vector components satisfy $k_x^2 - \kappa_z^2 = (\omega/c)^2$. After simple algebra we find that such a wave also carries a nonzero SAM density component, which is perpendicular to the propagation and the attenuation direction:⁹⁴

$$\mathbf{s}_T \propto \text{Re} \mathbf{k} \times \text{Im} \mathbf{k} \quad (11)$$

This component of SAM arises due to the elliptical polarization of the electric field in the propagation plane, Figure 4a, and is known as the transverse spin angular momentum.^{94,95}

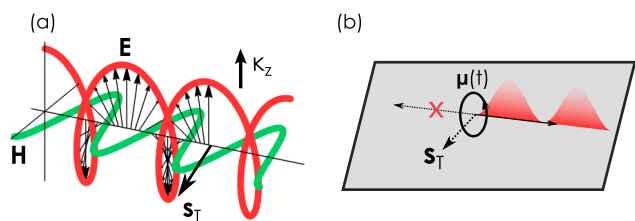


Figure 4. Relation between chirality and spin. (a) Illustration of the spatial distribution of the electric and magnetic fields in a TM-polarized evanescent wave propagating along the x axis and exponentially decaying along the z axis. Elliptical polarization of the electric field produces a transverse component of the spin angular momentum density \mathbf{s}_T perpendicular to the linear momentum of the wave. (b) Spin-momentum locking in evanescent waves. An elliptically polarized electric dipole source placed near a waveguiding surface features directional coupling to guided waves due to the spin-orbit coupling.

This property of evanescent fields leads to a fundamental connection between light's SAM density and linear momentum near planar surfaces and enables unidirectional excitation of waveguide modes in various nanophotonic platforms.^{95–97} Consider a TM-polarized bound mode supported by an interface (such as a surface wave propagating along a metallic surface, or a waveguide mode of a dielectric film). An electric

dipole with an appropriate circular or elliptical polarization placed near a waveguiding surface will produce an electromagnetic field that will couple preferentially to those guided modes, whose transverse SAM density matches that of the circular-polarized source, Figure 4b. An analogous spin-momentum locking arises for TE-polarized bound modes.⁹⁸

It is crucial to emphasize the similarities and the differences between the SAM density and the chirality of light. SAM density is a time-odd vector, while chirality density is a time-even pseudoscalar. The SAM density of a circularly polarized homogeneous wave is collinear with its momentum density. Correspondingly, time reversal leaves its handedness unchanged, but flips the SAM density. Contrary to that, in the case of a waveguide mode excited by a spinning dipole in the above examples, the evanescent field of these modes has purely transverse SAM density and zero chirality density.⁹⁹ Likewise, circularly polarized sources involved in these scenarios are also not chiral as they lack the magnetic dipole component.

A lot of excellent works dealing with this mechanism of unidirectional excitation have used terms “chiral coupling”, “chiral emission”, and alike (see, e.g., refs 97, 100–103), while the studied systems had little to do with the true chirality of light. Chirality involves chiral sources represented by a combination of collinear electric and magnetic dipoles, as opposed to circularly polarized electric dipole engaged in the effect of spin-orbit coupling.

Orbital angular momentum (OAM) is another characteristic of the electromagnetic field that should be put into the context of chirality. While local chirality density, eq 4, determines the response asymmetry in dipolar light-matter interactions,⁴⁰

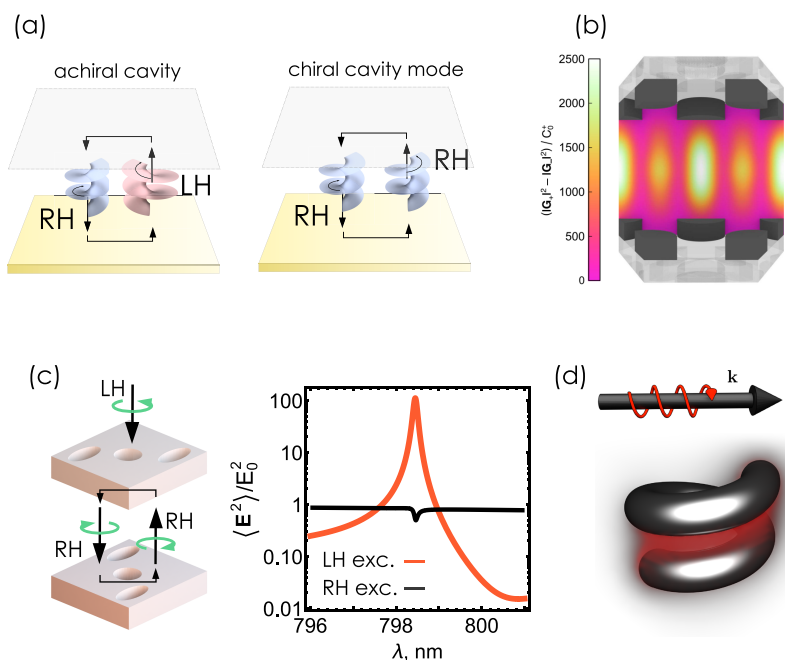


Figure 5. Handedness-preserving optical cavities. (a) Illustration of an ordinary Fabry-Pérot cavity, and a handedness-preserving planar cavity. In an ordinary Fabry-Pérot cavity a circularly polarized plane wave flips its handedness after experiencing a single reflection at a normal incidence, resulting in a nonchiral standing wave with a series of nodes and antinodes. Mirrors of a handedness-preserving cavity, on the contrary, maintain the field handedness resulting in a chiral standing wave. (b) Sketch of the handedness-preserving cavity composed of two dielectric photonic crystal mirrors. The color shows the optical chirality density of the resulting standing wave. (c) Left: single-handedness chiral cavity realized by stacking two dielectric low-symmetry mirrors. Right: simulated electric field enhancement spectra. (d) A compact maximally chiral optical cavity represented by a metallic helix producing a resonant response only to one incident handedness and being nearly transparent to the other handedness. Panel (b) adapted with permission from ref 107. Copyright 2020 APS. Parts of panel (c) adapted with permission from ref 81. Copyright 2022 ACS. Panel (d) was adapted with permission from ref 108. Copyright 2022 ACS.

utilizing structured light beams carrying nonzero OAM expands the palette of chiral optical effects accessible with higher-order multipoles of molecular transitions.¹⁰⁴ In particular, the interaction of molecular electric quadrupoles with optical vortices of different handedness gives rise to the so-called helical dichroism.¹⁰⁵

4. CONSTRUCTING CHIRAL POLARITONS

Now we are in a position to discuss the notion of a chiral polariton, by which we are going to refer to the coupled state of an interacting light-matter system, where both the optical mode and the material excitation are chiral. Maxwell's equations in free space admit solutions in the form of chiral photons, so one could already examine chiral polaritons emerging in this situation. However, from the practical standpoint, we are usually interested in strong interaction with confined optical modes. Thus, it would seem natural to load an ordinary resonator, such as a Fabry–Pérot cavity, with chiral matter and expect illumination of chiral polaritons upon excitation of such a system with a circularly polarized electromagnetic field. This kind of system has been realized in ref 22 by coupling chiral metallic meta-atoms to the normal-incidence resonance of a Fabry–Pérot cavity. A similar setup was realized in ref 23 by coupling chiral organic emitters to a nonchiral surface plasmon mode of a metallic film.

The simple intuition outlined above faces a fundamental obstacle. To exemplify the problem, consider a perfect electric mirror illuminated at normal incidence by an LCP or an RCP plane wave $\mathbf{E}_{\text{inc}}(\mathbf{r}) \propto (1, \pm i\lambda, 0)^T e^{ikz}$, $\lambda = \pm 1$. The field continuity at the surface of the mirror requires that the reflected wave is described by the same complex polarization $(1, \pm i\lambda, 0)^T$. Thus, reflection of the circularly polarized wave at a normal by a metallic mirror preserves its SAM density, but reverses its wave vector, which in the end flips the handedness of the reflected wave. This handedness flipping of the wave traveling between two mirrors creates a standing wave with zero chirality density, Figure 5a. As a result, the resonant modes of a Fabry–Pérot cavity at normal incidence do not possess any handedness. This property of circularly polarized standing waves imposes severe constraints on the behavior of polaritonic systems. In particular, this helicity flipping ultimately limits the magnitude of CD that can be observed with a chiral film strongly coupled to an ordinary Fabry–Pérot cavity despite the resonant enhancement of the electromagnetic field inside the cavity.²²

The problem of handedness flipping poses a quest for optical cavities supporting resonant modes of well-defined handedness, whose performance is schematically illustrated in Figure 5a.¹⁰⁶ In this hypothetical scenario, a circularly polarized plane wave retains its handedness after reflection from a carefully designed mirror, resulting in a chiral standing wave. A natural question then arises: what design rules does one need to follow in order to engineer a cavity that preserves the handedness of electromagnetic field upon scattering? This turns out to be a more fundamental issue, which we address below.

4.1. Handedness-Preserving Cavities. Handedness of light may be converted in different ways upon interaction with scatterers, even nonchiral ones. As we showed above, any field distribution satisfying Maxwell's equations can be expanded into two components of well-defined handedness \mathbf{G}_{\pm} . Imagine a scenario when an incident field $\mathbf{E}_{\text{inc}}(\mathbf{r})$ of a certain handedness (for example, a purely LH field) interacts with an arbitrary scatterer, such as a metasurface or a compact nanoparticle. For this field only, the \mathbf{G}_{+} component is different from zero. The

scattered field, on the other hand, would generally contain both handedness components: $\mathbf{G}_{+}^{\text{scat}}(\mathbf{r}) \neq 0, \mathbf{G}_{-}^{\text{scat}}(\mathbf{r}) \neq 0$.

Some cavities, such as plasmonic and dielectric nanoantennas, exhibit spatial regions of enhanced chirality density even upon excitation with linearly polarized light,^{74,109,110} but the resonant modes of these systems still do not possess a well-defined pure handedness. In this context, the concept of duality¹¹¹ plays an important role. Using the framework of Riemann–Silberstein vectors, one can show that a piece-wise homogeneous and isotropic system preserves the handedness of any incident electromagnetic field at a frequency ω if and only if all the materials have a constant impedance across all media constituting the system, including the environment:¹¹¹

$$\frac{\varepsilon(\mathbf{r}, \omega)}{\mu(\mathbf{r}, \omega)} = \frac{\varepsilon_{\text{env}}(\mathbf{r}, \omega)}{\mu_{\text{env}}(\mathbf{r}, \omega)} = \text{const } \forall \mathbf{r} \quad (12)$$

Structures that satisfy this criterion are referred to as dual. Correspondingly, if the structure is surrounded by free space, eq 12 requires equal permittivity and permeability of the resonator, $\varepsilon(\mathbf{r}, \omega) = \mu(\mathbf{r}, \omega)$.

As one can see, duality is a very stringent requirement that calls for magnetic materials, $\mu \neq 1$. Since they are very rare in the visible range, this motivates the search for nonmagnetic handedness-preserving structures. Feis et al.¹⁰⁷ demonstrated a handedness-preserving cavity formed by a pair of periodic dielectric mirrors, Figure 5b. Each mirror operates by virtue of first-order diffraction into large transverse momentum (k_{\parallel}) modes. Thanks to the presence of an inversion center, the system itself is achiral, meaning it supports both the LH and the RH resonant modes at the same time. Voronin et al. pushed this idea further and studied a single-handedness chiral optical cavity.⁸¹ By utilizing low-symmetry dielectric mirrors adopted from ref 80, they designed a Fabry–Pérot cavity that supports a QNM of a well-defined handedness and does not support resonant modes of the opposite handedness in the relevant wavelength range, Figure 5c.

In addition to planar infinitely extended resonator, there has been a progress in designing compact nanostructures with chiral optical resonances. Garcia et al. experimentally demonstrated what is called a maximally chiral object³⁸ of a finite size operating in the IR.¹⁰⁸ Their structure is a helix-shaped metallic nanoresonator, Figure 5d, that is nearly transparent for incident light of a certain handedness, while excitation with the opposite handedness produces resonant extinction. Any maximally chiral object is necessarily dual,³⁸ implying that the excited resonant modes should have a well-defined handedness. The interior of the resulting nanocavity can be loaded with an excitonic material similar to ref 112, which studied theoretically a similar plasmonic nanostructure interfaced with an achiral excitonic material.

4.2. A Theoretical Model for Chiral Polaritonics. The availability of a handedness-preserving cavity is only one part of the story, next we have to understand how to utilize it. Exploring the possibilities of chiral polaritonics is no small endeavor and will demand ample work on both theoretical and experimental side. Intuition, often generated by simple models as illustrated in this section, serves as an important catalyst. We refer the interested reader to ref 113 for a detailed derivation.

The starting point for all theoretical descriptions is the nonrelativistic minimal-coupling Hamiltonian. Since molecules are usually small in relation to the wavelength of the confined modes it is beneficial to apply the Power–Zienau–Woolley transformation and retain only the electric and magnetic dipolar

terms as well as electric quadrupoles.^{114,115} The lowest-order Hamiltonian for chiral interaction takes, therefore, the form

$$\hat{H} = \hat{H}_M + \hat{H}_L - \frac{1}{\epsilon_0} \sum_n \hat{\mu}_n \cdot \hat{\mathbf{D}}_\perp(\mathbf{r}_n) - \sum_n \hat{\mathbf{m}}_n \cdot \hat{\mathbf{B}}(\mathbf{r}_n) + \hat{H}_{LMc} \quad (13)$$

with the electric and magnetic transition-dipole moments $\hat{\mu}_n$, $\hat{\mathbf{m}}_n$ related by the transition elements $\mathbf{m}_n^{01} = -ic\xi\mu_n^{01}$, displacement $\hat{\mathbf{D}}_\perp(\mathbf{r}_n)$ and magnetic $\hat{\mathbf{B}}(\mathbf{r}_n)$ field. Bare matter \hat{H}_M

and field \hat{H}_L Hamiltonian feature the bare matter $\hbar\omega_m$ and cavity $\hbar\omega_{\text{cav}}$ excitation energy, respectively. The corrections collected in \hat{H}_{LMc} are essential for gauge-invariance, realistic descriptions, and large interaction strength.¹¹³ Importantly, the dipolar moments are defined with respect to the center of mass of each individual molecule. Following ref 113, we can obtain an intuitive solution for the interaction between N strongly simplified chiral emitters and the standing chiral field. In a simplified form, the analytic solution reads:

$$\omega_\pm \approx \frac{1}{\sqrt{2}} \sqrt{\omega_{\text{cav}}^2 + \omega_m^2 + 8\xi\lambda g^2 \pm \sqrt{[\omega_{\text{cav}}^2 - \omega_m^2]^2 + 16g^2(\omega_{\text{cav}} + \omega_m\xi\lambda)(\omega_{\text{cav}}\xi\lambda + \omega_m)}} \quad (14)$$

where λ is the eigenvalue of the helicity operator describing either a LH ($\lambda = +1$) or a RH ($\lambda = -1$) cavity mode, ξ is the matter chirality parameter, and g is the fundamental coupling strength. Figure 6a illustrates the resulting energy spectrum of an

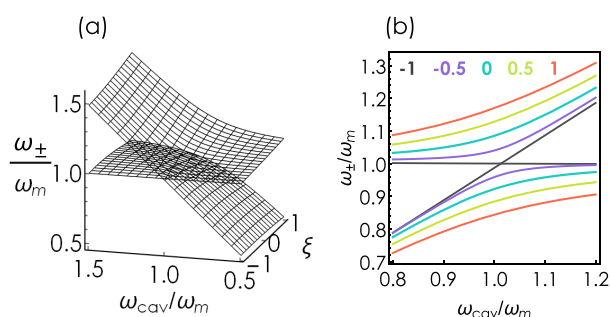


Figure 6. (a) Spectrum of polaritonic eigenvalues ω_\pm of the chiral Hopfield model with a left-handed cavity mode as a function of the cavity frequency ω_{cav} in relation to the matter excitation ω_m and chiral factor ξ . The eigenvalues are calculated with typical values for dye molecules and account for corrections via \hat{H}_{LMc} (see ref 113 for details). (b) Same as (a) but as a series of 1D plots for different fixed chirality parameters ξ .

ensemble of chiral emitters coupled to a LH cavity with $\lambda = +1$. As expected, emitters with matching handedness ($\xi = +1$) couple strongly to the cavity mode, whereas opposite enantiomers feature a gapless energy spectrum. Figure 6(b) shows this transition as ξ varies between -1 and $+1$.

The handedness preserving mirrors are therefore able to lift the degeneracy between same ($\lambda\xi > 0$) and opposite ($\lambda\xi < 0$) combinations, controlling the chiral cavity provides thus selective control over how strong a given enantiomer is coupled. A considerable interaction between light and matter results in a correlated ground-states, i.e., the binding of virtual chiral photons. While it sounds like a dream come true, it is important to realize that the degree of chirality is often weak and the energetic difference between the enantiomers therefore small. Nevertheless, chiral polaritonics suggests a plethora of possible applications, some will demand better engineered fields, others might work out-of-the-box. In the following, we will discuss some of those applications, debating short-term challenges and long-term prospects. Furthermore, we briefly discuss which theoretical approaches might be suited and how existing techniques can be extended.

5. PROSPECTS AND CHALLENGES IN CHIRAL POLARITONICS

Chirality is a long-standing and widely impactful concept in natural science. If we add sugar to our coffee, enjoy a good meal, or are in the need of medication, chirality has a defining influence at every point of our life and even the existence of life, as we know it, itself. Understanding and controlling the chiral state of a substance is thus pivotal. Early work in chiral catalysis was awarded in 2001 with the Nobel prize in chemistry.¹¹⁶ In the following, we will illustrate a selected set of promising directions, discuss associated challenges, and highlight recent development in the theoretical description of chiral polaritonics.

5.1. Anticipated Novel Phenomena. Controlling Spontaneous Emission. In the weak coupling regime, a chiral QE, such as an organic molecule or a lanthanide complex, would experience spontaneous decay accompanied by (partially) circularly polarized luminescence.^{89,117,118} In an achiral environment, two enantiomers of such a source would decay with equal rates, as the achiral environment is symmetric with respect to inversion. A single-handedness cavity could enable unequal asymmetric emission rates for left- and right-handed enantiomers of chiral sources. The notion of a chiral Purcell factor was introduced by Yoo and Park back in 2015,¹¹⁹ however, their description can be questioned because the authors assumed unequal emission rates of LH and RH enantiomers in free space.

Voronin et al. studied emission of chiral point sources coupled to their single-handedness cavities and observed a strong asymmetry in the emission intensities, suggesting that the fluctuating electromagnetic field within a single-handedness cavity acquires a strong chiral character.⁸¹ Such an observation follows intuitively from the handedness-dependent mode density in a chiral environment that gives rise to handedness-dependent Purcell factors. Thus, electronically excited states of opposite enantiomers of a chiral molecule would acquire different lifetimes, Figure 7b, which could be interesting in the context of selective de-excitation of chiral molecules.⁸⁶ Recent studies demonstrate intrinsic asymmetry of photoluminescence from chiral excitons hosted in J-aggregates;¹²⁰ single-handedness cavities may further enhance this emission asymmetry.

Red-Shifting Chiral Transitions. Either symmetric two-handedness or asymmetric single-handedness chiral cavities can be utilized for engineering of chiral polaritons by loading them with resonant Pasteur media, which could have promising implications for chiral sensing. Indeed, chiral electronic transitions of the majority of biomolecules are located in the UV range, where spectroscopic measurements are challenging. The two polaritons of a strongly coupled system are expected to experience an anticrossing, upon which the lower polariton

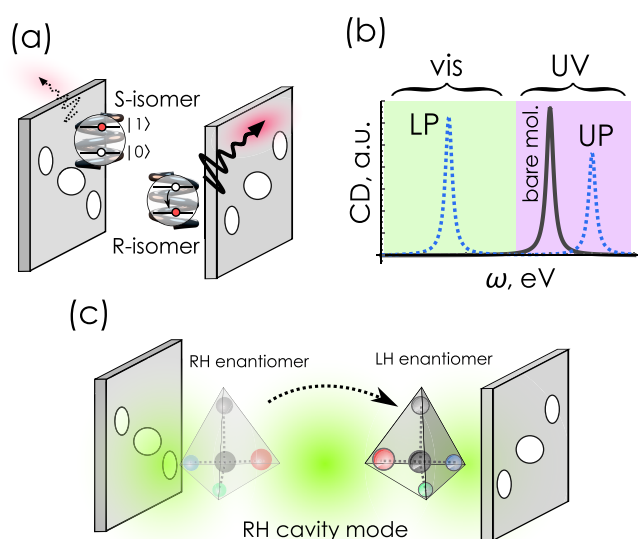


Figure 7. Potential implications of chiral strong coupling. (a) Selective de-excitation of chiral molecules. Two opposite enantiomers of a chiral molecule coupled with an asymmetric single-handedness optical cavity. Asymmetric coupling strength leads to unequal spontaneous decay rates from the excited states of two enantiomers. (b) Red-shifting chiral transitions by strong coupling. A single chiral electronic transition of a molecule located in the UV range. Strongly coupling this molecule with a photonic mode causes of the lower polariton (LP) to red-shift toward the visible range while the upper polariton (UP) is shifted deeper into the UV domain. (c) Steering the equilibrium of an ensemble of racemic mixture by ultrastrong coupling of chiral emitters to a single-handedness optical cavity.

shifts toward the visible range, Figure 7a, where measuring CD and characterizing the enantiomeric state of a racemic would be easier. Recent theoretical efforts begin to explore this strategy. For example, Feis et al. and Beutel et al. studied the response of a symmetric handedness-preserving cavity loaded with a non-resonant Pasteur medium and shown enhancement of CD,^{107,121} while Mauro et al. examined the behavior of a single-handedness cavity loaded with resonant chiral medium.¹²²

Leveraging Chiral Vacua. The chiral nature of vacuum fluctuations in single-handedness cavities might enable unusual vacuum energy landscapes. In a simplified picture, each polariton of a two-mode coupled system is an independent harmonic oscillator associated with its own vacuum (a.k.a. zero-point or ground-state) energy of $\hbar\omega_{\pm}/2$. The vacuum energy of the entire system therefore is $U_{\text{vac}} = \hbar(\omega_{+} + \omega_{-})/2$, where ω_{\pm} are the two polaritonic transition energies.^{123,124} Recent independent theoretical efforts suggest that the changes in the ground state energy will differ for each enantiomer and increase with the molecular concentration as N or \sqrt{N} for small or large hybridization, respectively.^{113,125}

This hints at a possibility that chiral molecules will experience different ground-state energies inside a single-handedness cavity depending on their enantiomeric state, thus steering the molecular structure to a different equilibrium. Similar proposals for affecting the vacuum energy of chiral enantiomers utilizing so-called “chiral atmosphere” have been put forward.¹²⁶

Irrespective of the exciting possibilities, a few obstacles remain. First, molecular chirality is small, a challenge and opportunity to be revisited in the following. Second, simplified few-mode theories are well suited to describe spectral effects but

can be expected to provide only a qualitative trend for the correlated ground state energy that would be predicted following Casimir.^{127,128}

Enhancing the Weak Chirality. The parameter ξ , characterizing the degree of matter chirality, is commonly small for molecular systems ($\xi \sim 10^{-3}$ – 10^{-6} , see refs 88, 90, and 91). Would we couple only a single pair of right and left enantiomers to the chiral cavity, we would observe only a minute asymmetry of the polaritonic energy spectra. The collective interaction in chiral polaritonics can enhance this by increasing the number of collectively coupled molecules according to $\sqrt{N}g_0\lambda\xi \propto \sqrt{N/V}\lambda\xi$. The achievable concentration N/V defines therefore an upper limit for this approach and has to outperform the small parameter ξ . While a conservative estimate indicates that observable differences will be present for common concentrations,¹¹³ it would be clearly desirable to enhance the differences by ‘enhancing’ the degree of chirality. Such an approach might be needed to improve the recognition capabilities, lower thresholds, and extend the methodology to a wider class of optically chiral systems.

One possibility to address this issue is to design a chiral cavity that would compensate for the smallness of ξ by adjusted relation between the electric and magnetic fields of the optical mode. Indeed, ξ enters eq 14 via the product $\lambda\xi$, where λ characterizes the relationship between the electric and magnetic fields of the chiral optical mode as $\mathbf{ZH} = -i\lambda\mathbf{E}$. This suggests that chiral molecules with $|\xi| \ll 1$ would produce a more substantial energy asymmetry if they are coupled to a chiral optical mode with $|\mathbf{ZH}| \gg |\mathbf{E}|$. This is not possible in purely transverse chiral standing waves, where the electric and magnetic field are related via $\mathbf{ZH} = \pm i\mathbf{E}$. However, in subwavelength cavities, where the field has a substantial longitudinal component it does no longer hold. Thus, the issue could be addressed by designing a compact chiral nanocavity, as in ref 108, whose quasi-normal mode is dominated by the longitudinal magnetic field and maintains a chiral character.

Exploring Autocatalysis and Homochirality. Why does sugar (sucrose) and many other substances exist in nature in such high excess compared to their chiral images? What leads to this large imbalance between enantiomers? This simple question remains unanswered, although it marks a defining problem for the development of life.¹²⁹ While still debated, it is conjectured that an initial unbalance between the enantiomers was amplified by autocatalytic reactions of chemical and/or biological nature.¹³⁰ The origin of this unbalance remains however unknown, and speculations range from pure chance due to statistical fluctuations to the parity symmetry breaking in weak interactions.¹³¹ Without a way to carefully adjust minute changes in the environmental conditions, it is challenging to observe and manipulate a possible mechanism.

Chiral polaritonics might provide here a unique possibility. The optical fields inside the chirality-preserving cavity undergo vacuum fluctuations that break the chiral symmetry of free space.¹¹³ How strong the electromagnetic environment varies inside the cavity from the free-space conditions can be well controlled by changing size, shape and quality of the optical mirrors. It has been demonstrated that optical cavities can be used to control anything from single atoms,¹³² over chemical reactions,¹³³ up to biomolecules and bacteria.¹³⁴ Such a sensitive tool could now be used to fine-tune the degree to which the electromagnetic environment prefers a given handedness. Control over the chiral environment allows then control over

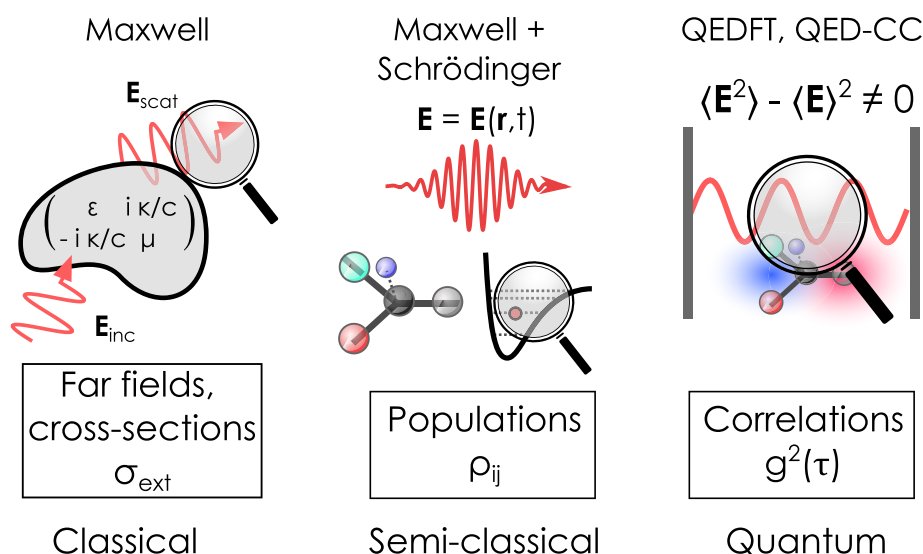


Figure 8. Summary of classical and quantum theoretical methods for description of strong chiral light–matter interaction. Left: description/modeling of chiral systems using Maxwell’s equations in terms of macroscopic constitutive parameters gives access to spectroscopic far-field quantities, such as cross sections. Middle: semiclassical description using combined treatment with Maxwell’s equations for the field and Schrödinger equation for matter gives access to, e.g., population dynamics of the matter encoded by its density matrix with feedback on the optical fields. Right: full quantum description of chiral light–matter interaction gives access to quantum correlated features, such as ground-state changes and combined statistics.

the initial conditions of homochirality. Furthermore, as the chiral polaritonic interaction depends on the number of collectively coupled emitters with the corresponding handedness, this effect is inherently self-catalyzing. While the details of this approach remain to be investigated, chiral polaritonics could serve as a novel tool to explore homochirality.

5.2. Development of Theoretical Descriptions. Simplified analytical models are mandatory to build intuition, the foundation for innovative developments and starting point for sophisticated descriptions. However, a faithful description of experimental reality, which provides in the long run the necessary microscopic understanding, will inevitably require sophisticated microscopic theory. How complex such a microscopic description has to be will depend heavily on the system at hand and the relevant observable, as sketched in Figure 8. The value of the classical approximation for light should not be underestimated. Providing Maxwell’s equations with an adequate polarizability will often suffice to obtain accurate far-field spectra. As an example, consider the typical Hopfield system with a set of quantum harmonic oscillators describing molecular dipoles and a quantized photonic mode. In the linear regime, its spectrum is identical to the purely classical solution obtained from Maxwell’s equations.^{135,136} Clearly, Maxwell’s equations do not provide access to the microscopic dynamics governed by quantum mechanics—the moment we intend to control the material we are bound to consider its full complexity. However, it is often sufficient to combine quantum matter with classical light.

The complexity of quantum matter imposes a necessity for efficient descriptions such as time-dependent density-functional theory¹³⁷ which can be combined with a self-consistent propagation of classical light.^{138–141} This approach remains accurate in predicting the eigenstates of the combined system even in the case of strong interaction with optically confined modes.¹⁴² Naturally, the major limitation of this approach is that quantum fluctuations of the electromagnetic field are not considered. While mixed quantum-classical approaches are partially able to compensate for the statistical nature of quantum

fluctuations,^{143–146} much remains to be desired. Changes in the correlated ground-state are for instance entirely caused by quantum fluctuations.

Following the canonical quantization procedure,^{115,147} the photonic fields are represented as a sum over many quantum harmonic oscillators. This vastly enlarges the already excessive size of the material Hilbert space and renders a direct solution of the associated Schrödinger equation impossible for anything remotely realistic. Typical coping strategies assume, for instance, a strong simplification of the material.^{113,148,149} In general, however, this approach is best suited to collect intuition and extensions to a more faithful representation of the material become important when working with, e.g., chemical reactions. The complexity of light and matter is dominated by the complexity of the material. For weak light–matter interaction, the associated Fock space can be efficiently truncated. Ultrastrong interactions require effective photon-free and nonperturbative approaches.^{150,151}

If the complexity of the material represents the major limitation, the solution should be to adjust existing many-body techniques to include quantized light–matter coupling. Two such approaches are quantum-electrodynamical density-functional theory (QEDFT)^{150,152–154} and QED coupled-cluster (QED-CC).^{155–158} Their QED adapted form inherits the fundamental strength and weaknesses of their respective quantum mechanical counterparts. While this novel field of *ab initio* QED¹⁵⁹ is still in its infancy, already the initial development provides access to real-space resolved Lamb-shifts,¹⁶⁰ modification of chemical reactivity,³⁴ and intermolecular interactions.¹⁶¹ Chiral polaritonics calls now for an intensified development in two directions.

Beyond the electric dipole. While many optical effects, such as Mie-scattering, imply matter to be of the size of the optical wavelength, the molecular constituents of the material are of much smaller size and the electric dipole commonly dominates the interaction. This convenient feature led to a clear dominance of the electric dipole approximation for the interaction between quantized fields with matter—to a point that the implications of

this approximation had been partially forgotten.^{162,163} Now, within the realm of chiral strong-coupling, it will be required to remedy this development. It seems natural to extend the description simply to the next order in the multipolar expansion¹⁴⁷ and the multipolar framework is known to perform well in the single mode limit of strong coupling.¹⁶³ In addition, full minimal coupling descriptions could complement this process, providing an important sanity check via the restrictions enforced by gauge invariance. The latter is only intact for the full Hilbert space. Riso et al. have recently taken first steps in this direction by minimally coupling a single cavity mode to chiral molecules described by coupled-cluster theory.¹²⁵ Furthermore, a resolution of the photonic momentum might question the single-mode approximation, bringing the field in closer contact to Casimir physics. While van-der-Waals interactions are omnipresent in chemistry and are an important ingredient in the design of quantum chemistry approaches, a rigorous extension of dispersive interactions into the retarded and nondipolar domain remained, thus far, firmly under (quantum) optical supremacy.^{164,165} Unfortunately, the latter lack for example the necessary framework to reliably handle chemical reactions.

A more cost-efficient alternative to coupled-cluster and similar techniques is based on extensions of (current-)density functional theory (CDFT).^{150,152,166,167} Quantum electrodynamical density-functional theory in dipolar approximation is build on the bilinearity in the density-potential pair (n, v) .^{150,152} Moving beyond the dipolar approximation requires to use the effectively nonlocal current-vector-potential pair (\mathbf{j}, \mathbf{A}) as descriptors.¹⁶⁶ While the development of the associated CDFT functionals is notoriously difficult, a simplified description in terms of the Kohn–Sham current-density might serve as a promising starting point for future developments.¹⁶⁸ Overall, the electric dipole approximation provides a unique comfort for established methods, yet being the seed for various issues which range from the conservation of momentum to the coupling with extended systems. Exploring the undiscovered country beyond the dipolar approximation will not only enable chiral polaritonics but also aid our understanding of light and matter in the first place.

Scaling up. The most elegant or rigorous theory is useless if unable to predict and understand the problem at hand. Thus, we are facing the question: Given a satisfying theoretical description of a chiral molecule, how do we account for the chiral environment comprising chiral cavities and nanoplasmonic particles? The recent debate around the theoretical description of ground-state polaritonic chemistry^{133,169–171} illustrates the limitation of oversimplified models. While *ab initio* QEDFT calculations³⁴ have shown qualitative agreement with experiments, much remains to be understood and the simplified description of the photonic system to be scrutinized. Collective light-matter interaction and complex environments represent now the next challenge.¹³⁹ Conceptually, this is closely related to other multiscale problems, such as impurities in condensed matter¹⁷² or active centers in biological structures.^{173,174} While parallelization strategies can account, under severe approximations, for a few hundred of molecules,¹⁷⁵ mesoscopic ensembles and realistic macroscopic environments will only become available when efficient embedding strategies are employed.^{139,176–181} Lastly, plasmonic structures will take a prominent role for chirality,¹⁸² especially due to their capability to enhance the inherently weak chirality (see section 5.1). Charge migration and the microscopic surface structure renders

simple eigenmode quantization strategies questionable if our chiral molecule of interest is in close proximity to the nanoparticle. Density-functional theory presents a reliable choice where first connections to optical cavities are already available.¹³⁸ The explicit simulation of sizable plasmonic structure is, however, too costly. Mixed descriptions along the lines of quantum hydrodynamics¹⁸³ or the embedding of quantum-dynamics into classical permittivity for larger fractions of the system^{139,184} could help to alleviate some of the computational weight necessary to describe realistic plasmonic systems.

6. CONCLUSIONS

To conclude, we have presented our vision of a potentially new area of nanophotonics: chiral polaritonics. Guided by the notion of chirality of electromagnetic field and matter, we established the general requirements to resonant optical systems in which chiral polaritonic eigenstates may emerge. Recent theoretical efforts discussed in this Perspective already indicate that chiral polaritonic systems may feature nontrivial optical phenomena, where the interplay of light and matter chirality is of key importance for determining the eigenfunctions of the system, as well as its response to external electromagnetic fields.

We have speculated on the potential of a collection of novel effects that can be enabled by strong coupling between chiral light and matter. Established directions for the utilization of chirality involve plasmonic or biological nanostructures,¹⁸² the here proposed usage of chiral polaritonics adds further versatility. Dispersive interactions, which are critical for chemical and biological systems, are based on the exchange of photons. The addition of strong light–matter coupling is therefore more than a mere hurdle; it naturally connects to the existing work and extends our understanding of chirality. Finally, development of existing and new theoretical tools might be necessary in order to accurately describe various observables of a strongly coupled chiral system, such as far-field response functions, molecular populations, and quantum correlations. Due to the multifaceted nature of the problem, a coordinated effort of researchers with backgrounds in classical electromagnetism, quantum optics, and material science will be needed in order to succeed in the hunt for chiral polaritons.

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Notes

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