

Chapter 2

Chirality in Nature and Science

Abstract Geometrical chirality in molecules or plasmonic nanostructures can lead to unique optical responses such as circular dichroism or optical rotatory dispersion. It is important to distinguish between such chiral responses and the underlying chiral geometry. In this chapter, we first discuss the geometrical properties of chiral objects from a mathematical point of view including planar chirality, the quantification of chirality, and different handedness definitions. After a short introduction to localized plasmons, we thoroughly derive the electromagnetic properties of geometrically chiral objects. Starting from the Born-Kuhn model for chiral media, we derive the chiral constitutive equations and, subsequently, the chiral wave equation. This wave equation provides the basis for a theoretical discussion of the resulting chiral far-field responses. Exemplary, we analyze the circular dichroism response of sugars and simple plasmonic nanostructures. Additionally, a short review of modern techniques for the fabrication of chiral plasmonic nanostructures is given.

2.1 Geometrical Chirality

The term *chirality*, which is derived from the Greek word $\chi\epsilon\iota\rho$ (*cheir*, hand), is used for objects that are not equivalent to their mirror images. It was introduced in 1884 by Lord Kelvin in his Baltimore Lectures [1]:

I call any geometrical figure, or group of points, chiral, and say that it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.

The best known example of such a geometrically chiral object is the human hand (cf. Fig. 2.1). The left and the right hand are mirror images of each other, but it is impossible to superpose them. Therefore, chiral objects are referred to as being *handed*. The two versions of geometrically chiral objects, which differ only in their handedness, are called *enantiomorphs* or, in the special case of chiral molecules, *enantiomers*¹ [3].

¹We will adopt this nomenclature and also speak of enantiomers in case of chiral plasmonic structures. This is common usage in recent literature and also fits to the concept of “plasmonic molecules” [2].

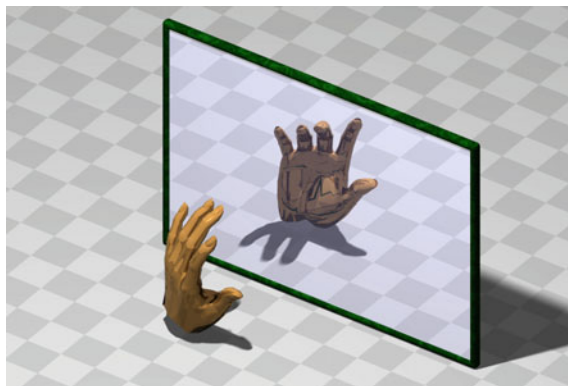


Fig. 2.1 The human hand is the most prominent example of a geometrically chiral object. The mirror images of a hand cannot be superposed by rotations or translations, leading to two enantiomorphs: The *left* and the *right* hand

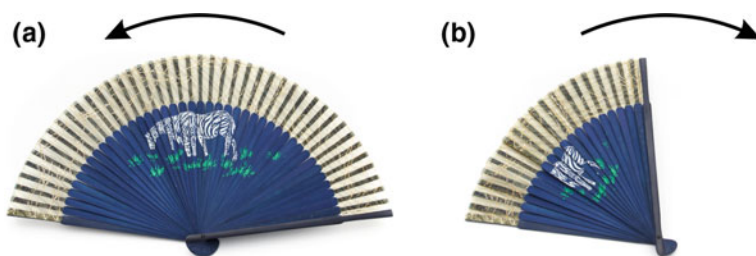


Fig. 2.2 An opened folding fan is a geometrically chiral object. Its handedness can be defined in two ways. **a** If the relative rotation of the sticks of the opened fan is considered, it is *left-handed*. **b** If we consider the movement necessary to open the fan, it is *right-handed*

It is noteworthy that, although there exist two enantiomorphs for every geometrically chiral object, there is no general rule to determine the left-handed or the right-handed one [4]. We show, on one simple example, that this choice is purely arbitrary: Consider the helical arrangement of sticks of a folding fan. The fan clearly is a geometrically chiral object, so we can assign a handedness to it. One might argue that the fan is left-handed because the helix formed by the sticks performs a left-handed rotation in space (cf. Fig. 2.2a). On the other hand, one could define the handedness by the clockwise twist necessary to open the fan (cf. Fig. 2.2b). With this argument, the fan could be labeled “right-handed”.

A more detailed discussion of this problem is given in Sect. 2.1.2. In this book, we will use the first method—following some sense of rotation in space—to define the handedness of geometrically chiral structures whenever possible, because it seems to be more intuitive.

Following Kelvin’s definition, geometrically chiral objects in three dimensions may in general not exhibit rotation-reflection axes of symmetry S_n . This includes

mirror planes (S_2) and inversion centers (S_1). However, rotational symmetry (C_n) is not forbidden. For example, n multiple intertwined helices (a structure that will be analyzed in detail in Chap. 8) exhibit n -fold rotational symmetry but the structure is still geometrically chiral.

Another important aspect of the definition given by Kelvin is that it is purely mathematical. One can directly decide whether an object is chiral or not just from looking at its geometry. This geometrical property can lead to physical responses that depend on the handedness of the structure. The fundamental properties of such responses are discussed in Sect. 2.1.3. Their presence implies that a different definition of chirality can be given by analyzing one specific response. In this case, the object is chiral if and only if the response can be detected.²

It is important to distinguish between these two different definitions. In this book, we deal with chiral optical responses that are visible both in the far-field as well as the near-field of plasmonic nanostructures. Hence, we term any object chiral that exhibits such a response. Whenever we refer to the mathematical concept of chirality, the term “geometrical chirality” is used.

2.1.1 Planar Geometrical Chirality

All considerations up to now were made in three-dimensional space. However, the concept of chirality can be also transferred to two dimensions. In this case, all rotations and translations are restricted to a two-dimensional plane. Apart from that, the definition is the same: An object is planar geometrically chiral when its mirror image cannot be brought into coincidence with itself by rotations and translations without lifting the object out of the plane. Some examples are shown in Fig. 2.3. The simplest planar geometrically chiral object would be an asymmetric triangle.

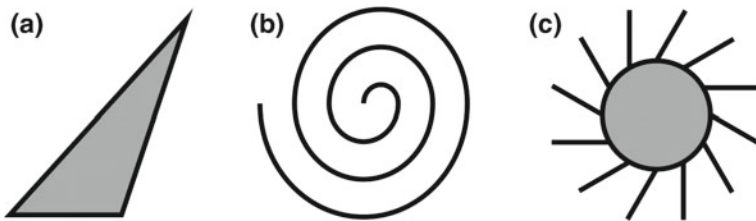


Fig. 2.3 Different examples of planar geometrically chiral structures. **a** The simplest example is an asymmetric triangle. **b** A spiral is the planar analogue of the helix. **c** Planar chiral objects may possess rotational symmetry such as the sketched blade wheel

²Note that it is possible to observe chiral responses for structures that are achiral from a geometrical point of view. This can, for example, occur when the combination of structure and incident wave vector form a chiral object. In some literature, such an arrangement is referred to as possessing “extrinsic chirality” [5].

The planar analogue of the helix is a spiral. Also, rotational symmetry can occur for planar geometrically chiral structures.

Note that any two-dimensional object, planar geometrically chiral or not, is geometrically achiral in three dimensions because the object plane is a trivial mirror plane in three dimensions: One can easily obtain the enantiomorph of a planar geometrically chiral object by flipping it over. This can be further generalized: Any object that is geometrically chiral in n dimensions will become achiral as soon as an additional dimension is added.

If we do not focus on geometrical chirality but look at chiral responses, it is needless to distinguish between planar and three-dimensional geometrical chirality. The structure might or might not show a specific response, independent of its geometrical chiral properties. However, most responses are defined for isotropically oriented chiral analytes and, therefore, cannot be observed for structures exhibiting only planar geometrical chirality.

2.1.2 Quantification of Chirality and Handedness

Kelvin's definition of geometrical chirality is binary: An object is either chiral or achiral. The definition does not allow for any ordering of different geometrically chiral objects. However, one might intuitively argue that, when comparing two helices of the same length, the one that rotates more often is "more chiral" or shows "stronger chirality" than the other.

Starting from Kelvin's definition, one can define measures that quantify the chirality of an object by simply looking at its geometry. One possibility is illustrated in Fig. 2.4: We start with the two enantiomorphs and align them in a way that the maximum overlap between the two structures is obtained. The overlap volume, normalized to the volume of the object, is a measure for the chirality. It results in a value between 0 and 1, where 1 (perfect overlap) describes an achiral object. The smaller the value gets, the higher the chirality of the object is in this measure.

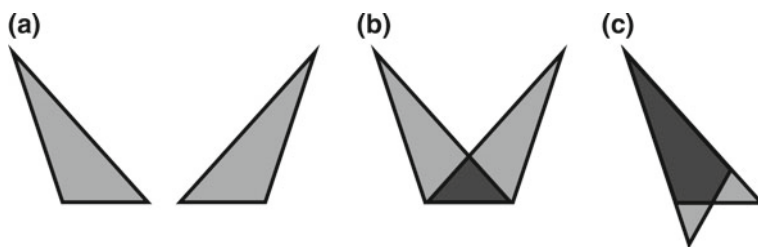


Fig. 2.4 A simple measure to quantify geometrical chirality. **a** Both enantiomers are taken and **b** overlapped. **c** The maximum overlap defines the degree of geometrical chirality for the structure

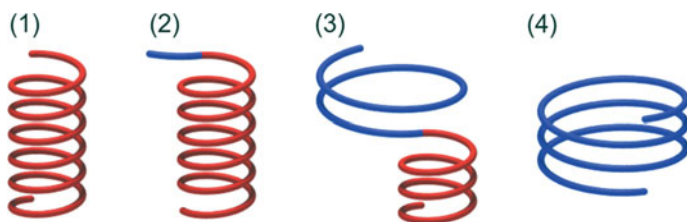


Fig. 2.5 A helix of one given handedness can be continuously transformed into a helix with opposite handedness by simply pulling at one end and rolling the wire up with a different radius. The different radii of both helices ensure that any intermediate state stays geometrically chiral

However, there are many more possibilities to define such geometrical measures for chirality [6, 7]. It has been shown that, starting from any chiral tetrahedron, one can construct a measure that leads to highest geometrical chirality for the object initially picked [8, 9]. Therefore, these measures provide no additional benefit from a mathematical point of view.

It becomes even more difficult, if we do not only want to define some degree of geometrical chirality, but try to quantify the handedness of a given structure by a geometrical measure. As already discussed in Sect. 2.1, there is no straightforward way to determine the handedness of an arbitrary geometrically chiral object.

Let's ask whether a mathematical way of defining the handedness can be found. We consider some measure that describes left-handed structures by positive values and right-handed structures by negative values. Enantiomorphs result in the same absolute value but with opposite sign, geometrically achiral structures result in the value 0. Of course, the measure should be continuous.

Let's now consider the helix depicted in Fig. 2.5 (1) and compare it to the one in state (4). The handedness of both helices is different. Therefore, the imaginary measure should result in values with opposite sign when analyzing these two structures. However, as shown in the intermediate sketches, one can continuously transform one helix into the other. This should result in a continuous change of the value of our measure leading to a configuration where the measure is zero. However, due to the different radii of the helices, all intermediate structures are geometrically chiral. Therefore, any such measure will label some geometrically chiral structures as achiral.³ In these cases, the resulting zero value is not due to geometrical achirality but due to the fact that the given measure cannot assign a handedness to this unique structure. This is a general problem of handedness measures, which is referred to as *chiral connectedness* in literature [10].

Recently, Efrati and Irvine introduced a tensorial measure for the handedness, which is locally defined [11]. In their description, a structure can be, depending

³One could also argue that, to resort this problem, both helices in the example must have the same handedness. However, it is straightforward to extend the transformation scheme to transform the structure back into the enantiomorph of the initial helix. Those two must have opposite sign in any useful handedness measure.

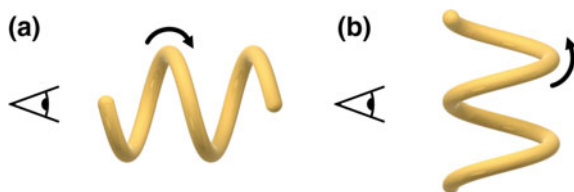


Fig. 2.6 If we define handedness by looking at the local deformation of a structure, the handedness of a helix depends on its orientation. **a** If we look along the axis of the helix, the wire bends to the right. **b** If we look perpendicular to the axis, the wire bends to the left. Therefore, opposite handednesses are observed for the different orientations

on the view, both left- and right-handed at the same time.⁴ For example, the local bending of a helically wound wire depends on the relative orientation of the helix and the observer (cf. Fig. 2.6), which would be reflected in this tensorial measure. This behavior has also been observed in an experiment where the chiroptical response of a helix changed its sign depending on the orientation, which indicates a handedness change [12]. However, this measure is unnecessarily complicated if one only needs to distinguish the two enantiomorphs of a given geometrically chiral structure.

2.1.3 Physical Manifestation of Geometrical Chirality

So far, we only discussed the geometrical implications of chirality. We will focus on the physical properties of geometrically chiral objects in this section. A *physical response* is a measurable quantity that results from the interaction of at least two different objects. A *chiral response* is a response that depends on the handedness of at least one of the objects. Therefore, chiral responses can be used to quantify the handedness of a given chiral analyte.

At first, we will discuss that both interacting objects must be geometrically chiral to obtain a chiral response. This can be motivated by purely geometrical considerations, as illustrated in Fig. 2.7. The two geometrically chiral keyholes “A” and “B” are enantiomorphs. A geometrically chiral key (“1” or “2”) of one handedness will fit in one of the enantiomorphic key-holes, but not in the other.⁵ A geometrically achiral key (“3”), on the other hand, fits or does not fit in both of the keyholes; the response is independent of the handedness. A similar result would be obtained if the keyhole itself is geometrically achiral (“C”). Then, both enantiomorphs of any geometrically chiral key would either fit or not fit. Only the combination of both a geometrically

⁴Additionally, tensors can change their sign in a continuous transformation without crossing zero.

⁵Note that the shapes of the keys are not the same as the shapes of the keyholes. This is not necessary to obtain a different response depending on the handedness of the key-hole, only the geometrical chirality is important.

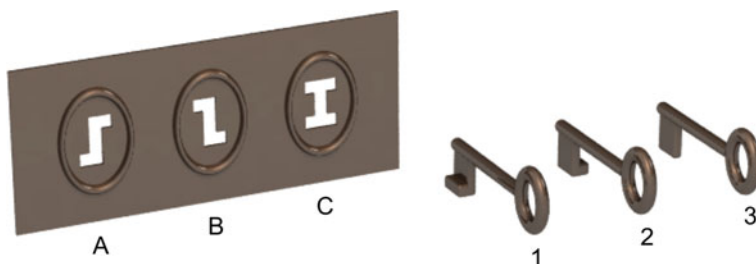


Fig. 2.7 Illustration of chiral interaction. Only when both the key and the keyhole are geometrically chiral, a different behavior depending on the relative handedness can occur

chiral key and a geometrically chiral keyhole leads to responses that depend on the handedness of both of the participants.⁶

This simple example can be extended to all kinds of interactions. Chiral responses can only be found when at least two of the participants are geometrically chiral. All other physical properties that can be analyzed without usage of a geometrically chiral probe do not depend on the handedness of the object.⁷ It is, for example, obvious that the mass of the enantiomorphs must be the same, because a mirror will not change the mass of the mirrored object.

This observation has an important implication: A second chiral object is required to probe the handedness of a given chiral analyte. Also, any chiral measure used to quantify the chirality of an object via its chiral response relies on other chiral objects. This second chiral object should be well-defined in order to be useful as a chiral probe.

Note that such chiral measures still suffer from the limitations discussed in Sect. 2.1.2. Especially, they respond zero for some geometrically chiral objects. Additionally, we will find objects that possess maximum chirality in such measures [17]. Connections between geometrical and physical chiral measures exist only for a limited number of systems [6].

2.2 Chiral Electrodynamics

After this rather intuitive introduction to geometrical chirality in Sect. 2.1, we will now discuss the electromagnetic response of such geometrically chiral molecules and plasmonic nanostructures. Classical electrodynamics in matter is based on the macroscopic Maxwell's equations [18]:

⁶Key and keyhole in this example are only planar geometrically chiral. However, it is straightforward to extend this example to three-dimensional geometrically chiral objects. The planar example has been chosen because it is easier to visualize.

⁷Strictly speaking, this is not true. Theoretical quantum chemistry predicts a small energy difference between two enantiomers because of the parity violation of the weak interaction [13, 14]. However, this difference is so small that it could not be measured by now [15, 16].

$$\nabla \cdot \mathbf{B} = 0, \quad (2.1a)$$

$$\nabla \times \mathbf{E} + \partial_t \mathbf{B} = 0, \quad (2.1b)$$

$$\nabla \cdot \mathbf{D} = \varrho, \quad (2.1c)$$

$$\nabla \times \mathbf{H} - \partial_t \mathbf{D} = \mathbf{j}. \quad (2.1d)$$

Here, $\mathbf{E}$ and $\mathbf{H}$ are the electric field and magnetic field strength, respectively, while $\mathbf{B}$ denotes the magnetic field and $\mathbf{D}$ is the electric displacement field. The free charges ϱ and currents $\mathbf{j}$ act as sources in the inhomogeneous equations. The material response is described by the linkage of $\mathbf{B}$ and $\mathbf{D}$ to $\mathbf{E}$ and $\mathbf{H}$ via the so-called *constitutive equations*, which can be arbitrarily complex in the most general case. In this book, we will restrict ourselves to linear materials. If we assume achiral media first, the constitutive equations read [18]

$$\mathbf{D} = \varepsilon_0 \bar{\bar{\varepsilon}} \mathbf{E}, \quad (2.2a)$$

$$\mathbf{B} = \mu_0 \bar{\bar{\mu}} \mathbf{H}. \quad (2.2b)$$

The response of the material is modeled by the relative permittivity $\bar{\bar{\varepsilon}}$ and permeability $\bar{\bar{\mu}}$. In the optical domain, the latter can be approximated as unity for most materials. In the general case of an anisotropic material, both quantities are 3×3 tensors. They reduce to scalars for isotropic media.

Electromagnetic waves in isotropic media must fulfill the wave equation [18]

$$\left(\nabla^2 - \frac{n^2}{c^2} \partial_t^2 \right) \mathbf{E} = 0. \quad (2.3)$$

Here, $c = 1/\sqrt{\varepsilon_0 \mu_0}$ is the speed of light in vacuum, $n = \sqrt{\varepsilon \mu}$ denotes the refractive index. A similar equation can be derived for the magnetic field.

A special solution of the wave equation are monochromatic plane electromagnetic waves given by

$$\mathbf{E} = E_0 \mathbf{J} e^{i(kz - \omega t)}, \quad (2.4)$$

where $\mathbf{J}$ is the Jones vector that describes the polarization state of the light while E_0 is the amplitude of the wave. Special cases of polarization states are linearly polarized light (LPL) with

$$J_{\text{LPL}}^\varphi = \begin{pmatrix} \cos \varphi \\ \sin \varphi \\ 0 \end{pmatrix} \quad (2.5)$$

for a polarization angle φ and circularly polarized light (CPL) with

$$J_{\text{CPL}}^\pm = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \\ 0 \end{pmatrix}. \quad (2.6)$$

For CPL, the y -component of the electric field is retarded (+) or advanced (−) by a factor of $\pi/2$ compared to the x -component. Therefore, the electric field vector rotates while the wave propagates. Such electromagnetic waves can be seen as geometrically chiral objects. The superscripts “+” and “−” are used to label the handedness.

As discussed, the definition of the handedness of a given geometrically chiral object is purely arbitrary (cf. Sect. 2.1). This has led to two distinct definitions for the handedness of CPL. In classical optics, the so-called *detector’s view* convention is usually used: The observer stands in the detector plane and looks in the direction of the *in-going* beam. The direction of rotation of the electric field vector in this plane defines the handedness of the light: Clockwise rotation belongs to right-handed circularly polarized light (RCP), counterclockwise rotation to left-handed circularly polarized light (LCP). If we freeze time, the intuitive handedness of the helix of the electric field vector in space matches the handedness of the circular polarization.

A different interpretation is made by the *source view* convention: Instead of the detector plane, the observer stands in the source plane and looks in the direction of the *out-going* beam. Again, the rotation of the electric field vector in this plane defines the handedness. However, the handedness of CPL in these two conventions is exactly opposite.⁸ The source view convention is commonly used in quantum optics and engineering.

In this book, we use the detector’s view convention. In this convention, “+” in (2.6) denotes LCP, while “−” labels RCP.⁹

Although the constitutive equations (2.2) can be used to describe wave propagation in a wide range of materials such as dielectrics, metals, and even more sophisticated materials such as magneto-optically active media, they are not sufficient for chiral media. A more general version of such constitutive equations will be derived in Sect. 2.2.2.3. Before that, we will discuss the properties of achiral metallic nanoparticles.

2.2.1 Electrodynamics of Metallic Nanoparticles

2.2.1.1 Dielectric Function of Metals

The characteristic optical properties of metals (mainly, the high reflectivity and absorbcency) can be attributed to the quasi-free electrons in the metal [19]. These electrons provide the main contribution to the optical response because they oscillate with the incident electric field. In a simple plasma model, this oscillation can be described as a damped harmonic oscillator driven by the external monochromatic field without an additional restoring force [20]:

⁸This can be intuitively understood as follows: The rotation in a plane is a planar geometrically chiral system. Depending on the convention, we look from opposite sides on this system, which changes its handedness.

⁹In principle, this additionally depends on the handedness of the coordinate system. Usually, a right-handed coordinate system is used.

$$\partial_t^2 \mathbf{u} + \gamma \partial_t \mathbf{u} = -\frac{e}{m^*} \mathbf{E}_0^{\text{ext}} e^{-i\omega t}. \quad (2.7)$$

Here, $\mathbf{u}$ is the displacement of an oscillating electron with charge e and effective mass m^* . The amplitude of the monochromatic external driving field is denoted by $\mathbf{E}_0^{\text{ext}}$. The collision frequency γ , which is the inverse of the relaxation time of the free electron gas, quantifies the damping in the system. Note that no term proportional to $\mathbf{u}$ occurs in (2.7) because no restoring force is present. Therefore, no resonance can be found in the system.

Using a time-harmonic ansatz, the solution for $\mathbf{u}$ can be found as

$$\mathbf{u} = \frac{e}{m^*} \frac{1}{\omega^2 + i\gamma\omega} \mathbf{E}_0^{\text{ext}}. \quad (2.8)$$

For N electrons in the unit volume, the polarization $\mathbf{P}$ of the metal can be written as

$$\mathbf{P} = -Ne\mathbf{u}. \quad (2.9)$$

The relation

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (2.10)$$

in combination with (2.2a) leads to the dielectric function of the free electron gas:

$$\varepsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}. \quad (2.11)$$

This is the well-known Drude model for isotropic metals. Here, the plasma frequency ω_p has been introduced:

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m^*}}. \quad (2.12)$$

The lone parameters necessary to describe the optical response of a given metal in the Drude model are ω_p and γ . Of course, this model is only a rough approximation because all resonances of the material (e.g., due to interband transitions) are ignored. However, it works well in the IR regime far off those resonances.

Figure 2.8a shows the real and imaginary part of the dielectric function of a hypothetical Drude metal close to the plasma frequency. Below the plasma frequency, the metallic behavior is observed: The real part of the permittivity is negative while the imaginary part is non-vanishing, which results in a high absorptivity of the material. For frequencies above the plasma frequency, the real part of the permittivity becomes positive. Additionally, the decreasing imaginary part results in lower losses of the material. Therefore, the Drude metal behaves as a lossy dielectric for frequencies above the plasma frequency. For $\omega \gg \omega_p$, the losses can be neglected and $\varepsilon = 1$ is approached. A physical interpretation of this behavior is that, for higher frequencies, the free electrons are not versatile enough to follow the external stimulus.

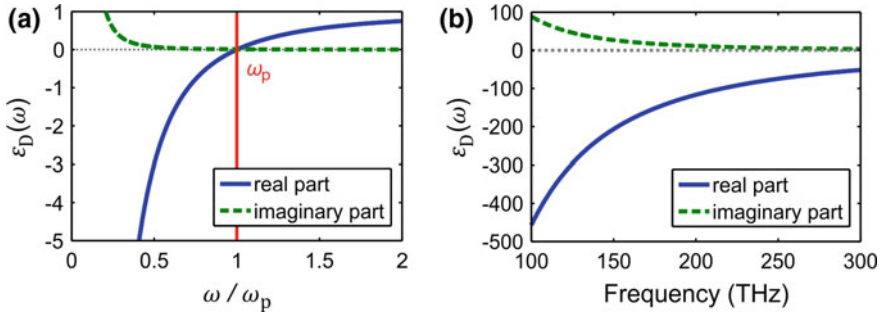


Fig. 2.8 Dielectric function of a Drude metal. **a** The metal has a negative real permittivity below the plasma frequency, which results in the metallic behavior. Above the plasma frequency, the permittivity becomes positive, resulting in the behavior of a lossy dielectric. The values on the x -axis are given as fractions of the plasma frequency. **b** Gold (modeled with $\omega_p = 1.37 \times 10^{16} \text{ rad s}^{-1}$ and $\gamma = 1.22 \times 10^{14} \text{ rad s}^{-1}$) is purely metallic in the NIR regime. On the x -axis, the frequency $f = \omega/2\pi$ is given

Figure 2.8b plots the Drude parameters that are used in this book to model the response of gold in the NIR region. They have been adopted from [21]:

$$\omega_p = 1.37 \times 10^{16} \text{ rad s}^{-1} \quad (2.13a)$$

and

$$\gamma = 1.22 \times 10^{14} \text{ rad s}^{-1}. \quad (2.13b)$$

It can be seen that the behavior of this “Drude gold” is purely metallic in the complete range below 300 THz ($1 \mu\text{m}$).

Note that the Drude model is a very simple parametrization of the response of metals. Especially the damping parameter γ depends strongly on the frequency. Therefore, one fit that works for all frequencies is not possible. These issues are discussed in detail in [22].

However, these issues are only problematic when we try to qualitatively and quantitatively predict the response of a given metallic nanostructure. In such cases, tabulated data should be considered. In the plasmonics community, the data of Johnson and Christy is usually used to model the response of gold in the visible spectral region [23]. Recent measurements that span a broad spectral range from 300 nm (1000 THz) to $25 \mu\text{m}$ (12 THz) have been reported in [24]. An extensive list of tabulated dielectric data for gold and respective Drude fits is given in [22]. An overview of tabulated data for noble metals as well as aluminum, lead, and tungsten with the respective Drude fits can be found in [25].

The Drude model offers a simple and easy parametrization for a fundamental analysis where the behavior of metals (but not the exact response of one specific metal) is needed. Therefore, we use the Drude model with the parameters given in (2.13) for the demonstration of different concepts in this book. The modeling of the

materials should be reconsidered as soon as potential resulting devices should be optimized.

As already discussed, strong deviations from the theoretical behavior of the metal are expected close to interband transitions. These resonances of the bound electrons substantially distort the dielectric function. However, they can be described by a similar model, which includes an additional restoring force. The differential equation of this so-called Lorentz model is given by [26]

$$\partial_t^2 \mathbf{u} + \gamma \partial_t \mathbf{u} + \omega_0^2 \mathbf{u} = -\frac{e}{m^*} \mathbf{E}_0^{\text{ext}} e^{-i\omega t}. \quad (2.14)$$

Here, ω_0 is the resonance frequency of the transition. Note, that m^* is the effective mass of the bound electron in the Lorentz model, while it denoted the effective mass of the free electron in case of the Drude model. The stationary solution is given by

$$\mathbf{u} = -\frac{e}{m^*} \frac{1}{\omega_0^2 - i\gamma\omega - \omega^2} \mathbf{E}_0^{\text{ext}} e^{-i\omega t}. \quad (2.15)$$

Similar considerations as for the Drude model result in the dielectric function

$$\varepsilon_L(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - i\gamma\omega - \omega^2}. \quad (2.16)$$

It is important to note that the Lorentz model describes the behavior of the bound electrons for one possible transition, while the Drude model describes the behavior of the free electrons of the metal. The total dielectric function of the metal with all transitions as well as the contribution of the free electrons can be obtained by summing up the respective terms with the correct weights [27]. Dielectrics can be modeled by ignoring the Drude term.

2.2.1.2 Polarizability of Metallic Nanoparticles

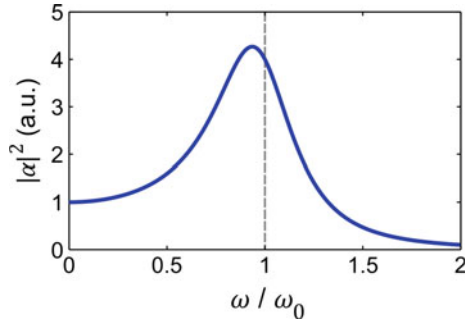
If we do not consider bulk metals but metallic nanoparticles, boundaries due to the finite dimensions of the particle occur. The particle acts as a cavity for the plasma oscillations. This results in non-propagating excitations—the so-called *localized* or *particle plasmons*—at the respective resonance frequency [20].

Let's consider a metallic nanoparticle. The incident electric field $\mathbf{E}_0$ induces a dipole moment $\mathbf{p}$ in the particle. This connection is described by the polarizability $\bar{\bar{\alpha}}$

$$\mathbf{p} = \bar{\bar{\alpha}} \mathbf{E}_0, \quad (2.17)$$

which is, in general, a tensorial quantity. For a spherical particle in vacuum with a radius r much smaller than the wavelength of the incident light, where the electrostatic approximation holds, one obtains the isotropic polarizability

Fig. 2.9 Polarizability of a metallic sphere with $\gamma = \omega_0/2$. One observes a clear Lorentzian lineshape. Note that the maximum polarizability is red-shifted with respect to ω_0



$$\bar{\alpha} \equiv \alpha = 4\pi\epsilon_0 r^3 \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2}. \quad (2.18)$$

The polarizability diverges for

$$\epsilon(\omega) = -2, \quad (2.19)$$

which is the special case of Fröhlich's condition for a sphere in vacuum [20]. Using the Drude model (2.11) for the permittivity $\epsilon(\omega)$ of the sphere,¹⁰ we obtain

$$\alpha = 4\pi\epsilon_0 r^3 \frac{\omega_0^2}{\omega_0^2 - i\gamma\omega - \omega^2}. \quad (2.20)$$

The polarizability shows a resonant behavior with a Lorentzian lineshape. The resonance frequency is given by

$$\omega_0 = \frac{\omega_p}{\sqrt{3}}, \quad (2.21)$$

where ω_p is the plasma frequency of the Drude metal. Note that the polarizability is purely imaginary at resonance indicating a $\pi/2$ phase shift between incident field and the response of the particle, as it is common in resonant systems.

Figure 2.9 shows the resonant behavior of such a particle. In this figure, $|\alpha|^2$ is plotted for different fractions of the resonance frequency for a strongly damped system with $\gamma = \omega_0/2$. As it can be seen, the spectrum does not peak at ω_0 but is red-shifted. The peak is observed at

$$\omega_{\text{peak}} = \sqrt{\omega_0^2 - \frac{\gamma^2}{2}}. \quad (2.22)$$

¹⁰It has been shown that the material properties of metal clusters are similar to those of bulk metals down to cluster sizes of a few nanometers [28]. Therefore, the same Drude parameters as for bulk metals can be used.

Its amplitude is given by

$$|\alpha|_{\text{peak}}^2 = (4\pi\epsilon_0 r^3)^2 \frac{4\omega_0^4}{4\omega_0^2\gamma^2 - \gamma^4} . \quad (2.23)$$

The resonance frequency is independent of the radius for small spherical Drude metal particles. The response depends on the radius as soon as retardation effects come into play. More complicated particles do have polarizabilities that strongly depend on the geometry. For example, the resonance position of linear rod antennas depends on the aspect ratio of the antenna [29].

However, the distinct resonances keep the Lorentzian lineshape. Therefore, they can be modeled as a damped harmonic oscillator similar to the Lorentz model. The resulting response has the same functional form as (2.15). The induced dipole moment can be written as

$$\mathbf{p} = -e\mathbf{u} . \quad (2.24)$$

Comparison with (2.17) leads to

$$\alpha = -\frac{e^2}{m^*} \frac{1}{\omega_0^2 - i\gamma\omega - \omega^2} . \quad (2.25)$$

Note that γ does not denote the damping of the material but the damping of the plasmonic resonance in this case. Of course, the material damping has an influence on this quantity.

2.2.1.3 Plasmon Hybridization in Coupled Plasmonic Nanoparticles

A special class of complex plasmonic nanostructures are coupled nanoparticles. Several simple particles such as spheres are combined to achieve complex optical responses [30, 31]. It has been suggested already in 1985 that the collective response can be derived from the properties of the single nanoparticles similar to molecular orbital theory [32]. Such an analogous model has been introduced in 2003. In the so-called *plasmon hybridization model*, the plasmons of the coupled nanoparticles hybridize and form new collective resonances [33].

The general idea is the following: Consider two plasmonic particles in vacuum with resonances ω_1 and ω_2 . If the cross-coupling ω_{cc} between the particles is weak (i.e., $\omega_{cc} \ll |\omega_1 - \omega_2|$), the individual resonances are only slightly shifted due to the presence of the second particle. In a simple coupled oscillator model, one obtains

$$\omega'_1 = \omega_1 + \frac{\omega_{cc}}{4(\omega_1 - \omega_2)} , \quad (2.26a)$$

$$\omega'_2 = \omega_2 - \frac{\omega_{cc}}{4(\omega_1 - \omega_2)} . \quad (2.26b)$$

Both resonances are weakly split by the same amount as shown in Fig. 2.10a.

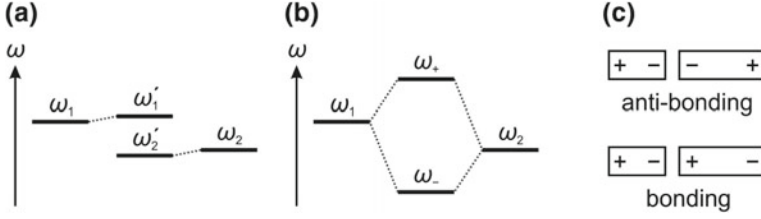


Fig. 2.10 Hybridization of two plasmonic resonances ω_1 and ω_2 . **a** In a weakly coupled system, both resonances are only slightly shifted. **b** In a strongly coupled system, an energy splitting between the two hybrid modes ω_+ and ω_- is observed. **c** The symmetric mode ω_- is lowered in energy while the anti-symmetric mode ω_+ is increased in energy due to the additional electrostatic interaction

In the case of a strongly coupled system with $\omega_{cc} \gg |\omega_1 - \omega_2|$, new hybrid modes ω_+ and ω_- are formed. Their resonance frequencies can be described by

$$\omega_{\pm} = \frac{\omega_1 + \omega_2}{2} \pm \frac{\omega_{cc}}{2}. \quad (2.27)$$

Those hybrid modes split symmetrically around the mean resonance frequency of the two initial plasmon modes (cf. Fig. 2.10b).

One can also look at this splitting from a fundamental physical view, as sketched in Fig. 2.10c. The lower-energy bonding mode is symmetric in its current distribution for both particles: The currents flow in phase. The anti-symmetric anti-bonding mode is higher in energy because additional electrostatic energy is stored in the coupled system due to the charge accumulations.

Note that not all of the hybrid modes are necessarily excitable by an external light source. The bonding mode shows always a strong dipole moment, but the anti-bonding mode results in a charge distribution with lower dipole moment. The dipole moment can vanish in special cases such as two identical particles on the same layer. Such *dark modes* cannot be excited by far-field radiation. Therefore, excitation is not possible by plane waves but may be realized by near-field interaction with other plasmonic nanoparticles.

The plasmon hybridization model not only explains the new hybrid resonances qualitatively, but predicts the resonance energies accurately. However, the coupling between the single plasmons must be quantified, which depends on the specific system. The initial article [33] demonstrated the model for a metallic shell, which can be described as a hybridization of the modes of a sphere and a spherical cavity. The effects of dielectric background media as well as the extraction of polarizabilities for the shell are discussed in [34]. The treatment of dimers consisting of two spherical particles is shown in [35].

2.2.2 *Electronic Models of Chiral Materials*

As shown in Sect. 2.2.1.2, the response of metals can be described by a harmonic oscillator model. However, a single harmonic oscillator (and, accordingly, a single electron in a harmonic potential) is not sufficient to describe the behavior of chiral systems. Several extensions and alternative models for the description of chiral materials have been proposed over more than the last 100 years. A general overview of electronic theories of chiral materials is given in [36]. A more detailed discussion of selected models can be found in [37].

2.2.2.1 Overview of Historic Models

First extensions of the simple oscillator model have been proposed by Drude in 1896, who discussed an electron oscillating on a helical path [38]. However, the model was criticized due to the arbitrary choice of the path [39]. Additionally, Kuhn showed in 1933 that the chiroptical response arising from the model is due to some negligence Drude introduced during his derivation [40].

Condon established a working single-electron model in 1937. Instead of Drude's helical path, the electron is situated in a general chiral potential [41]. This model describes an oscillator in a chiral environment that enforces a helical oscillation. A plasmonic analogue of the Condon model would be a single geometrically chiral nanostructure such as a nanohelix. However, such structures are complicated to fabricate.

As discussed in Sect. 2.2.1.3, the response of many complex plasmonic systems is obtained because of the coupling between several equally contributing oscillators. In this case, a single-electron model seems to be unnatural.

Chiral plasmonic systems of coupled achiral constituents are well described by the so-called Born-Kuhn model, which uses two coupled orthogonal harmonic oscillators with an external driving force to model the chiral behavior [39, 42–44]. Each damped harmonic oscillator describes an electron performing a linear motion. The chiral response originates from the coupling between the electrons.

2.2.2.2 Details of the Coupled Oscillator Model

The system of coupled equations for the Born-Kuhn model is given by [45]

$$\partial_t^2 u_x + \gamma \partial_t u_x + \omega_0^2 u_x + \omega_c^2 u_y = -\frac{e}{m^*} E_{0,x}^{\text{ext}} e^{i(k(z_0 + \frac{d}{2}) - \omega t)}, \quad (2.28a)$$

$$\partial_t^2 u_y + \gamma \partial_t u_y + \omega_0^2 u_y + \omega_c^2 u_x = -\frac{e}{m^*} E_{0,y}^{\text{ext}} e^{i(k(z_0 - \frac{d}{2}) - \omega t)} \quad (2.28b)$$

for a molecule located at $\mathbf{r}_0 = (x_0, y_0, z_0)$ illuminated with a plane wave propagating in z -direction. Note that the $\omega_0^2 u_i$ terms are necessary because chiral responses are

only present at molecular resonances. Therefore, a model without a restoring force (i.e., coupled Drude-like terms) is not sufficient.

Equations (2.28) are similar to the Lorentz oscillator model for resonant media or nanostructures. The Born-Kuhn model additionally implements a coupling between the two oscillators via the coupling parameter ω_c .

However, the coupling alone will not result in a chiral system. Additionally, there must be a non-zero distance d between the two oscillators. It is introduced by the additional phase terms in the driving field. Note that, although the model accounts for the distance between the oscillators in the driving field, the coupling is still instantaneous.

The description of coupled oscillators is similar to our discussion of plasmon hybridization for the special case of two identical oscillators. Therefore, we expect two hybrid modes that are split in energy.

In the following, we will show how this system can be solved. The system of two coupled equations can be decoupled via the transformation

$$u_{\pm} := \frac{1}{\sqrt{2}}(u_x \pm u_y), \quad (2.29)$$

which leads to

$$\partial_t^2 u_{\pm} + \gamma \partial_t u_{\pm} + (\omega_0^2 \pm \omega_c^2) u_{\pm} = -\frac{e}{m^*} E_{\pm}^{\text{ext}} e^{\hat{i}(kz_0 - \omega t)} \quad (2.30)$$

with

$$E_{\pm}^{\text{ext}} = \frac{1}{\sqrt{2}} \left(E_{0,x}^{\text{ext}} e^{\hat{i}k\frac{d}{2}} \pm E_{0,y}^{\text{ext}} e^{-\hat{i}k\frac{d}{2}} \right). \quad (2.31)$$

As expected, we obtain two uncoupled oscillators that describe the normal modes of the coupled system. The resonance frequency without an external driving force is modified by the coupling constant. The lower energy case u_- corresponds to an in-phase oscillation of the two oscillators, while the u_+ case describes the counter-oscillating mode. The system can now easily be solved and reads

$$u_{\pm} = -\frac{e}{m^*} \frac{1}{(\omega_0^2 \pm \omega_c^2) - \hat{i}\gamma\omega - \omega^2} E_{\pm}^{\text{ext}} e^{\hat{i}(kz_0 - \omega t)}. \quad (2.32)$$

We now consider CPL with $\lambda = 4d$ as an external field. This choice leads to

$$e^{\pm \hat{i}k\frac{d}{2}} = e^{\pm \hat{i}\frac{\pi}{4}} = \frac{1}{\sqrt{2}}(1 \pm \hat{i}). \quad (2.33)$$

In this case, we obtain different relations for $E_{\pm}^{\text{ext}}$ depending on the handedness. For LCP, we obtain

$$E_+^{\text{ext}} = E_{0,+} e^{i\frac{\pi}{4}}, \quad (2.34a)$$

$$E_-^{\text{ext}} = 0, \quad (2.34b)$$

where E_0 is the amplitude of the incident electromagnetic field. For RCP, the result is opposite:

$$E_+^{\text{ext}} = 0, \quad (2.35a)$$

$$E_-^{\text{ext}} = E_{0,-} e^{i\frac{\pi}{4}}. \quad (2.35b)$$

Each handedness of CPL excites only one specific normal mode of the coupled oscillators when the wavelength is tuned accordingly to the distance between them. The additional phase term can be attributed to the propagation to the center of the molecule, which is separated by $d/2$ from the first resonator. Any other polarization will excite a superposition of both modes.

2.2.2.3 Constitutive Equations

Throughout the derivation of the constitutive equations of a Born-Kuhn type chiral material, we will use the abbreviation

$$\Omega := \sqrt{\omega_0^2 - i\gamma\omega - \omega^2} \quad (2.36)$$

for convenience.

At first, we have to transform the result from (2.32) back to the Cartesian coordinate system:

$$u_x = -\frac{e}{m^*} \left(\frac{\Omega^2 E_{0,x}^{\text{ext}} e^{ik\frac{d}{2}} - \omega_c^2 E_{0,y}^{\text{ext}} e^{-ik\frac{d}{2}}}{\Omega^4 - \omega_c^4} \right) e^{i(kz_0 - \omega t)}, \quad (2.37a)$$

$$u_y = -\frac{e}{m^*} \left(\frac{\Omega^2 E_{0,y}^{\text{ext}} e^{-ik\frac{d}{2}} - \omega_c^2 E_{0,x}^{\text{ext}} e^{ik\frac{d}{2}}}{\Omega^4 - \omega_c^4} \right) e^{i(kz_0 - \omega t)}. \quad (2.37b)$$

The distance d between the two oscillators leads to a retardation in the excitation between the oscillators for one specific external field $\mathbf{E}_0^{\text{ext}}$.

Of course, the radiation emitted from these oscillators will reach an observer at different times as well. Therefore, the optical response of this system can not be obtained as easily as in the Lorentz model. Instead, both electrons and the finite distance d between them must be considered.

The following derivation is based on [45]. Each single electron of the Born-Kuhn molecule adds $-e\mathbf{u}$ to the induced dipole moment. The first electron, which oscillates only in x -direction, is located at $z_0 = -d/2$, the second one (oscillating in y -direction) at $z_0 = d/2$. Therefore, the polarization of N identically oriented

Born-Kuhn molecules can be calculated using (2.37) as

$$\mathbf{P} = -\varepsilon_0 \frac{\omega_p^2}{\Omega^4 - \omega_c^4} \begin{pmatrix} \Omega^2 & -\omega_c^2 e^{-\hat{i}kd} & 0 \\ -\omega_c^2 e^{\hat{i}kd} & \Omega^2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \mathbf{E}_0^{\text{ext}} e^{-\hat{i}\omega t}. \quad (2.38)$$

The terms proportional to $e^{\pm \hat{i}kd}$ stem from the finite distance d between the electrons. In the limit of small molecules compared to the wavelength ($kd \ll 1$), this exponential term can be expanded to

$$e^{\pm \hat{i}kd} \approx 1 \pm \hat{i}kd. \quad (2.39)$$

The term linear in k describes optical responses due to first-order spatial dispersion [46].

A plane wave propagating in z -direction has no E_z component. Therefore, the external field fulfills

$$\nabla \times \mathbf{E}_0^{\text{ext}} = \begin{pmatrix} -\hat{i}k E_{0,y}^{\text{ext}} \\ \hat{i}k E_{0,x}^{\text{ext}} \\ 0 \end{pmatrix}. \quad (2.40)$$

With this, (2.38) can be rewritten as

$$\mathbf{P} = -\varepsilon_0 \frac{\omega_p^2}{\Omega^4 - \omega_c^4} \left[\begin{pmatrix} \Omega^2 & -\omega_c^2 & 0 \\ -\omega_c^2 & \Omega^2 & 0 \\ 0 & 0 & 0 \end{pmatrix} - d\omega_c^2 \nabla \times \right] \mathbf{E}_0^{\text{ext}} e^{-\hat{i}\omega t}. \quad (2.41)$$

After averaging over all orientations of the Born-Kuhn molecules, one finally obtains the constitutive equation

$$\mathbf{D} = \varepsilon_0 \varepsilon_{\text{BK}} \mathbf{E} + \varepsilon_0 \Gamma \nabla \times \mathbf{E} \quad (2.42)$$

with

$$\varepsilon_{\text{BK}} = 1 + \frac{2}{3} \frac{\omega_p^2 \Omega^2}{\Omega^4 - \omega_c^4} \quad (2.43)$$

and

$$\Gamma = -\frac{d}{3} \frac{\omega_p^2 \omega_c^2}{\Omega^4 - \omega_c^4}. \quad (2.44)$$

The factor $2/3$ in the second term of (2.43) stems from the isotropic averaging because we have only two orthogonal oscillators but three spatial directions. The molecules do not respond to illumination perpendicular to both oscillators. A similar argument explains the factor $1/3$ in (2.44).

Note that ε_{BK} also depends on the coupling parameter ω_c . This means that the presence of a strong chiral response also influences the achiral electrodynamic interaction.

We will now consider the limit of weak chirality, i.e., $\omega_c^4 \ll \Omega^4$. On resonance, this condition reduces to $\omega_c \ll \sqrt{\gamma\omega_0}$. This indicates that any chiral material should be absorptive in this description. After revoking the abbreviation (2.36), we obtain

$$\varepsilon_{\text{BK}} \approx 1 + \frac{2}{3} \left(\frac{\omega_p^2}{\omega_0^2 - \hat{i}\gamma\omega - \omega^2} \right), \quad (2.45)$$

$$\Gamma \approx -\frac{d}{3} \left(\frac{\omega_p^2}{\omega_0^2 - \hat{i}\gamma\omega - \omega^2} \right) \left(\frac{\omega_c^2}{\omega_0^2 - \hat{i}\gamma\omega - \omega^2} \right). \quad (2.46)$$

In the weak chirality limit, ε_{BK} is very similar to the result of the Lorentz model (2.16). The difference is again due to the presence of two orthogonal oscillators and the missing oscillator in the third spatial direction. For Γ , an additional Lorentzian is multiplied, but the coupling parameter ω_c replaces the plasma frequency.

Equation (2.42), together with a similar equation for the magnetic field

$$\mathbf{B} = \mu_0 \mu_{\text{BK}} \mathbf{H} + \mu_0 \frac{\mu_{\text{BK}}}{\varepsilon_{\text{BK}}} \Gamma \nabla \times \mathbf{H}, \quad (2.47)$$

are the Drude-Born-Fedorov constitutive equations for reciprocal chiral media [47]. We will not give the explicit form of μ_{BK} here, because in most realistic systems the magnetic permeability can be set to unity in the optical domain.

For numerical calculations, the Drude-Born-Fedorov form is difficult to handle because of the curl. However, one can transform it to a simpler set of constitutive equations:

$$\mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} - \frac{\hat{i}\kappa}{c} \mathbf{H}, \quad (2.48a)$$

$$\mathbf{B} = \mu_0 \mu \mathbf{H} + \frac{\hat{i}\kappa}{c} \mathbf{E}. \quad (2.48b)$$

The transformation is given via [48]

$$\varepsilon = \frac{\varepsilon_{\text{BK}}}{1 - \frac{\omega^2}{c^2} \frac{\mu_{\text{BK}}}{\varepsilon_{\text{BK}}} \Gamma^2}, \quad (2.49a)$$

$$\mu = \frac{\mu_{\text{BK}}}{1 - \frac{\omega^2}{c^2} \frac{\mu_{\text{BK}}}{\varepsilon_{\text{BK}}} \Gamma^2}, \quad (2.49b)$$

$$\kappa = \frac{\frac{\omega}{c} \mu_{\text{BK}} \Gamma}{1 - \frac{\omega^2}{c^2} \frac{\mu_{\text{BK}}}{\varepsilon_{\text{BK}}} \Gamma^2}. \quad (2.49c)$$

If we assume that the chirality is weak enough that ε and μ do not depend on the chirality of the material, we can approximate the denominator by unity. With the additional approximation $\mu_{\text{BK}} = 1$, we obtain

$$\varepsilon \approx \varepsilon_{\text{BK}}, \quad (2.50a)$$

$$\mu \approx 1, \quad (2.50b)$$

$$\kappa \approx \frac{\omega}{c} \Gamma. \quad (2.50c)$$

Note that κ —exactly as ε and μ —is a dimensionless parameter in this description, while Γ has the dimension of a length.

All these parameters are scalars because we assume an isotropic chiral medium, i.e., the interaction of incident light is independent on the propagation direction. A thorough theoretical description of the electrodynamics of anisotropic chiral materials can be found in [49].

2.2.3 Chiral Optical Far-Field Responses

For isotropic chiral media, the homogeneous wave equation can be obtained similarly as in normal linear media. In the following, we will show this derivation in detail.

Maxwell's curl equation (2.1b) in combination with the constitutive equation for $\mathbf{B}$ (2.48b) leads to

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B} = -\mu_0 \mu \partial_t \mathbf{H} - \frac{\hat{\imath} \kappa}{c} \partial_t \mathbf{E}. \quad (2.51)$$

Then, we can derive

$$\nabla \times \nabla \times \mathbf{E} = -\mu_0 \mu \partial_t \underbrace{\nabla \times \mathbf{H}}_{=\partial_t \mathbf{D}} - \frac{\hat{\imath} \kappa}{c} \partial_t \nabla \times \mathbf{E}. \quad (2.52)$$

Here, the second curl equation (2.1d) has been used. Applying the constitutive equation for $\mathbf{D}$ (2.48a) results in

$$\nabla \times \nabla \times \mathbf{E} = -\frac{n^2}{c^2} \partial_t^2 \mathbf{E} + \mu_0 \mu \frac{\hat{\imath} \kappa}{c} \partial_t^2 \mathbf{H} - \frac{\hat{\imath} \kappa}{c} \partial_t \nabla \times \mathbf{E}. \quad (2.53)$$

Using

$$\partial_t^2 \mathbf{H} = \frac{1}{\mu_0 \mu} \partial_t \left(\underbrace{\partial_t \mathbf{B}}_{=-\nabla \times \mathbf{E}} - \frac{\hat{\imath} \kappa}{c} \partial_t \mathbf{E} \right), \quad (2.54)$$

which is obtained from (2.1b) and (2.48b), one arrives at

$$\nabla \times \nabla \times \mathbf{E} = -\frac{n^2 - \kappa^2}{c^2} \partial_t^2 \mathbf{E} - 2\frac{\hat{t}\kappa}{c} \partial_t \nabla \times \mathbf{E} \quad (2.55)$$

after some sorting.

Equation (2.55) is the chiral wave equation. As for achiral media, we can use the identity

$$\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}. \quad (2.56)$$

The electric field $\mathbf{E}$ can be written as sum of terms proportional to $\mathbf{D}$ and $\mathbf{B}$. Therefore, $\nabla \cdot \mathbf{E} = 0$ for isotropic media and we obtain the following form of the wave equation:

$$\left(\nabla^2 - 2\frac{\hat{t}\kappa}{c} \partial_t \nabla \times - \frac{n^2 - \kappa^2}{c^2} \partial_t^2 \right) \mathbf{E} = 0. \quad (2.57)$$

A similar equation can be derived for the magnetic field.

In isotropic achiral media, the wave equation can be trivially split into three decoupled scalar equations, one for each spatial component (cf. (2.3)). Therefore, any initial polarization state is preserved for isotropic materials [50].

In case of a chiral medium, the appearing curl term leads to a cross-coupling between the spatial components. For a plane electromagnetic wave propagating in z -direction (cf. (2.4)), (2.57) reduces to

$$\left(-k^2 - 2\hat{t}\kappa \frac{\omega}{c} \mathbf{k} \times + \frac{\omega^2}{c^2} (n^2 - \kappa^2) \right) \mathbf{E} = 0 \quad (2.58)$$

with $\mathbf{k} = k\hat{e}_z$. Equation (2.58) results in a system of two coupled equations:

$$\underbrace{\begin{pmatrix} k^2 - \frac{\omega^2}{c^2} (n^2 - \kappa^2) & -2\hat{t}\kappa \frac{\omega}{c} k \\ 2\hat{t}\kappa \frac{\omega}{c} k & k^2 - \frac{\omega^2}{c^2} (n^2 - \kappa^2) \end{pmatrix}}_{=: \bar{\bar{M}}} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = 0. \quad (2.59)$$

We now transform this system into a circular basis using the transformation matrix

$$\bar{\bar{T}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & \hat{t} \\ 1 & -\hat{t} \end{pmatrix}. \quad (2.60)$$

In this system, $\bar{\bar{M}}$ becomes diagonal:

$$\bar{\bar{T}} \bar{\bar{M}} \bar{\bar{T}}^\dagger = \begin{pmatrix} k^2 - 2\kappa \frac{\omega}{c} k - \frac{\omega^2}{c^2} (n^2 - \kappa^2) & 0 \\ 0 & k^2 + 2\kappa \frac{\omega}{c} k - \frac{\omega^2}{c^2} (n^2 - \kappa^2) \end{pmatrix}. \quad (2.61)$$

The corresponding electric field vector is given as

$$\begin{pmatrix} E_+ \\ E_- \end{pmatrix} := \bar{T} \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} E_x + \hat{i} E_y \\ E_x - \hat{i} E_y \end{pmatrix}. \quad (2.62)$$

In a circular basis, the single components of the electric field correspond to circular polarization states. We directly see that E_+ corresponds to LCP, while E_- corresponds to RCP. After this transformation, the system (2.59) simplifies to

$$\left(k^2 \mp 2\kappa \frac{\omega}{c} k - \frac{\omega^2}{c^2} (n^2 - \kappa^2) \right) E_{\pm} = 0. \quad (2.63)$$

This equation shows that the circular polarization states $E_{\pm}$ are the eigenpolarizations of waves propagating in isotropic chiral media. We can derive the corresponding propagation constants $k_{\pm}$ by solving (2.63). These quadratic equations lead, in general, to two solutions:

$$k_{\pm,1} = \frac{\omega}{c} (n \pm \kappa), \quad (2.64)$$

$$k_{\pm,2} = \frac{\omega}{c} (-n \pm \kappa). \quad (2.65)$$

If we enforce $k = \omega n / c$ for vanishing κ , the second solution must be omitted. Therefore, we obtain

$$k_{\pm} = \frac{\omega}{c} n_{\pm}, \quad (2.66)$$

where the refractive indices for the two circular polarizations are given by

$$n_{\pm} = n \pm \kappa. \quad (2.67)$$

Therefore, chiral media are also referred to as a kind of *bi-isotropic medium* in literature.¹¹ The refractive index n can be interpreted as averaged refractive index. It appears for example for unpolarized incident light.

Any non-circular polarization state is altered while propagating through a chiral medium [51]. A special case is obtained for linear polarization. Any linear polarization state can be decomposed into a superposition of LCP and RCP with similar magnitudes. The polarization angle is determined by the relative phase between the circular components. Regarding to (2.67), both components experience a different phase velocity within the chiral medium due to the difference in the real part of the refractive index. This leads to a change of the relative phase of

¹¹ In general, the term “bi-isotropic medium” comprises a wider class of materials with more general constitutive equations (cf. [47]). They are all characterized by two orthogonal eigenpolarizations with opposite handedness.

$$\Delta\phi = 2 \Re(\kappa) l \frac{\omega}{c} \quad (2.68)$$

after a propagation length l .

Due to this phase change, the polarization angle of the light rotates. The rotation angle Θ is given by

$$\Theta = \frac{\Delta\phi}{2} = \Re(\kappa) l \frac{\omega}{c}. \quad (2.69)$$

Additionally, the imaginary part of κ has further influence on propagating plane waves as it induces a differential absorbance for CPL with opposite handedness. Absorbance in a medium with complex refractive index $n_{\pm}$ after a path length l can be written as

$$A_{\pm} = 1 - e^{-2 \Im(n_{\pm}) l \frac{\omega}{c}}. \quad (2.70)$$

This assumes that all attenuation of the intensity is due to absorption; no scattering is observed. Then, the differential absorbance is given by

$$\Delta A = -e^{-2 \Im(n) l \frac{\omega}{c}} \underbrace{\left(e^{-2 \Im(\kappa) l \frac{\omega}{c}} - e^{2 \Im(\kappa) l \frac{\omega}{c}} \right)}_{=-2 \sinh(2 \Im(\kappa) l \frac{\omega}{c})}. \quad (2.71)$$

Compared to (2.70), the first exponential is connected to the averaged absorbance A in the medium. Therefore, we obtain

$$\Delta A := A_{+} - A_{-} = 2(1 - A) \sinh \left(2 \Im(\kappa) l \frac{\omega}{c} \right), \quad (2.72)$$

For small values of κ , which is normally the case, a first-order Taylor expansion of the hyperbolic sine in (2.72) results in

$$\Delta A \approx 4(1 - A) \Im(\kappa) l \frac{\omega}{c}. \quad (2.73)$$

Note that A also depends on l . Therefore, ΔA does in general not depend linearly on l , but is approximately linear in $\Im(\kappa)$.¹²

Equations (2.68) and (2.73) describe the so-called *optical rotatory dispersion* (ORD) (or *natural optical activity*) and the *circular dichroism* (CD), respectively. Those are the most common chiroptical responses that can be observed.

Note that κ is dispersive, as discussed in Sect. 2.2.2.3. Its real and imaginary part are Kramers-Kronig related [52]. Figure 2.11 shows typical results obtained from the

¹²In chemistry, the differential molar extinction coefficient is often used instead of the differential absorbance. This quantity describes the chiroptical properties of a chiral molecule independent of external influences such as path length or concentration (cf. Appendix A).

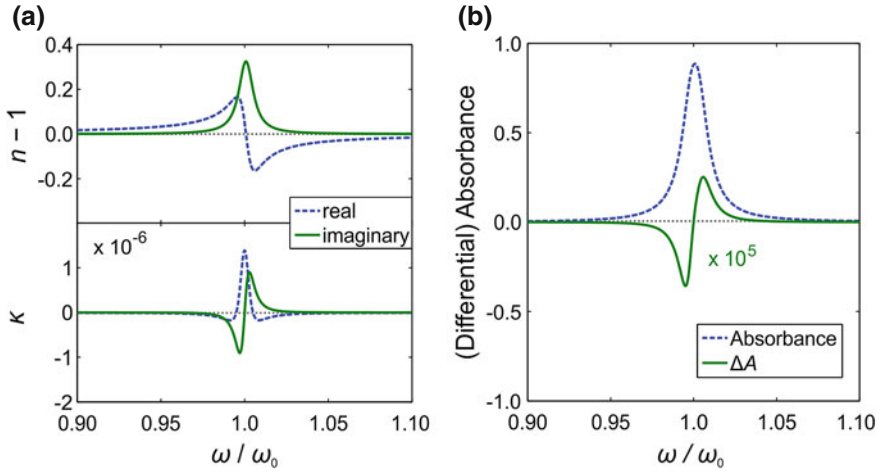


Fig. 2.11 Results of the Born-Kuhn model for a hypothetical chiral material. **a** Refractive index n and chirality parameter κ . The real part of n has been shifted by -1 . **b** Absorbance and resulting CD. The chiral response is five orders of magnitude smaller than the achiral one. All frequencies are relative to ω_0

Born-Kuhn model.¹³ The CD is five orders of magnitude smaller than the absorbance. ORD would follow exactly the same shape as the real part of κ . Note that the CD curve shows a bisignate lineshape. This is due to the different modes that are selectively excited by the respective circular polarization.

2.3 Realization of Chiral Materials

After the theoretical considerations in Sect. 2.2, we will now focus on natural as well as artificial chiral materials, for which the discussed responses can be observed.

2.3.1 Chiral Molecules

A very important example for geometrical chirality in nature can be found in biochemistry. In fact, most biomolecules such as, e.g., all of the essential amino acids, are geometrically chiral [53].

¹³The following parameters have been used: $\omega_0 = 500$ THz, $\omega_p = 50$ THz, $\gamma = 5$ THz, $\omega_c = 2.5$ THz and $d = 1$ nm. The path length $l = 2$ μ m has been chosen such that strong absorption on resonance is obtained. Therefore, the absorption per unit length is much stronger than for most natural chiral materials.

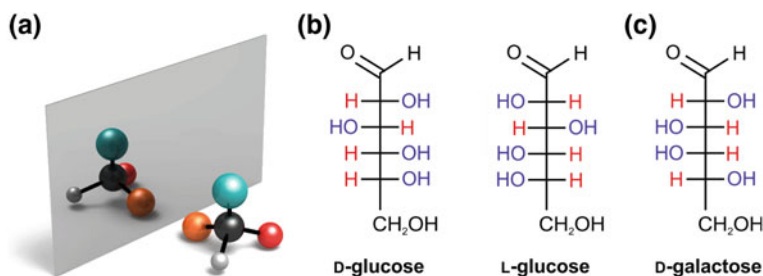


Fig. 2.12 **a** A carbon atom bound to four differently sized atoms is geometrically chiral. This configuration is the prototypical example of a chiral molecule. **b** Real chiral molecules, such as the glucose molecule, can consist of several chiral centers. **c** If only some of the chiral centers are changed, one obtains a diastereomer

One geometrical origin of chirality in molecules is sketched in Fig. 2.12a. It depicts a carbon atom that is bound to four atoms of different sizes. These size differences render the whole configuration geometrically chiral. An intuitive handedness definition is not possible for such an arrangement.

However, one can compare the spatial configurations of molecules via their Fischer projection and, in this way, find a nomenclature where the relative handedness is consistent. Glyceraldehyde has been chosen as a reference molecule to introduce an absolute nomenclature. The two enantiomers are labeled D (*dexter*, right) and L (*laevus*, left) [54]. However, several other naming conventions are used in stereochemistry [55].

Figure 2.12b sketches a more complex example: the glucose molecule, which consists of four carbon atoms with different groups attached. In nature, one commonly finds the right-handed D-glucose. If not all but only few of the chiral centers change their handedness, one speaks of *diastereomers* (cf. Fig. 2.12c).¹⁴

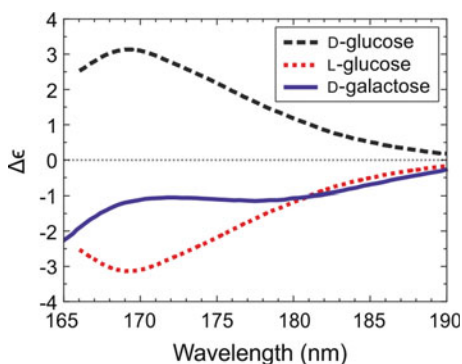
Figure 2.13 depicts the UV part of the CD spectra of these three sugars.¹⁵ The values for D-glucose and D-galactose have been measured in [56]; the values for L-glucose have been calculated from those of D-glucose for demonstration purposes. Theory predicts that they must be exactly opposite.

Note that the spectra of the diastereomers differ significantly. While glucose has only one chiroptically active band in the depicted region, one can identify two for galactose. Additionally, the plot shows that it is difficult to extract handedness information from CD measurements. D-glucose and D-galactose are both in their D-form, but exhibit different signs of their CD signal in the same wavelength range. Therefore, one needs substantial knowledge about the analyzed system to extract information from CD studies.

¹⁴Strictly speaking, only L-glucose and D-galactose are diastereomers. D-glucose and D-galactose, who differ in exactly one chiral center, are called *epimers*.

¹⁵In this figure, $\Delta\epsilon$ is the molar differential extinction coefficient. Please refer to Appendix A for an explanation of the different units used in CD spectroscopy.

Fig. 2.13 CD response of the sugars depicted in Fig. 2.12. The data for the D-sugars has been obtained from [56]. The curve for L-glucose has been calculated from D-glucose [Adapted with permission from [56]. Copyright 1972 American Chemical Society.]



In addition to simple chiral centers around carbon atoms, larger molecules can form geometrically chiral arrangements. The best-known example is DNA with its double-helix, other examples include the secondary structure of proteins or helicene, which is a helical arrangement of benzene rings [57].

2.3.2 Chiral Plasmonic Nanostructures

Metallic nanoparticles can be used to create systems that exhibit much higher chiroptical responses. The induced electric and magnetic dipole moments in plasmonic nanostructures are several orders of magnitude higher than those in any natural molecule because of the large number of electrons involved. Therefore, similar effects as found in natural molecules can be studied in *plasmonic molecules*, but with much stronger responses [2].

The “atoms” of such plasmonic molecules are single nanoparticles, whose collective response is studied. As discussed in Sect. 2.2.1.3, the response of such complex plasmonic molecules can be obtained by the plasmon hybridization model. Examples for complex collective behavior include artificial aromatic molecules [58], Fano resonances [59], or electromagnetically induced transparency [60, 61] and absorption [62, 63].

Of course, the effects of geometrical chirality can also be studied in such plasmonic molecules [64]. The analogue of the chiral molecule discussed in Fig. 2.12a would be a tetrahedral arrangement of four differently sized plasmonic particles as introduced in [65]. However, the CD response of such an arrangement is rather weak because the single particles are detuned in resonance frequency and oscillator strength. Therefore, they couple only weakly and act more like individual particles.

Stronger coupling is obtained for similar particles. The tetrahedral arrangement of similar spherical particles, however, is geometrically achiral. Therefore, it has been suggested to use similar particles, but arrange them in a way that leads to geometrical chirality. Such structures are called *chiral plasmonic oligomers* [66].

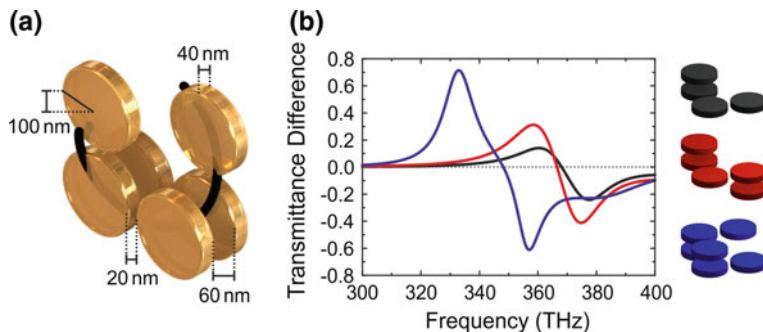


Fig. 2.14 **a** Sketch of a chiral plasmonic oligomer. The arrangement of the gold disks mimics the geometrically chiral structure of a left-handed helix. **b** Calculated transmittance difference for different chiral plasmonic oligomers. The absolute values increase with the number of gold disks

The implementation is sketched in Fig. 2.14a. The chiral plasmonic oligomer is based on a bi-layer structure. Each layer consists of three gold disks which are arranged in an L-shaped configuration. The second layer is twisted by 90° to emulate the chiral layout of a helix. The dimensions chosen in the sketch lead to a resonance in the near-IR with maximum chiroptical response at 333 THz (900 nm).

Figure 2.14b shows the simulated chiroptical far-field response of the structure aligned in a periodic array with an unit cell of 650 nm.¹⁶ Note that one does not need six disks to obtain geometrical chirality and the subsequent chiroptical response. Four particles, correctly arranged, are sufficient. Therefore, Fig. 2.14b additionally contains the simulated response for chiral plasmonic oligomers with five and four particles. However, by reducing the number of disks, the chiroptical response is weakened.

Additional disks lead to a stronger chiral coupling and, therefore, a stronger chiroptical response. Of course, adding these disks must not destroy the geometrical chirality of the structure. Therewith, the maximum performance of such designs is limited. Note that the theoretical response of such a monolayer with a thickness well below one micron is several orders of magnitude larger than for natural chiral molecules measured with a path length in the range of millimeters.

The simple design with four individual disks (but slightly different dimensions) has been experimentally investigated in [66], the six-disk structure is discussed in [67]. Figure 2.15a depicts the obtained transmittance difference of the four-disk oligomer. Both the mirror symmetry of the response of the enantiomers as well as the independence of the response to the orientation of the sample can be clearly seen. The transmittance difference of more than 7% is much higher than for any natural chiral molecule.

¹⁶For most plasmonic systems, we show the transmittance difference ΔT instead of ΔA . Both responses contain equivalent information as long as no differential reflectance occurs (cf. Appendix A).

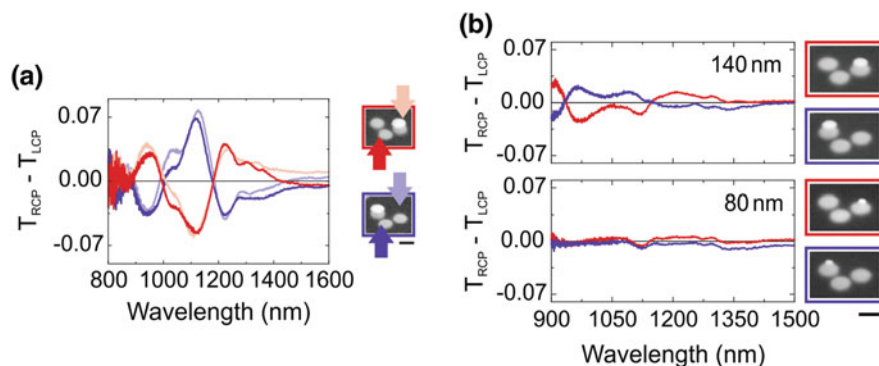


Fig. 2.15 **a** Differential transmittance of a four-disk chiral plasmonic oligomer illuminated from top and from bottom [Reprinted in part with permission from [66]. Copyright 2012 American Chemical Society.] **b** The differential signal vanishes when the upper disk becomes smaller [Reprinted in part with permission from [66]. Copyright 2012 American Chemical Society.]

Note that a supercell of four oligomers has been used for the periodic arrangement to ensure C_4 symmetry of the whole array. It can be shown by group theory that only symmetry groups C_3 or higher support CPL as eigenpolarization [68]. For lower symmetries, elliptical birefringence would lead to circular polarization conversion that could be erroneously interpreted as transmittance difference signal [69].

Figure 2.15b demonstrates the importance of resonant coupling: Reducing the size of the disk in the upper layer and, thereby, detuning of the resonance will significantly weaken the chiroptical response. By this means, the chiroptical response vanishes, although the structure stays geometrically chiral. However, from a plasmonic point of view, we obtain several weakly coupled achiral structures instead of one chiral geometry.

The combination of several of these oligomers in one plasmonic molecule leads to a plasmonic analogue of diastereomers [70]. It could be shown that the chiroptical response of such diastereomers can be decomposed into the sum of the responses of the single chiral centers as long as these centers in the plasmonic molecule are sufficiently decoupled. More details about different combinations of these chiral centers can be found in [71].

The chiroptical response of plasmonic oligomers can in principle be explained by the Born-Kuhn model because it arises due to coupling between similar constituents. The direct plasmonic realization of this model is obtained by two corner-stacked bars [72].

The simulated response is shown in Fig. 2.16a for the right-handed enantiomer. The length of each rod is 223 nm, the width and thickness 40 nm. The structure has been calculated in a C_4 arrangement with a periodicity of the supercell of 800 nm. The system has been embedded in an environment with a refractive index of $n = 1.5$. We obtained almost perfect selective excitation of the two normal modes (cf. Sect. 2.2.2.2) due to the matched distance (120 nm) between the rods.

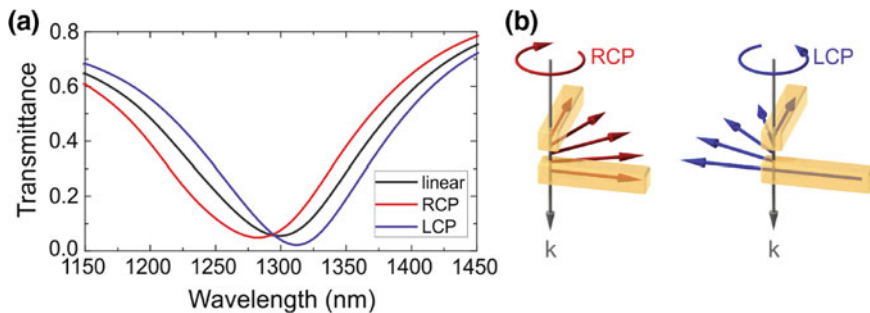


Fig. 2.16 **a** Simulated response of a right-handed corner-stacked rod structure illuminated with linear polarization and CPL. **b** The two hybrid modes are selectively excited by RCP and LCP if the distance between the rods is chosen accordingly

An intuitive explanation of this selective excitation can be obtained by analyzing the normal modes of the system via a plasmon hybridization approach. As shown in Fig. 2.16b, the anti-bonding and the bonding mode are selectively excited by RCP and LCP, respectively. The electric field vector rotates while traveling the distance between the two rods.¹⁷ Depending on the handedness of the light, either an out-of-phase or an in-phase oscillation of the second rod is induced. Both modes hybridize, with the out-of-phase mode being of higher energy due to the accumulation of charges of the same sign at the corner. Therefore, a strong transmittance difference for the two polarizations is obtained.

The strength of the chiroptical response depends on the coupling strength (and, therefore, the splitting) as well as the width and the modulation of the plasmonic resonance. Note that a reduced distance will lead to a reduced suppression of the second mode for one circular polarization. However, the chiroptical response might still be larger due to the stronger coupling. Additional theoretical insights into chiral plasmonic dimers can be obtained from [73–75].

So far, only coupling of similar geometrically achiral constituents has been discussed. However, complex plasmonic structures can lead to sophisticated responses without coupling. A simple example of such a geometry is the so-called split-ring resonator (SRR), which is depicted in Fig. 2.17a. When the structure is excited parallel to the gap, an electric dipole moment is induced in the gap. However, the charge oscillation must follow the bend of the structure. This leads to an induced ring current. Therefore, the structure also exhibits a magnetic dipole moment pointing out of the plane.

The orthogonality of the dipole moments can be eliminated when one of the ends of the SRR is uplifted. In this case, a helical geometry, which is geometrically chiral, is achieved. The magnetic dipole moment will still point along the axis (as in a coil), but the electric dipole moment is rotated to point from one end to the other

¹⁷ In the detector's view convention, LCP rotates to the left while RCP rotates to the right. Therefore, such analysis can be performed rather intuitively in the chosen convention.

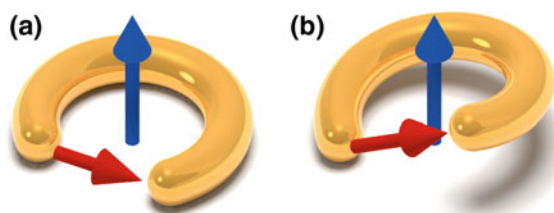


Fig. 2.17 **a** A SRR exhibits an electric (*red*) and magnetic (*blue*) dipole moment. **b** When one of the ends is bent upwards, both dipole moments are not orthogonal anymore. The resulting helical geometry is chiral

of the structure. Thus, both dipole moments feature parallel components. Following Rosenfeld's calculations, this will lead to a chiroptical response in case of molecules [76]. Therefore, such structures are also expected to show chiroptical response in the plasmonic case.

One recent realization of this idea is given in [77], where a gold ramp has been fabricated.¹⁸ Interestingly, even the response of this complex design can be explained qualitatively by the Born-Kuhn model. In this case, higher-order modes are used instead of the hybridized collective modes.

However, the Born-Kuhn model breaks down when the complexity is further increased. Specifically designed helices with two turns can lead to a broadband transmittance dip for one circular polarization, which involves coupling of three plasmonic modes [78, 79]. Theoretical discussions of complex three-dimensional chiral nanostructures such as Möbius strips are given in [80–82].

Fabrication of geometrically chiral plasmonic structures is non-trivial. Figure 2.18 shows some examples of nanostructures fabricated with different methods.

The chiral plasmonic oligomer has been fabricated via electron-beam lithography (EBL) using a stacking procedure first described in [21]. Such two-layer geometrically chiral metamaterials have been extensively studied in literature [84–90]. Additional layers lead to even more sophisticated designs [91, 92]. A special class of lithographically defined chiral metamaterials works without stacking at all. Here, a geometrically planar chiral structure is fabricated on top of a substrate. Therefore, the mirror symmetry is broken in propagation direction [93–97]. This demonstrates that not only the plasmonic structure but also its surrounding play a crucial role for the chiroptical response. However, the interaction of at least two plasmonic modes is necessary to obtain the reported CPL transmittance difference [98]. Besides the symmetry-breaking due to the substrate, also fabrication imperfections that lead to differences between the top and the bottom of the structure play an important role for such responses [99].

¹⁸Note that the fabrication method does not allow for C_3 or C_4 symmetry. However, the structure has been measured from both sides to eliminate the influence of circular conversion dichroism, which exhibits opposite sign for backward illumination.

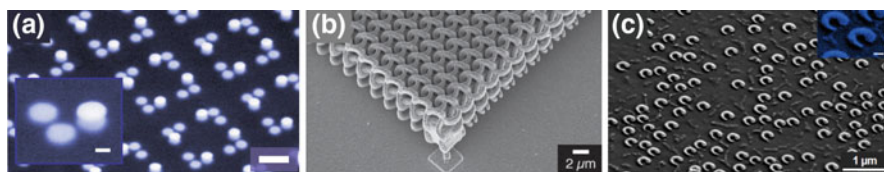


Fig. 2.18 Different examples for complex geometrically chiral nanostructures fabricated with different methods. **a** Chiral plasmonic oligomer fabricated by two-step EBL. [Reprinted in part with permission from [66]. Copyright 2012 American Chemical Society.] **b** Bi-chiral plasmonic crystal fabricated by DLW. [Reprinted in part with permission from [83]. Copyright 2011, John Wiley & Sons, Ltd.] **c** Plasmonic ramp fabricated by colloidal lithography with tilted angle evaporation [Reprinted in part with permission from [77]. Copyright 2012 American Chemical Society.]

Although EBL is a powerful and well-established technique, it is restricted to layered geometries. More sophisticated designs are possible by combination with other techniques. For example, lithographic steps [100–102] or asymmetric evaporation [103] on a prestructured template can lead to fully three-dimensional geometrically chiral structures. Other fabrication techniques for such designs include direct laser writing (DLW) [78, 83, 104, 105], glancing angle deposition (GLAD) [106, 107], electron- and ion-beam induced deposition [108–112], anisotropic etching [113] or colloidal lithography with tilted angle evaporation [77]. GLAD has also been used to fabricate chiral templates, on which achiral plasmonic nanoparticles can be attached in a subsequent step [114, 115]. An even more exotic technique utilizes the strain in heterostructured films [116]. The chiroptical response of such so-called Swiss-roll metamaterials has been analyzed in [117].

In recent years, self-assembly techniques have been adopted to fabricate geometrically chiral nanostructures that are fully three-dimensional. In these methods, small nanoparticles are linked together to a precisely controllable geometry, for example via a DNA template. Both tetrahedral arrangements of differing nanoparticles [65, 118–120] as well as geometrically chiral arrangements of similar building blocks [121–129] have been demonstrated.

Additional complexity can be added to steer the chiral properties of such metamaterials. In the THz region, silicon can be switched into the conducting state under optical illumination. This mechanism has been combined with a sophisticated design to obtain a metamaterial with switchable handedness [130]. Phase change materials, such as germanium antimony telluride, allow for control over the chiroptical response in the NIR [131]. Magnesium has been used for a simple on/off switching of the chiroptical response with hydrogen [132]. Geometric reorientation of the chiral structures with respect to the incident light [12], or even reconfiguration of the structure itself [133], is possible with self-assembly techniques.

Much work has been devoted into control and tailoring of the chiroptical far-field response of artificial chiral materials. This is useful to study chirality and influences of the geometry on the resulting chiroptical spectra. Additionally, any application related to circular polarization such as circular polarizers or polarization converters highly benefit from this research. However, the chiroptical response is obtained by

the choice of the structure. The problem of enantiomer discrimination needs a method of increasing the response of a specific chiral analyte, which will be discussed in the following chapters.

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