Formulation of phase retardation effects in coupled nanorods

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Abstract

We derive a formula for phase retardation effects in plasmonic systems. We analyze the circular dichroic response (CD) of two orthogonal Au nanorods in detail and we show that, although the circular dichroism stems from the dipole-dipole interaction between the particles, CD response of the system can be much greater for weakly coupled particles.

Introduction

Achiral and chiral configurations of coupled plasmonic nanorods manifest circular polarization effects due to the phase difference between the light scattered from different parts of the system [1–6]. In this note we study the case of two orthogonal metallic nanorods and derive a formula for the far field circular dichroic response (CD) of the system that depends on two different phase factors besides the electromagnetic interaction coefficient. We observe that the phase due to the chiral geometry is doubled and show that the CD response of the system can be much greater for weakly coupled particles.

We study a chiral configuration of coupled oriented dipoles (nanorods) (Fig.1). Particles are excited by a plane wave that propagates along the $z$-axis. Far field scattering intensities $I_{RCP}$ and $I_{LCP}$ corresponding to $RCP$ and $LCP$ excitation polarization states are calculated in the $z$-direction.

Figure 1: Coupled dipoles (nanorods). CD response is maximum for weak coupling.
It is shown that far field CD response of the coupled system can be written as

$$\Delta I(R, Z, \lambda) = 8gg^* \sin\left(\frac{2\pi Z}{\lambda}\right) \Re\left(\alpha\delta e^{i2\pi R/\lambda}\right)$$

(1)

where $\Delta I(R, Z, \lambda) = I_{RCP} - I_{LCP}$ that quantifies the differential scattering between right- and left-circular polarization, $\alpha$ is the Lorentzian polarizability associated with the dipoles, $\delta$ is the interaction coefficient, $g$ is the overall factor defined in the next section.

There are two phase factors in Eq.(1). $e_2 = e^{i2\pi Z/\lambda}$ is the phase due to the 3D chiral geometry and $e_1 = e^{i2\pi Z/\lambda}$ is the phase that involved in the dipole-dipole interaction. Only the imaginary part of $e_2$ appears in Eq.(1) as explained in the next section. For $Z = 0$, $\Delta I = 0$, hence, there is no chiroptical effect for a scattering in the $z$-direction.

By playing with the spatial parameters involved in $e_1$ and $e_2$ it is possible to maximize $\Delta I$. For nanorods with length $> 200$ nm $R$ can be very large compared to the size of the rod. As an example, for nanorods with length 400 nm and radius 50 nm, by setting $X = Y = 430$ nm and $Z = 240$ nm ($R = 654$ nm) $\Delta I$ can be made $1/3$ of the total intensity $[(I_{RCP} - I_{LCP})/(I_{RCP} + I_{LCP}) \approx 1/3]$ at the wavelength $\lambda_{LSPR}$ (single particle plasmon resonance wavelength). BEM simulations for this configuration is given in Fig.2. Dashed line is for $\Delta I$.

![Figure 2: Scattering intensities $I_{RCP}$, $I_{LCP}$ and $\Delta I$ for nanorods of length 400 nm and radius 50 nm with $X = Y = 430$ nm, $Z = 240$ nm.](image)

**Derivation of the formula: Analytic approach with the Jones matrix**

For simple nano systems it is enough to investigate the behavior of the system under a single excitation polarization. However, in case of coupled nanorods, one usually needs to study different excitation polarizations and employ matrix methods [6,8].

Nanorods are the basic elements of a class of more complex systems. Their optical response can be modeled as oriented dipoles with polarization characteristics similar to that of linear polarizers in a certain interval of photon energy. We assume that the polarizability

\[^1\text{For } Z = 0, \Delta I \neq 0 \text{ in other scattering directions [4]}\]
of each rod is fully anisotropic, i.e., it can only polarize along a particular direction. Hence, scattering properties of a nanorod can be represented by a linear polarizer Jones matrix:

\[ J = \alpha \begin{pmatrix} \cos^2 \theta & \cos \theta \sin \theta \\ \cos \theta \sin \theta & \sin^2 \theta \end{pmatrix} \]  

(2)

where \( \alpha \) is the Lorentzian polarizability associated with the particle and \( \theta \) is the orientation angle in the \( x-y \) plane (Fig. 3).

Assuming a plane wave excitation with electric field components \( E_{0x} \) and \( E_{0y} \) at \( z = 0 \) we calculate the components of the far field electric vector for two orthogonal nanorods depicted in Fig. 1 by taking into account the mutual interactions as described in the Appendix.

\[ E_x = \frac{F(e_2 \varepsilon \alpha E_x + e_1 \varepsilon \alpha^2 \delta E_y)}{1 - e_1^2 \varepsilon^2 \alpha^2 \delta^2} \]  

(3)

\[ E_y = \frac{e_2 F(e_1 e_2 \varepsilon \alpha^2 \delta E_x + \varepsilon \alpha E_y)}{1 - e_1^2 \varepsilon^2 \alpha^2 \delta^2} \]  

(4)

where \( \varepsilon \) is the permittivity of the medium, and \( F \) is the far field factor. \( e_1 = e^{i2\pi R/\lambda} \), \( e_2 = e^{i2\pi Z/\lambda} \), \( \delta \) is the interaction coefficient defined as \( \delta = -XYk^2B/R^2 \) (\( B \) is given in the Appendix). There is an extra \( e_2 \) in \( E_y \) because the vertical rod is behind the horizontal rod at a distance \( Z \).

From the far field components we extract the Jones matrix of the system:

\[ J = \frac{\varepsilon \alpha F}{1 - e_1^2 \varepsilon^2 \alpha^2 \delta^2} \begin{pmatrix} e_2 & e_1 \alpha \delta \\ e_1 e_2^* \alpha \delta & e_2 \end{pmatrix} \]  

(5)

We calculate the CD response of the system directly from the Jones matrix. Let \( \Delta I(R, Z, \lambda) = I_{RCP} - I_{LCP} \), where \( I_{RCP} \) and \( I_{LCP} \) are the scattering intensities corresponding to right- and left-handed circular polarization:

\[ \Delta I(R, Z, \lambda) = 2i(-J_{11} J_{12}^* + J_{12} J_{11}^* - J_{21} J_{22}^* + J_{22} J_{21}^*) \]  

(6)

where \( J_{ij} \) are elements of the Jones matrix. Using the property \( J_{11} = J_{22} \) Eq. (6) simplifies to

\[ \Delta I(R, Z, \lambda) = -4\text{Im}(J_{11}^* (J_{12} - J_{21})) \]  

(7)

In terms of the elements of the Jones matrix given in Eq. (5)

\[ \Delta I(R, Z, \lambda) = 8gg^* \sin \left( \frac{2\pi Z}{\lambda} \right) \text{Re}(\alpha \delta e^{i2\pi R/\lambda}) \]  

(8)

where \( g = \varepsilon \alpha F/(1 - e_1^2 \varepsilon^2 \alpha^2 \delta^2) \). It is worth to emphasize that \( \Delta I \) given in Eq. (8) depends on the interaction coefficient, \( \delta \). When the nanorods are well separated from each other, \( \delta \to 0, \Delta I \to 0 \).
Appendix

The induced electric dipole moment vector, $\mathbf{P}$, on a nanorod is proportional to the incident electric field, $\mathbf{E}_0(\mathbf{r})$:

$$\mathbf{P} = \varepsilon \mathbf{J} \mathbf{E}_0(\mathbf{r}),$$  \hspace{1cm} (9)

where $\varepsilon$ is the permittivity of the medium at the dipole position.

When we put two particles close to each other we have to consider mutual interaction contributions. Each one of the dipoles experience the field of the other dipole which should be taken into account to find the actual dipoles of the particles:

$$\mathbf{P}_1 = \mathbf{J}_1[\varepsilon \mathbf{E}_0(\mathbf{r}_1) + k^2 \mathbf{G}(\mathbf{r}_1 - \mathbf{r}_2) \cdot \mathbf{P}_2],$$ \hspace{1cm} (10a)

$$\mathbf{P}_2 = \mathbf{J}_2[\varepsilon \mathbf{E}_0(\mathbf{r}_2) + k^2 \mathbf{G}(\mathbf{r}_2 - \mathbf{r}_1) \cdot \mathbf{P}_1],$$ \hspace{1cm} (10b)

where $k$ is the wavenumber, $\mathbf{J}_1$, $\mathbf{J}_2$ are the Jones matrices of individual particles and $\mathbf{G}$ is the free-space electric dyadic Green’s function with the following effect on a dipole vector:

$$\mathbf{G} \cdot \mathbf{P} = \frac{1}{4\pi R} \left[ \left( 1 + \frac{i}{k R} - \frac{1}{k^2 R^2} \right) \mathbf{P} + \left( -1 - \frac{3i}{k R} + \frac{3}{k^2 R^2} \right) (\hat{\mathbf{u}} \cdot \mathbf{P}) \hat{\mathbf{u}} \right],$$  \hspace{1cm} (11)

where $R$ is the distance and $\hat{\mathbf{u}}$ is the unit vector between the center of masses of particles. The notation can be simplified if we let,

$$A = \frac{1}{4\pi R} \left( 1 + \frac{i}{k R} - \frac{1}{k^2 R^2} \right),$$ \hspace{1cm} (12a)

$$B = \frac{1}{4\pi R} \left( -1 - \frac{3i}{k R} + \frac{3}{k^2 R^2} \right),$$ \hspace{1cm} (12b)

thus,

$$\mathbf{G} \cdot \mathbf{P} = A \mathbf{P} + B(\hat{\mathbf{u}} \cdot \mathbf{P}) \hat{\mathbf{u}}.$$  \hspace{1cm} (13)

We study the circular polarization effects for the geometry given in Fig.3 where $\mathbf{r} (|\mathbf{r}| = R)$ is the vector between the dipoles. A plane wave excites $\mathbf{P}_1$ first and excites $\mathbf{P}_2$ after a delay. According to Fig.3 $e_1 = e^{i 2\pi R/\lambda}$ is the phase difference between the dipoles along the distance $R$ and $e_2 = e^{i 2\pi Z/\lambda}$ is the phase difference in the $z$-direction.

Jones matrix of the first dipole is fixed along the $y$ axis:

$$\mathbf{J}_1 = \alpha_1 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$  \hspace{1cm} (14)

The second dipole is tilted at an angle of $\theta$:

$$\mathbf{J}_2 = \alpha_2 \begin{pmatrix} a & b \\ b & c \end{pmatrix}$$  \hspace{1cm} (15)

where $\alpha_1$ and $\alpha_2$ are the Lorentzian polarizabilities of the dipoles and $a = \cos^2 \theta$, $b = \cos \theta \sin \theta$, $c = \sin^2 \theta$.

Let $C_1 = \cos \phi_1$, $S_1 = \sin \phi_1$, $C_2 = \cos \phi_2$, $S_2 = \sin \phi_2$ then the unit vector along $\mathbf{r}$ can be written as

$$\hat{\mathbf{u}}(\mathbf{r}_2 - \mathbf{r}_1) = (C_1C_2, S_1, C_1S_2)$$  \hspace{1cm} (16)
We calculate $P_1$ and $P_2$ with the Green function contributions:

$$P_1 = \varepsilon J_1 \begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix} + k^2 J_1 \begin{pmatrix} e_1 AP_{2x} + (C_1C_2P_{2x} + S_1P_{2y})C_1C_2e_1B \\ e_1 AP_{2y} + (C_1C_2P_{2x} + S_1P_{2y})S_1e_1B \end{pmatrix}$$  \hspace{1cm} (17)$$

$$P_2 = \varepsilon J_2 \begin{pmatrix} e_2 E_{0x} \\ e_2 E_{0y} \end{pmatrix} + k^2 J_2 \begin{pmatrix} C_1C_2S_1e_1BP_{1y} \\ e_1AP_{1y} + S_2^2e_1BP_{1y} \end{pmatrix}$$  \hspace{1cm} (18)$$

$E_{0x}, E_{0y}$ are the components of the planewave excitation at $z = 0$.

We solve the components of the dipoles at the far field for scattering in the $z$-direction and we find the scattering matrix (Jones matrix) of the interacting system:

$$J = \frac{\varepsilon F}{N} \begin{pmatrix} e_2\alpha_1 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} + e_2\alpha_2 \begin{pmatrix} a & b \\ b & c \end{pmatrix} + e_1\alpha_1\alpha_2 \begin{pmatrix} 0 & \Delta_1 \\ \Delta_1 & (1 + e_2^2)\Delta_2 \end{pmatrix} \end{pmatrix}$$  \hspace{1cm} (19)$$

where $N = 1 - e_1^2\alpha_1\alpha_2(2b\delta_1\delta_2 + c\delta_1^2 + a\delta_2^2)$, $F$ is the far field factor, $\delta_1 = k^2(A + S_1^2B)$, $\delta_2 = k^2(C_1C_2S_1B)$, $\Delta_1 = b\delta_1 + a\delta_2$ and $\Delta_2 = c\delta_1 + b\delta_2$ are the interaction coefficients that result from the dipole-dipole interaction. Here we write the Jones matrix of the system as a linear combination of three Jones matrices, first two of them corresponding to the symmetric linear polarizer Jones matrices of individual (noninteracting) dipoles and the third one is an asymmetric Jones matrix due to the interaction and phase ($e_2$). All elements of the interaction Jones matrix are scaled by interaction coefficients which are functions of the distance between the dipoles so that for distant particles this coupling term consistently vanishes.

As a special case we study a simpler geometry given in Fig.4 where we let $a = 1, b = 0, c = 0, \alpha_1 = \alpha_2 = \alpha$, with $\Delta_1 = \delta_2 = \delta$ and $\Delta_2 = 0$. Eq. (19) reduces to the following Jones matrix:

$$J = g \begin{pmatrix} e_2 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + e_2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} + e_1 \begin{pmatrix} 0 & \alpha\delta \\ \alpha\delta & 0 \end{pmatrix} \end{pmatrix} = g \begin{pmatrix} e_2 \begin{pmatrix} 1 & e_1\alpha\delta \\ e_1\alpha\delta & e_2 \end{pmatrix} \end{pmatrix}$$  \hspace{1cm} (20)$$
where

\[ g = \frac{\varepsilon \alpha F}{1 - e_1^2 \alpha^2 \delta^2} \]  \hspace{1cm} (21)

Figure 4: Two orthogonal dipoles separated by a distance \( Z \) along the \( z \)-axis.

Extremum points of the denominator of the overall factor \( g \) determines the intensity peaks corresponding to the hybridized modes which occur at the energies that make \( \text{Re}(\varepsilon_1 \alpha \delta) = \pm 1 \). Separation between the higher and lower energy modes decreases and eventually they overlap for large \( R \), but two modes can still be monitored by means of the parameter \( \varepsilon_1 \alpha \delta \) which can be found from the simulated Jones matrix.

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