

Interpreting Chiral Nanophotonic Spectra: The Plasmonic Born–Kuhn Model

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Supporting Information

ABSTRACT: One of the most intuitive ways to classically understand the generation of natural optical activity in chiral media is provided by the coupled oscillator model of Born and Kuhn consisting of two identical, vertically displaced, coupled oscillators. We experimentally realize and discuss its exact plasmonic analog in a system of corner-stacked gold nanorods. In particular, we analyze the arising circular dichroism and optical rotatory spectra in terms of hybridized electromagnetic modes and retardation. Specifically, we demonstrate how tuning the vertical distance between the nanorods can lead to a selective excitation of the occurring bonding and antibonding chiral plasmonic modes.



KEYWORDS: Chirality, plasmonics, circular dichroism, optical rotation, optical activity, plasmon ruler

Tatural optical activity sparked the development of stereochemistry. The discovery of its intimate link with chirality, that is, the property of an object of not being superimposable onto its own mirror image,¹ inevitably implied three-dimensional molecular structures. For more than a century, its manifestation as circular dichroism (CD) and optical rotatory dispersion (ORD) in optical spectra of chiral molecules has been used as a powerful analytic tool ranging from the determination of sugar concentration in wine to quality control in pharmaceutically relevant processes.² In particular, CD-spectroscopy is well-suited for conformational and structural analysis in complex biomolecules such as proteins,³ thereby having revealed secondary and tertiary structures. However, these chiroptical spectroscopy methods only work well for high concentrations of chiral analytes. Recently, it has been suggested to use plasmonic nanostructures to boost the sensitivity of this method by generating superchiral electromagnetic near-fields⁴⁻¹² or exploiting their acute response to their immediate environment.¹³⁻¹⁷ These efforts ultimately aim at boosting the limit of detection of chiroptical spectroscopy to the single molecule level as has already been demonstrated for plasmonically enhanced absorption spectros-copy.¹⁸⁻²¹ To this end, it is instructive to study the optical modes of chiral plasmonic structures themselves. A lot of work has already been done in this field, demonstrating that, indeed, artificially engineered systems can give rise to natural optical activity.²²⁻²⁸ Furthermore, the associated calculated and measured effects are orders of magnitude larger than in naturally occurring substances, thereby also paving the way for a range of applications such as ultrathin wave-plates^{29,30'} and negative index metamaterials.^{31–33} While chiral structures were initially largely fabricated using top-down methods such as electron beam lithography, progress in bottom-up fabrication

techniques has enabled DNA-self-assembled chiral plasmonic structures. $^{\rm 34-38}$

In this Letter, we take a systematic look at the most fundamental chiral plasmonic structure to provide a tool to intuitively dissect, analyze, and understand more complex situations. Drawing inspiration from the classical theories of optical activity, we investigate a plasmonic version of the simplest system exhibiting chiroptical responses: two coupled, vertically displaced electrons of mass m that carry out orthogonal harmonic oscillations driven by an external light field (Figure 1a).^{39,40} The ansatz of using an oscillating charged particle is well-known from the derivation of optical properties of materials within the Drude-Lorentz model. The Born-Kuhn model differs in that it employs two instead of one charged particle and that these are coupled to each other. It is intuitively clear that such a system will lead to polarization rotation for incident linearly polarized light. Let incident linearly polarized light that is polarized along the y-direction strike the upper oscillator, which is confined to movement in y-direction. The coupling between the two particles will set the second oscillator oriented along the *x*-direction into movement as well. The resulting direction of the oscillation of the centerof-mass of the system will, therefore, differ from the y-direction, thus leading to a polarization rotation. One can immediately see that this describes a chiral system by drawing out the right (D) - and left (L)-handed enantiomers.

In order to study the value of the rotation and its associated circular dichroism, one needs to determine the resulting complex refractive indices of left-and right-handed circularly

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Figure 1. (a) Right (D)- and left (L)-handed classical coupled-oscillator models of optical activity. (b) Optical rotatory dispersion (ORD) and circular dichroism spectra (CD) calculated from the right-handed coupled-oscillator model.

polarized light.³ Consequently, one proceeds analogously to the derivation of permittivity within the Drude–Lorentz model by setting up and solving the equations of motion as treated in Svirko and Zheludev⁴¹

$$\ddot{x}(t) + \gamma \dot{x} + \omega_0^2 x(t) + \xi y = -\frac{e}{m} E_x e^{-i\omega t + ik(z_0 + d/2)} + \text{c.c.}$$
(1a)

$$\ddot{y}(t) + \gamma \dot{y} + \omega_0^2 y(t) + \xi x = -\frac{e}{m} E_y e^{-i\omega t + ik(z_0 - d/2)} + \text{c.c.}$$
(1b)

where c.c. means the complex conjugate, γ denotes the loss in the oscillators, ω_0 is the eigenfrequencies of the uncoupled oscillators, ξ is the coupling constant between the two oscillators, *m* is their masses, *e* is their charges, z_0 is the position of their center, and *d* is the distance between them. The remaining variables are used according to standard notation as in, for example, Jackson.⁴² Note the different phase factors of eqs 1a and 1b resulting from their different relative positions on the *z*-axis. This results in a polarization density for isotropically oriented molecules of

$$\mathbf{P}(\omega, r) = \varepsilon_0(\varepsilon - 1)\mathbf{E}(\omega, \mathbf{r}) + \Gamma \nabla \times \mathbf{E}(\omega, \mathbf{r})$$
(2)

where

$$\varepsilon = 1 + \frac{2N_0 e^2}{3m} \frac{\omega_0^2 - i\gamma\omega - \omega^2}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2}$$
(3a)

$$\Gamma = \frac{dN_0 e^2}{3m} \frac{\xi}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2}$$
(3b)

From eq 2 and using the relation $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$, we obtain the constitutive equation

$$\mathbf{D}(\omega, \mathbf{r}) = \varepsilon_0 \varepsilon \mathbf{E}(\omega, \mathbf{r}) + \varepsilon_0 \Gamma \nabla \times \mathbf{E}(\omega, \mathbf{r})$$
(4)

which is the Drude–Born–Fedorov form of the constitutive equation for isotropic reciprocal spatially dispersive media with nonlocality parameter Γ . Solving the respective Fresnel equation for propagation in *z*-direction⁴⁴ results in

$$n_{\rm R,L}^2 = \overline{n}^2 \pm \Gamma \overline{n} \tag{5}$$

where $\overline{n} = (n_{\rm L} + n_{\rm R})/2$ is the average refractive index of the chiral material. The associated modes correspond to right-handed and left-handed circularly polarized light described by the ratios $E_x = \mp i E_y$.⁴³ The difference between the refractive indices $\Delta n = n_{\rm R} - n_{\rm L}$ for right-handed circularly polarized light (RCP) and left-handed circularly polarized light (LCP) determines CD and ORD and can be obtained from eq 5 as $\Delta n = \Gamma$. Note that Γ and, therefore, Δn are complex quantities whose real parts are responsible for optical rotatory dispersion (per unit length) through the relation

$$\theta = \frac{\Delta nk}{2} = \frac{\omega}{2c} \mathcal{R}e(\Gamma) \tag{6}$$

Furthermore, the differential absorption of LCP and RCP light is governed by $Im(\Delta n)$. Employing Lambert–Beer's law of absorption (per unit length)

$$A_{\rm L} - A_{\rm R} = 2\frac{\omega}{c} Im(\Gamma) \tag{7}$$

yields a CD-spectrum with a typical bisignate shape (Figure 1b). Note that CD and ORD are Kramers-Kronig-related as they are derived from the same expression.

The molecular analog of the Born–Kuhn model can be, for example, found in the two-chromophore coupling of optically active molecules, where each of the chromophores by itself is achiral. A chemical compound that can be described in such a way is 1,1'-bi-2-naphthol (BINOL),⁴⁵ which exhibits the characteristic bisignate line shape in the UV spectral range of its CD-spectrum.

The plasmonic version of the Born-Kuhn configuration can be realized as two identical corner-stacked, vertically displaced nanorods that have a 90° angle between them because the collective excitation of the electron cloud in a nanorod can be well approximated by a harmonic oscillator^{46,47} (Figure 2a). The coupling between the plasmonic resonators can be mediated conductively or capacitively through near-field coupling. Similar configurations have been evaluated in the literature, however, without a full analysis and discussion of the chiral optical modes.^{48,49} In more complex plasmonic chiral systems, the Born–Kuhn system is oftentimes contained as a subsystem; sometimes even more than once.^{30,50–53} Therefore, understanding its chiral optical modes can help explain more complicated spectra. These corner-stacked orthogonal nanorods can be thought of as the chiral equivalent to the plasmonic dimer,⁵⁴⁻⁵⁷ which consists of two nanorods that are positioned next to each other on the same plane either along their long or short axis. Therefore, one can easily understand the sign and spectral position of the arising optical modes in terms of a hybridization model. For a qualitative assessment, we assume a vertical spacing d that corresponds to an effective phase difference of $\pi/2$ between the two nanorods. This stems from the retardation that occurs due to the finite velocity of the electromagnetic perturbation. Given the D-enantiomer, we can study its interaction with right-and left-handed circularly polarized light. RCP incident light traveling in -z-direction is assumed to have its polarization aligned with the upper nanorod when it strikes it. The helix drawn out in space by the field vector at this fixed time is right-handed and its field vector is aligned with the lower nanorod as well because it is positioned at an effective quarter wavelength distance in -z-direction (Figure 2b).



Figure 2. (a) Left- and right-handed plasmonic realizations of the Born–Kuhn model. (b) Modes excited by right- and left-handed circularly polarized light for the D-enantiomer with rods spaced at an effective quarter-wavelength. (c) Hybridization model for chiral plasmonic Born–Kuhn modes.

Therefore, it will drive the electron oscillations in both nanorods in phase at every time. Hence, the symmetry of the light implies the excitation of a mode that corresponds to the antisymmetric case in the coupled oscillator model. This can be thought of as an antibonding mode (Figure 2c) as charges of the same sign will accumulate at the ends of the two nanorods. Similarly, LCP incident light first impinges on the upper nanorod, rotates counter-clockwise for a quarter wavelength and then antialigns with the lower nanorod (Figure 2b). Therefore, due to its inherent symmetry, LCP excites a bonding mode with opposite charges located at the corner where the nanorods are stacked. The resulting energy level for the bonding mode is lower than that of the individual nanorod due to the favorable arrangement of charges whereas the antibonding mode lies at higher energies (Figure 2c). Note that due to the choice of the vertical displacement, one obtains a selective excitation of bonding and antibonding modes. The reasoning for the L-enantiomer is analogous and leads to swapped bonding and antibonding modes.

In contrast to naturally occurring molecules, the plasmonic Born–Kuhn system has the advantage that one can tune various parameters at will, specifically the inter-rod distance. This conveniently allows us to tailor the distance such that we realize the effective $\pi/2$ phase difference assumed above. In nature, the

distances between chromophores are much smaller than a quarter wavelength, therefore rendering a selective excitation of the described modes impossible. Also, the nanorods do not have to be corner-stacked in order to show optical activity. For example, a geometry where the nanorods are stacked at their center has been theoretically proposed.⁵⁸ However, this setup does not allow for particles that have a 90° angle between them to be chiral.

We carried out finite full-field simulations using a self-written code implementing the Fourier Modal Method with adaptive spatial resolution⁵⁹ of the plasmonic Born-Kuhn setup using gold nanorods that have length l = 223 nm, height h = 40 nm, and width w = 40 nm. The nanorods are arranged in a C_4 -symmetric supercell^{24,60} in order to avoid anisotropy effects that lead to polarization conversion. These supercells serve as unit cells for our simulations that are periodic with period p =800 nm in x- and y-direction. The excitation is implemented via a plane wave source angled at 17°, which corresponds to the average excitation angle we have in our measurement setup. The whole system is embedded in a dielectric environment with refractive index n = 1.5 (corresponding to PC403). By varying the vertical interparticle distance and monitoring the induced currents and transmission spectra for LCP and RCP light, we found that, indeed, a selective excitation of bonding and antibonding modes occurs for d = 120 nm as shown in Figure 3. ORD has been calculated by evaluating the orientation of the polarization-ellipse upon illumination with linearly polarized light.

Using these optimized parameters, we experimentally realized the plasmonic Born-Kuhn system using a two-step electron beam lithography procedure 61 (Figure 3c) (Supporting Information). The spectra for left-and right-handed circularly polarized light passing through a D-enantiomer are plotted in (Figure 3b, upper plot). One can clearly see two Lorentzian curves for the circularly polarized transmittance spectra. As expected from our simple qualitative reasoning, the RCP mode lies at lower wavelengths (1290 nm), that is, higher energies, therefore, corresponding to a bonding mode. Additionally, the LCP mode is located at longer wavelengths (1325 nm), that is, lower energies and can be identified as the bonding mode. The transmittance spectrum of linearly polarized light corresponds to the average of the LCP and RCP transmittance spectra because linearly polarized light is composed of equal parts of LCP and RCP light. Its peak is located at 1300 nm. The CD spectrum exhibits the characteristic bisignate line shape that can be associated with pure Born-Kuhn type systems with extrema appearing at 1250 and 1350 nm. The CD spectra for D- and L-enantiomer are exactly mirror symmetric to each other. It is clear how the signs of the CD peaks are determined. Evaluating the expression $\Delta T = T_{\rm R} - T_{\rm L}$ for the D-enantiomer, one obtains a negative sign of the CD peak at 1250 nm and a positive sign for the peak at 1350 nm with a zero crossing at 1300 nm. Similarly, the L-enantiomer exhibits the opposite behavior due to its switched modes. These properties can be directly predicted by our chiral hybridization model. The fabricated structures show no detectable polarization conversion. Additionally, the spectra remain identical when being recorded from the reverse, which is the hallmark of truly biisotropic, that is, chiral systems because it means that the structures are time reversal symmetric (S1 in Supporting Information). The ORD curves for D- and L-enantiomers follow the line shape of the Kramers-Kronig-related curve of the CD spectrum with a maximum rotation angle of 20° at 1300 nm.

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Figure 3. (a) Full-field simulations of transmittance, CD, and ORD spectra of the C₄-symmetrically arranged right-handed enantiomer with 120 nm vertical separation. (b) Measured transmittance, CD, and ORD spectra of fabricated structures (c) SEM micrograph of fabricated left-handed enantiomer.

We simulated and prepared a second sample with an interlayer distance of d = 60 nm, whose spectra can be seen in (Figure 4). Here, the transmittance spectra for RCP and LCP do not follow a single Lorentzian line shape anymore. Moreover, one can see that RCP light not only excites the higher energy antibonding mode but also the lower energy bonding mode. However, the antibonding mode is still excited with much greater efficiency due to its preferred symmetry for RCP light. Likewise, the antibonding mode is also excited with small efficiency by LCP light. This behavior, again, can be explained with our simple qualitative model. At distances d shorter than an effective quarter wavelength between the two nanorods, the polarization vector of the light does not fully align with the lower nanorod. Therefore, it also possesses a component of its electric field vector that can drive the mode of opposite symmetry to the preferred one. In principle, one could use this effect and tune the distance d to $3\pi/4$ phase difference and flip the sign of the CD and ORD responses. In practice, this cannot be achieved because the near-field coupling vanishes.⁶² The antibonding and bonding modes are spectrally more separated due to the stronger near-field coupling. At the same time, the amplitude of the CD spectrum doubles in



Figure 4. (a) Full-field simulations of transmittance, CD and ORD spectra of the C_4 -symmetrically arranged right-handed enantiomer with 60 nm vertical separation. (b) Measured transmittance, CD, and ORD spectra of fabricated structures.

comparison to the wider spaced sample. The maximum value $\Delta \ln(T)_{max} = 1.25$ corresponds to an ellipticity of 41 250 mdeg $(\theta(\text{mdeg}) \approx 33\,000 \cdot \Delta \text{A})^{.63}$ This value can become even larger for smaller interlayer separations. Compared to the perfectly spaced sample, the ORD spectrum in Figure 4 is broader because the two modes that contribute to it are separated further. Interestingly, the linear transmittance spectrum shows around 40% transmission in the region between 1250 and 1400 nm. Thus, the thin layer containing the stacked nanoparticles operates as a broadband waveplate in this region. This is a property that one can easily play with by changing the structure parameters, thereby, conveniently achieving high rotation angles. Note that while we chose a system where the nanorods are capacitively coupled for our demonstration, the same reasoning holds when the two nanorods are conductively coupled to each other via a gold connection. In this case, the bonding mode would redshift further.

To demonstrate the accuracy with which the coupledoscillator model describes the plasmonic Born–Kuhn model, we carried out a fit of the CD-spectrum of the left-handed enantiomer with 60 nm vertical spacing (Figure 5a) using the analytic fitting formula

$$\ln(T_{\rm R}) - \ln(T_{\rm L}) = \frac{1}{\omega^2} Im \left(\frac{A\xi\omega}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2} \right)$$
(8)

where the amplitude coefficient *A*, ω_0 , γ , and ξ were fitting parameters. A phenomenological Drude factor of $1/\omega^2$ was included to account for the bulk gold material properties. The extracted parameters were $\omega_0 = 1450$ THz, $\gamma = 100$ THz, and $\xi = 1.84 \times 10^{29}$ s⁻². Inserting the obtained fit parameters into

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Figure 5. (a) Measured CD-spectrum (gray) and fit (dashed red) using the analytic Born–Kuhn expression for a left-handed enantiomer with 60 nm vertical separation. (b) Measured ORD-spectrum (gray) and plotted ORD-curve with parameters extracted from fitting of the CD-spectrum (dashed red).

$$\theta = \frac{1}{\omega^2} \mathcal{R}e\left(\frac{B\xi\omega}{(\omega_0^2 - i\gamma\omega - \omega^2)^2 - \xi^2}\right)$$
(9)

where *B* is an amplitude factor, reproduces the measured ORD spectrum (Figure 5b). The discrepancy between analytic fit and measured spectrum is larger for the ORD spectrum than for the CD spectrum because the ORD spectrum depends on the incident angle and we measured under a broad range of angles centered around 17° .

Chirality as a field of study at the intersection of chemistry, life-sciences, and physics is truly multidisciplinary. With recent progress in DNA-assisted self-assembly, for example, and since the amplitude of the CD-signal depends on the angle between the two nanorods,⁶⁴ one can envision an angle sensitive version of the plasmon ruler concept:^{60,65,66} a plasmonic angle ruler made of nanorods that are attached to two nanoscopic objects whose relative angle would be encoded in the far-field CD-spectrum of the compound system.

In summary, we have shown that a C_4 -symmetric cornerstacked metallic nanorod system acts as the exact plasmonic analog of the Born-Kuhn model of chiral media. Since arbitrarily complex chiral plasmonic systems can often be decomposed into nonparallel rod-type segments, the results of this paper provide the required insight to predict their chiroptical spectra. Therefore, our study of the plasmonic Born-Kuhn model will open the door to novel plasmonic designs in a wide range of applications, allowing researchers to specifically tune response, bandwidth, spectral position, and size of the chiroptical effect, by intuitively understanding how to couple the basic chiral building blocks together.

ASSOCIATED CONTENT

S Supporting Information

Forward and backward transmittance spectra, conversion spectrum, and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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