Unified treatment for scattering, absorption, and photoluminescence of coupled metallic nanoparticles with vertical polarized excitation

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Abstract

Optical properties of coupled metallic nanoparticles (MNPs) have been widely reported due to their unique characteristics such as peak shift/splitting of the coupling spectra and electromagnetic enhancement at subwavelength scale, etc. In a previous work, we have investigated the coupling spectra of two coupled MNPs with parallel polarized excitation. In this study, we investigate the vertical polarization case in detail. Different from the parallel one, the vertical one has its unique properties: (a) three coupling coefficients; (b) positive coupling terms in the coupling equations; (c) blue-shifts of the peaks with the increasing coupling strength for identical MNPs spectra, including scattering, absorption, and photoluminescence (PL). The model shows that for the two resonant MNPs, the spectra reveal only one mode that blue shifts as the coupling strength increases; while for the two non-resonant MNPs, the spectra reveal two splitting modes, one of which blue shifts and the other of which red shifts as the coupling strength increases. The relative intensity of the two modes varies with the coupling strength. Furthermore, the PL efficiency (relative to the scattering) is about the order of $10^{-2}$. Comparison with published experimental results shows the validity of this model. This work provides a deeper understanding on the optical properties of coupled MNPs and is beneficial to relevant applications.

1. Introduction

The optical properties of coupled metallic nanostructures, or metallic nanoparticles (MNPs) have attracted wide interest of researchers due to the ability and potential to control the electromagnetic field at subwavelength scale. Numerous applications have been driven by these studies, such as optical biosensing [1–4], chiral optics, [5–7], plasmonic devices, [8–10], and nonlinear optics [11–13].

There are numerous coupling models using harmonic oscillator system. Joe et al [14] used both the classical and quantum systems to describe the Fano resonance. In their classical model, two oscillators couple with each other with the external force driving one of them. The phase of these two are detailed analyzed to explain the formation of Fano line shape. In their quantum model, they analyzed the coupling between 2D electron waveguide with a quantum dot, and the Fano resonance results from the interference between a propagating wave and an evanescent wave. Quantum oscillator models could explain the coupling in a similar way. Fan et al [15], present a model to describe a single optical resonance coupled with multiple input and output ports. Yang et al [16], used the quantum oscillator model to explain electromagnetically induced transparency in their all-dielectric metasurface. These examples that employ oscillator models are successful. However, some details are missing. Especially, the coupling coefficients are not clarified. That is, when considering a practical situation, e.g. MNPs with certain separation distance, the coupling coefficients are usually uncertain. Researchers often fit the curves of experiments to determine the coefficients in general.
Furthermore, the coupling coefficients may vary with several quantities, thus influencing the coupling process.

In a previous work, we have presented a practical model to investigate the coupled MNPs with parallel polarized excitation. In this study, we also present a practical model to investigate the optical properties of two coupled MNPs with vertical polarized excitation. The results in this work show great difference from the parallel polarized one in at least three points: (a) there are three coupling coefficients for vertical polarization, while there are only two for parallel polarization; (b) vertical polarization has positive coupling terms in the coupling equations, while parallel polarization has negative ones; (c) for identical MNPs, as the coupling strength increases, vertical polarization shows blue-shift in the spectra, including scattering, absorption, and photoluminescence (PL), while parallel polarization shows red-shift. These phenomena are explained by this model. This work would help to understand the coupling phenomena of MNPs in a classical way more deeply.

2. Model

Figure 1 shows the schematic of this model in $x$-$y$ view. Two MNPs are treated as two oscillators with ions (positive charged) staying at rest and electrons (negative charged) oscillating around the ion. Here, the two oscillators are on the $x$-axis, and the distance between them is $r_0$. The $y$-polarized external electromagnetic field with angular frequency $\omega_{\text{ex}}$ and amplitude $E_0$ propagates along the $z$-axis and illustrates the coupled MNPs. Therefore, the polarization of the excitation light is perpendicular to the line between the two oscillators (vertical polarized excitation). We assume that the free electrons are forced to oscillate only along $y$-axis. Define $y_j(t)$, $\dot{y}_j(t)$, and $\ddot{y}_j(t)$ as the displacement, velocity, and acceleration in $y$-direction of the $j$th electron with $j = 1, 2$, respectively. The equations of the two electrons are written as:

\[
\ddot{y}_1 + \beta_0 \dot{y}_1 + \omega_0^2 y_1 - \frac{F_{11}}{m_e} = C_1 \exp(-i \omega_{\text{ex}} t),
\]

\[
\ddot{y}_2 + \beta_0 \dot{y}_2 + \omega_0^2 y_2 - \frac{F_{12}}{m_e} = C_2 \exp(-i \omega_{\text{ex}} t).
\]

Here, $m_e$ is the electron mass, $C_1 = -eE_1/m_e$, $C_2 = -eE_2/m_e$, $e$ is the elementary charge. Usually, $E_1 = E_2 = E_0$ is a good approximation due to the subwavelength distance between them; $\omega_0$ and $\beta_0$ are the eigenfrequency (angular) and the damping coefficient of the $j$th oscillator, respectively; $F_{11} = -eE_{11}$ and $F_{12} = -eE_{12}$ are the interaction forces between the two oscillators, which can be derived from [17]:

\[
E = \frac{q}{4\pi \varepsilon_0} \frac{r}{(r \cdot u)^3} \left[ (c^2 - v^2) u + r \times (u \times a) \right],
\]

where $E$ is the electric field introduced by the moving charge $q$, $\varepsilon_0$ is the permittivity of vacuum, and $c$ is the velocity of light in vacuum; $u \equiv cr/r - v$; $r$, $v$, and $a$ are the displacement vector from the charge to the field point, velocity, and the accelerate of the charge, respectively, with $r = |r|$ and $v = |v|$. Therefore, the electric field $E_{21}$ and $E_{12}$ can be written as:

\[
E_{21} \approx \frac{e}{4\pi \varepsilon_0 r_0^3} \left( \frac{y_2}{r_0} + \frac{\dot{y}_2}{c} + \frac{\ddot{y}_2}{c^2} \right),
\]

\[
E_{12} \approx \frac{e}{4\pi \varepsilon_0 r_0^3} \left( \frac{y_1}{r_0} + \frac{\dot{y}_1}{c} + \frac{\ddot{y}_1}{c^2} \right).
\]

Here, we use the conditions $v/c \ll 1$, $y/r_0 \ll 1$, and $r_0 \ddot{y}/c^2 \ll 1$, and ignore the higher-order infinitesimal for approximation. Due to the collective oscillation of large number of electrons in the MNPs, the interaction forces should be modified as $F_{21} = -N_1 eE_{21}$ and $F_{12} = -N_2 eE_{12}$, where $N_1$ and $N_2$ are the effective numbers of free electrons in Oscillator 1 and Oscillator 2, respectively. To make it clearer, we define the general coupling coefficients as:

\[
\frac{1}{\kappa} \approx \frac{e^2}{4\pi \varepsilon_0 m_e c^3}, \quad g_0^1 = \frac{1}{\kappa} \left( \frac{c}{r_0} \right)^3, \quad \gamma_0 = \frac{1}{\kappa} \left( \frac{c}{r_0} \right)^2, \quad \eta_0 = \frac{1}{\kappa} \left( \frac{c}{r_0} \right)^1,
\]

then the coupling coefficients are:

\[
g_1^2 = N_1 g_0^1, \quad \gamma_1 = N_1 \gamma_0, \quad \eta_1 = N_1 \eta_0,
\]

\[
g_2^2 = N_2 g_0^1, \quad \gamma_2 = N_2 \gamma_0, \quad \eta_2 = N_2 \eta_0.
\]
To obtain the PL spectrum, we should find the eigen solutions of the following equations:

\[ \dot{y}_1 + \beta_{01}y_1 + \omega_{01}^2 y_1 + \eta_0 y_2 + \gamma_2 y_2 + g_2^2 = C_1 \exp(-i\omega_{ex}t), \quad (6a) \]

\[ \dot{y}_2 + \beta_{02}y_2 + \omega_{02}^2 y_2 + \eta_1 y_1 + \gamma_1 y_1 + g_1^2 = C_2 \exp(-i\omega_{ex}t). \quad (6b) \]

For simplicity, we define \( \Omega_j(\alpha) = \omega_{0j}^2 + \beta_{0j}\alpha + \alpha^2 \) and \( G_j(\alpha) = g_j^2 + \gamma_j\alpha + \eta_j\alpha^2 \) for \( j = 1, 2 \) which would be used in the following derivation.

2.1. Scattering and absorption

To obtain the white light scattering spectra, \( \alpha \) is substituted by \(-i\omega_{ex}\), and we solve the following equations derived from equation (6) after assuming \( y_j(t) = A_j \exp(-i\omega_{ex}t) \) for \( j = 1, 2 \),

\[ \begin{pmatrix} \Omega_1(\alpha) & G_2(\alpha) \\ G_1(\alpha) & \Omega_2(\alpha) \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}, \]

with \( \alpha = -i\omega_{ex} \).

The solutions are:

\[ A_1(\omega_{ex}) = \frac{\Omega_2 C_1 - G_2 C_2}{\Omega_1 \Omega_2 - \Omega_1 G_2}, \quad A_2(\omega_{ex}) = \frac{\Omega_1 C_2 - G_1 C_1}{\Omega_1 \Omega_2 - \Omega_1 G_2}. \quad (8) \]

Therefore the total scattering spectrum is derived after substituting \( \omega_{ex} \) with \( \omega \):

\[ I_{sc}(\omega) = \omega^4 |N_1 A_1(\omega) + N_2 A_2(\omega)|^2. \quad (9) \]

Here, the term \( \omega^4 \) is due to the fact that the detected scattering field is usually the far field, which is proportional to \( \dot{y} \propto \omega^2 \).

To obtain the absorption spectrum [14], we notice that the absorption is introduced by the term \( \beta_{0j}\dot{y}_j \), thus the total absorption spectrum is written as:

\[ I_{abs}(\omega) = N_1 |\beta_{01} A_1(\omega)|^2 + N_2 |\beta_{02} A_2(\omega)|^2. \quad (10) \]

2.2. PL

To obtain the PL spectrum, we should find the eigen solutions of the following equations:

\[ \dot{y}_1 + \beta_{01}y_1 + \omega_{01}^2 y_1 + \eta_0 y_2 + \gamma_2 y_2 + g_2^2 = 0, \quad (11a) \]

\[ \dot{y}_2 + \beta_{02}y_2 + \omega_{02}^2 y_2 + \eta_1 y_1 + \gamma_1 y_1 + g_1^2 = 0. \quad (11b) \]
After assuming \( y_j(t) = B_j \exp(\alpha t) \) for \( j = 1, 2 \), the equations are written in matrix form:

\[
\begin{pmatrix}
\Omega_1(\alpha) & G_2(\alpha) \\
G_1(\alpha) & \Omega_2(\alpha)
\end{pmatrix}
\begin{pmatrix}
B_1 \\
B_2
\end{pmatrix}
= \begin{pmatrix}
0 \\
0
\end{pmatrix},
\]

with initial conditions:

\( y_j(0) = A_j, \quad \dot{y}_j(0) = 0, \quad \text{for } j = 1, 2. \) \hfill (12)

Obviously, to find a non-trivial solution, \( \alpha \) should satisfy

\[
\begin{vmatrix}
\Omega_1(\alpha) & G_2(\alpha) \\
G_1(\alpha) & \Omega_2(\alpha)
\end{vmatrix} = 0.
\] \hfill (13)

A particular case is that the two oscillators are identical, i.e. \( \omega_{01} = \omega_{02} = \omega_0, \beta_{01} = \beta_{02} = \beta_0, \)
\( N_1 = N_2 = N, g_1 = g_2 = g, \gamma_1 = \gamma_2 = \gamma, \eta_1 = \eta_2 = \eta, \) and \( C_1 = C_2 = C. \) In the rest of this section, we take this identical case as an example to illustrate the PL properties of the coupled system. The expressions derived from the general case (non-identical) are much more complicated than the identical one, but the solving processes of them are similar. Back to the identical case, the solutions of \( \alpha \) are:

\[
\alpha_{p\pm} = -\beta_0 - \gamma \pm i \sqrt{4(1 + \eta)(\omega_0^2 + g^2) - (\beta_0 + \gamma)^2},
\]

\[
\alpha_{m\pm} = -\beta_0 + \gamma \pm i \sqrt{4(1 - \eta)(\omega_0^2 - g^2) - (\beta_0 - \gamma)^2},
\] \hfill (14)

Notice that these solutions should satisfy \( \eta \neq 1 \) (Case 1). If \( \eta = 1 \) and \( \gamma \neq \beta_0 \) (Case 2), the solutions would be reduced to \( \alpha_{p\pm} \) and \( \alpha_{m\pm} \), with \( \alpha_m = \frac{\omega_0^2 - g^2}{\eta \omega_0^2 + g^2}. \) In this case, \( \alpha_m \) corresponds to the non-oscillation term with exponentially decreasing or increasing, depending on the sign of \( \alpha_m \), the latter of which should be removed from the solutions due to its divergence with time. If \( \eta = 1 \) and \( \gamma = \beta_0 \) (Case 3), the solutions would only remain \( \alpha_{p\pm} \). Incidentally, we can easily derive the relations of \( g = \gamma = \beta_0, \quad r_0 = c/\beta_0, \quad N = \kappa/\beta_0, \) and \( N_c = \kappa r_0 \) from Case 3. It is worth mentioning that Case 2 and Case 3 are not general cases, because they require a large number of electrons (large \( N \)) or small enough distance \( r_0 \) to achieve such strong coupling. Practically, Case 1 is a more general case when discussing coupled MNPs.

To make it clearer, we rewrite the solutions from equation (14) in a simple form:

\[
\alpha_1 = \alpha_{p-} = -\frac{\beta_1}{2} + i \omega_1, \quad \alpha_2 = \alpha_{p+} = -\frac{\beta_1}{2} - i \omega_1,
\]

\[
\alpha_3 = \alpha_{m-} = -\frac{\beta_2}{2} - i \omega_2, \quad \alpha_4 = \alpha_{m+} = -\frac{\beta_2}{2} + i \omega_2. \] \hfill (15)

Here, there are two new eigenfrequencies \( (\omega_1 \) and \( \omega_2 \)) and two new damping coefficients \( (\beta_1 \) and \( \beta_2 \)). Obviously, they could be written as:

\[
\omega_1 = \sqrt{\frac{\omega_0^2 + g^2}{1 + \eta} - \frac{\beta_1^2}{4}}, \quad \beta_1 = \frac{\beta_0 + \gamma}{1 + \eta},
\]

\[
\omega_2 = \sqrt{\frac{\omega_0^2 - g^2}{1 - \eta} - \frac{\beta_2^2}{4}}, \quad \beta_2 = \frac{\beta_0 - \gamma}{1 - \eta}. \] \hfill (16)

Then, the solutions of equation (12) for \( y_j(t) \) are written as:

\[
y_j(t) = \sum_{k=1}^{4} B_k \exp(\alpha_k t), \quad \text{for } j = 1, 2. \] \hfill (17)

There are eight undetermined coefficients \( (B_k) \), hence, we need eight equations, i.e. eight initial conditions. In equation (12), we list four of them, and the rest four conditions are determined by \( \bar{y}_j(0) \) and \( \bar{y}_j(0) \) which can be derived from equation (11):

\[
A_1(\omega_{01}) = A_2(\omega_{02}) := A_0(\omega_{0c}), \quad \bar{y}_1(0) = \bar{y}_2(0) = -\frac{\omega_0^2 + g^2}{1 + \eta}, \quad \bar{y}_4(0) = \bar{y}_2(0) = -\frac{\beta_0 + \gamma}{1 + \eta}, \quad \bar{y}_0 := \bar{y}_0. \] \hfill (18)
Here, $A_0$ could be simplified from equation (8):

$$A_0(\omega_{ex}) = \frac{C_0}{\Omega + G} = \frac{-C_0/(1 + \eta)}{(\omega_{ex} + \beta_1/2)^2 - \omega_1^2}. \tag{19}$$

The solutions of $B_{jk}$ could be given by the matrix equation:

$$\begin{pmatrix}
\alpha_1 & \alpha_2 & \alpha_3 & \alpha_4 \\
\alpha_2 & \alpha_3 & \alpha_4 & 0 \\
\alpha_3 & \alpha_4 & 0 & 0 \\
\alpha_4 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
B_{j1} \\
B_{j2} \\
B_{j3} \\
B_{j4}
\end{pmatrix}
= \begin{pmatrix}
A_j \\
\bar{y}_j(0) \\
\bar{y}_j(0) \\
\bar{y}_j(0)
\end{pmatrix}$$

for $j = 1, 2$. \tag{20}

Then, $B_{jk}$ are listed below:

$$B_{jk} = \frac{\bar{y}_j(0) - A_j \prod_{n \neq k}^4 \alpha_n - \bar{y}_j(0) \sum_{n \neq k}^4 \alpha_n}{\prod_{n \neq k}^4 (\alpha_k - \alpha_n)}$$

$$= \frac{(\omega_1^2 + \gamma)(\beta_1 + \gamma)}{(1 + \eta)^2} - \prod_{n \neq k}^4 \alpha_n + \frac{\omega_1^2 + \gamma}{1 + \eta} \sum_{n \neq k}^4 \alpha_n$$

$$= \frac{4}{\prod_{n \neq k}^4 (\alpha_k - \alpha_n)} A_0 := B_{0k}. \tag{21}$$

Therefore, the solutions of equation (11) are:

$$y_1(t) = y_2(t) = \sum_{k=1}^4 B_{0k} \exp(\alpha_k t) := y_0(t), \tag{22}$$

After removing the insignificant coefficients, i.e. factor $f = \frac{\varepsilon}{k \pi \varepsilon_{sep}^{eff}} \tag{18}$, where $d$ is the distance between the system and the far field point, the far field electric field is:

$$E_{far}(t) = N_1 \bar{y}_1(t) + N_2 \bar{y}_2(t) = 2N \bar{y}_0(t) := \sum_{k=1}^4 B_{0k} \exp(\alpha_k t), \tag{23}$$

where $B_{0k} = 2N \alpha_k^2 J_{0k}$. Hence, the emission spectrum can be evaluated by [19]:

$$I_{PL}(\omega) = \text{Re} \left( \int_0^\infty E_{far}(t) E_{far}(t + \tau) \exp(i\omega \tau) d\tau \right). \tag{24}$$

Similarly, after removing the insignificant coefficients, i.e. factor $F_I = \frac{1 - e^{-\eta/t_0}}{\beta_{01}} \tag{19}$, where $t_0$ is the interaction time between light and the system, the total PL spectrum can be written as:

$$I_{PL}^{\text{total}}(\omega) = \frac{\beta_1 |B_{01}|^2}{(\omega - \omega_1)^2 + \left(\frac{\beta_1}{2}\right)^2} + \frac{\beta_1 |B_{02}|^2}{(\omega + \omega_1)^2 + \left(\frac{\beta_1}{2}\right)^2}$$

$$+ \frac{\beta_2 |B_{03}|^2}{(\omega - \omega_2)^2 + \left(\frac{\beta_2}{2}\right)^2} + \frac{\beta_2 |B_{04}|^2}{(\omega + \omega_2)^2 + \left(\frac{\beta_2}{2}\right)^2}. \tag{25}$$

After ignoring the second and the fourth term due to the fact that they are far away from the resonance frequency, the PL spectrum can be evaluated as:

$$I_{PL}(\omega) = \frac{\beta_1 |B_{01}|^2}{(\omega - \omega_1)^2 + \left(\frac{\beta_1}{2}\right)^2} + \frac{\beta_2 |B_{02}|^2}{(\omega - \omega_2)^2 + \left(\frac{\beta_2}{2}\right)^2}. \tag{26}$$
Notice that for the identical case, \( B_{03} = B_{04} = 0 \) can be derived from equation (21). Hence, the identical PL spectrum is evaluated as:

\[
\frac{p_{\text{identical}}(\omega)}{\rho_{\text{identical}}(\omega)} = \frac{\beta_1 |B_{01}|^2}{(\omega - \omega_1)^2 + \left(\frac{\omega_0}{2}\right)^2}.
\]  

(27)

Here, we emphasize that the whole derivation for the PL spectra is only applicable to the identical case, resulting in equation (27). In order to calculate the one of the non-identical case, i.e. equation (26), we should follow these steps: (1), (numerically) solve equation (13) to obtain the right modes for equation (15); (2), derive the initial conditions for equation (18) using equation (11) and \( A_j(\omega_{ex}) \) that are solved from equation (8); (3), solve equation (20) to obtain the amplitudes \( B_{jk} \), also known as the first line of equation (21); (4), the rest is to follow equations (23)–(26).

### 2.3. PL efficiency

Now we evaluate the PL efficiency, which is a significant property of the MNP, by assuming that the far field emissions are from the oscillators that can be treated as dipoles. The total radiation power of a dipole with dipole moment \( p \) and angular frequency \( \omega_p \) can be evaluated by [17]:

\[
\langle S \rangle = \frac{p^2 \omega_p^4}{12\pi \varepsilon_0 c^2}.
\]  

(28)

When calculating the power emitted by the scattering process, the dipole moment of the \( j \)th MNP can be evaluated by \( p_{\text{scat}} = eN_j |A_j| \), with the emission angular frequency \( \omega_{ej} \); while calculating the one of the PL process, the dipole moment of the \( j \)th MNP with the \( k \)th mode can be evaluated by \( p_{\text{PL},k} = eN_j |B_{jk}| \) (we only consider \( k = 1, 3 \) here), with the corresponding emission angular frequencies \( \omega_1 \) and \( \omega_2 \). Therefore, the total power ratio of PL to scattering can be evaluated by:

\[
\text{Ratio} = \frac{N_1^2 |B_{13}|^2 + N_3^2 |B_{31}|^2}{N_1^2 |A_1|^2 + N_3^2 |A_3|^2} \frac{\omega_1^4}{\omega_{\text{ex}}^4} F_1 + \frac{N_1^2 |B_{13}|^2 + N_3^2 |B_{31}|^2}{N_1^2 |A_1|^2 + N_3^2 |A_3|^2} \frac{\omega_2^4}{\omega_{\text{ex}}^4} F_2.
\]  

(29)

The factor \( F_1 \) here is due to the integration of equation (24). This ratio represents the relative PL efficiency.

### 3. Results and discussions

After preparing these formulas employing this coupling model, the optical properties of the coupled system could be obtained easily.

#### 3.1. Coupling coefficients

First, we investigate the behavior of the coupling coefficients, i.e. \( g, \gamma, \) and \( \eta \), in the identical case.

Figure 2 shows these coupling coefficients varying with the electron number \( N \) and the distance \( r_0 \), calculated from equations (4) and (5). As \( N \) increases or/and \( r_0 \) decreases, they increase. The contour lines for \( g, \gamma, \) and \( \eta \) satisfy \( N \propto r_0^{-5}, N \propto r_0^2 \), and \( N \propto r_0 \), respectively. The dashed lines are the examples (\( g = 10^{16} \) Hz, \( \gamma = 10^{10} \) Hz, and \( \eta = 1 \)) to show the contour lines.

We emphasize here that when \( r_0 \) is small enough, i.e. \( r_0 < 1 \) nm, the electron tunneling effect makes it hard to evaluate the interaction between the oscillators employing only classical electromagnetic method which is used in this paper. Therefore, this model fails to describe the behaviors of the oscillators at the subnanometer scale, and we do not discuss this situation in this paper.

A particular case is when \( \eta \geq 1 \), which corresponds to a so strong coupling (very large \( g \) and \( \gamma \)) that the practical MNPs cannot reach easily. Hence, this situation is not discussed in detail in this paper.

#### 3.2. Eigen modes

Second, we investigate the eigen modes of the coupled system, i.e. \( \omega_j \) and \( \beta_j \) for \( j = 1, 2 \), in the identical case.

Figure 3 shows the eigen modes varying with the electron number \( N \) and the distance \( r_0 \), calculated from equation (16). As the coupling coefficients increase, it is obvious that \( \omega_1 \) and \( \beta_1 \) (Mode 1) increase; however, \( \omega_2 \) and \( \beta_2 \) (Mode 2) decrease in the case of \( \eta < 1 \), but they increase in the case of \( \eta > 1 \). Due to the behaviors at \( \eta < 1 \) (the general case), we could naturally call Mode 1 the blue branch or blue mode, and call Mode 2 the red branch or red mode. Here, unit ‘Hz’ and unit ‘eV’ could be translated by \( P(\text{eV}) = \frac{P}{2}\text{P(}\text{Hz)}\), where \( h \) is the reduced Planck constant and \( P \) is the parameter with unit ‘Hz’ or ‘eV’.
Figure 2. The coupling coefficients $g$ (a), $\gamma$ (b), and $\eta$ (c) varying with electron number $N$ and distance $r_0$. The color bar of (a) and (b) is in unit of Hz with log scale, i.e. $\log_{10}(g)$, and $\log_{10}(\gamma)$, respectively. Dashed lines stand for the contour line of the values $g, \gamma = 10^{16}$ Hz. The color bar of (c) employs log scale, i.e. $\log_{10}(\eta)$. Dashed line stands for the contour line of the value $\eta = 1$.

Figure 3. Eigen modes of the coupled system. $\omega_1$ (a), $\beta_1$ (b), $\omega_2$ (c), and $\beta_2$ (d) varying with the electron number $N$ and distance $r_0$. Here, the parameters of the individual MNP are $\beta_0 = 1.57 \times 10^{14}$ Hz (0.1034 eV), $\omega_0 = 3.14 \times 10^{15}$ Hz (2.0690 eV). The gray region in (c) and (d) stand for the vanishing of the red mode. The blue mode could blue-shift along with the increasing damping coefficient as the coupling strength increases, which is only limited by the MNPs themselves, i.e. $N$ is limited by the volume and $r_0$ is limited by the geometric structures or the electron tunneling effect. However, when it comes to the red mode, the behaviors are totally different. Both figures 3(c) and (d) show large areas filled with gray color, which indicates that the red mode vanishes in this area, i.e. only blue mode exists. The reason could be found in equation (16). Here, we take $\beta_2$ as an example to explain the reason. When $\eta < 1$, i.e. the denominator of $\beta_2$ is positive, as the coupling strength increases from 0, the numerator of $\beta_2$ decreases from $\beta_0$ until $\gamma$ increases to $\beta_0$. After $\gamma$ continuous to increase, $\beta_2$ would be negative, indicating that the solutions $\alpha_{m \pm}$ should be abandoned due to its non-physical process (exponentially increasing of $y_j(t)$). This possible region is indicated by $(\beta_0 > \gamma) \cap (\eta < 1)$, i.e. $N < \kappa \beta_0 r_0^2 / c^2$, as shown at the bottom right corner in figure 3(d). When $\eta > 1$, i.e. the denominator of $\beta_2$ is negative, hence, Mode 2 has physical meaning only when $\gamma$ is larger than $\beta_0$. As the coupling strength increases from a large value, $|\gamma - \beta_0|$ increases. This possible region is indicated by $(\beta_0 < \gamma) \cap (\eta > 1)$, i.e. $N > \kappa r_0 / c$, as shown at the top left corner in figure 3(d). Therefore, Mode 2 in the view of $\beta_2$ is forbidden at the gray region in figure 3(d), or Region $FR_{\beta_2}$: $\kappa \beta_0 r_0^2 / c^2 < N < \kappa r_0 / c$. We analyze $\omega_2$ similarly. When the value of $\omega_2$ is an imaginary number, the value of $\alpha_{m \pm}$ would be a real number,
indicating that Mode 2 is not an oscillation mode, thus abandoning Mode 2. Therefore, Mode 2 in the view of \( \omega_2 \) is forbidden at the gray region in figure 3(c), or Region \( \text{FR}_{\omega_2} : N_{\text{cut}1} < N < N_{\text{cut}2} \), where \( N_{\text{cut}1}(r_0) \) and \( N_{\text{cut}2}(r_0) \) are the two roots of the equation \( \left( \omega_0^2 - g^2 \right) / \left( 1 - \eta \right) - \beta_2^2 / 4 = 0 \), with \( N \) the uncertain number.

According to the above analysis and the parameters \( (\omega_0, \beta_0) \) we set in figure 3, the total forbidden region of Mode 2 should be \( \text{FR}_{\omega_2} \cup \text{FR}_{\beta_2} \), i.e. \( \kappa/\beta_0 r_0^2 / \epsilon^2 < N < N_{\text{cut}2} \).

### 3.3. Spectra

Third, we investigate the spectra of the coupled system, i.e. white light scattering spectra, absorption spectra, and PL spectra. Here, we choose \( g \) from \( (g, \gamma, \eta) \) to represent the coupling strength for clarity.

Figure 4 shows these spectra of resonant MNPs varying with the coupling strength \( g \), calculated from equations (9), (10) and (27). Here, ‘resonant MNPs’ stands for two identical MNPs, thus same resonant mode (both resonate at 600 nm). Two phenomena are illustrated. First, only one mode arises; second, the peaks blue shift and the line-width increases as \( g \) increases. The first phenomenon is due to the identical condition. In scattering and absorption view, equation (19) shows no information of \( \omega_2 \), indicating the vanishing of Mode 2; in PL view, the amplitude of Mode 2 is zero according to equation (27), also indicating the vanishing of Mode 2, thus only Mode 1 existing. The second phenomenon could be explained by equation (16) together with figures 3(a) and (b), where \( \omega_1 \) and \( \beta_1 \) increase as \( g \) increases. It is worth mentioning that this blue-shift phenomenon is opposite to the case of parallel polarized excitation as our previous work illustrates, where red-shift phenomenon is obtained [18]. This is essentially caused by the fact that the coupling terms in the coupling equations (equation (6)) of them have opposite sign, which are both derived from equation (2), i.e. positive sign for vertical polarization and negative sign for parallel polarization. Therefore, the primary peaks are different for these two cases. This phenomenon also agrees well with the experimental results of Pasquale et al [20], where they employed several structures consisted with different numbers of MNPs including dimers. The experimental scattering spectra of the dimer show blue shift and red shift with vertical and parallel polarized excitations, respectively.

Figure 5 shows these spectra of non-resonant MNPs varying with the coupling strength \( g \), calculated from equations (9) and (10). Here, ‘non-resonant MNPs’ stands for two different MNPs, thus different resonant modes (resonate at 500 nm and 600 nm, respectively). The formula to calculate the PL spectra is not shown in this paper because its amplitudes are pretty complicated as has been mentioned. Also, two phenomena are illustrated. First, there are two resonant peaks with different ratios of peak values for these three; second, as \( g \) increases, one peak blue shifts, the other red shifts. For the first phenomenon in detail, as \( g \) increases, for the scattering and PL spectra, the ratio of the amplitude of Mode 1 to the amplitude of Mode 2 increases;
Figure 5. Normalized scattering (black solid), absorption (black dashed), and PL spectra (red dotted) for non-resonant MNPs, with different coupling strengths. (a)–(d) stand for $g = 0.0$ eV, $g = 0.8$ eV, $g = 1.0$ eV, and $g = 1.2$ eV, respectively. Blue and red dashed arrows stand for the tracks of the blue-shifted (Mode 1) and red-shifted (Mode 2) resonant peaks, respectively. $N_1 = N_2 = 10^5$, $\beta_{01} = \beta_{02} = 1.034$ eV, $\omega_{01} = 2.0718$ eV, $\omega_{02} = 2.0690$ eV, and the excitation wavelength $\lambda_{ex} = 355$ nm.

Figure 6. Power ratio of PL to scattering as a function of coupling strength $g$, calculated from equation (29). The parameters of the MNPs and the excitation wavelength are the same as the ones in figure 5.

however for the absorption spectra, the ratio decreases. Furthermore, the line-width of Mode 1 increases and the one of Mode 2 decreases with the increasing $g$, which can be explained by equation (16) together with figures 3(b) and (d). Similar to the ‘resonant MNPs’ case, the second phenomenon could also be explained by equation (16) and figures 3(a) and (c). In figure 5(d), we notice that Mode 2 of PL vanishes. Because when $g = 1.2$ eV, Mode 2 of PL reaches the forbidden region as discussed in figure 3, thus only Mode 1 remaining.

3.4. PL efficiency

We use the power ratio of PL to scattering to represent the relative PL efficiency. As mentioned before, $t_0$ is the interaction time between light and the MNPs, therefore, we introduce a quantum explanation that $t_0$ can be evaluated by the PL lifetime of the MNPs, which is about the order of $10^{-14}$ s [21–23].

Figure 6 shows the ratio of the non-resonant MNPs as a function of $g$, the parameters of which are the same as the ones in figure 5. It indicates that as the coupling strength increases, the ratio first increases to its maximum and then decreases, with the values of the order of $2 \times 10^{-2}$. In equation (29), the first term plays a more important role than the second term does due to the facts that $\omega_1 > \omega_2$ and the peak of Mode 1 is closer to the excitation wavelength than the peak of Mode 2 does.

The behavior of the ratio varying with $g$ is due to two competing parameters. The first is the factor $F_1$ that decreases with the increasing $\beta_1$ which is introduced by the increasing $g$; the second is the PL amplitude of Mode 1 increases as its peak gets closer to the excitation wavelength which is introduced by the increasing $g$. 

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9
We notice that there is a sudden dip at around $g_{\text{cut}} = 1.1 \text{ eV}$. Because Mode 2 vanished when $g > g_{\text{cut}}$ as discussed in figure 3, the second term of equation (29) should be ignored when calculating the ratio, and the amplitudes $B_{12}$ and $B_{21}$ should be recalculated by solving the equations (steps are below equation (27)) in the case of only one mode. Moreover, equation (29) is an approximation to evaluate the relative PL efficiency, because we only consider the emission of the dipoles with single frequency, rather than considering the integral of the PL spectra. As a result, the curve suddenly varies when $g$ increases to $g_{\text{cut}}$ because of the sudden vanishing of Mode 2.

4. Conclusions

In conclusion, we develop a coupling model based on classical electromagnetic method to explain the coupling properties of two MNPs with vertical polarized excitation. There are three coupling coefficients that influence the coupling and they vary with both the free electron number and the separation distance. The scattering, absorption, and PL properties of coupled MNPs are illustrated. Particularly, the modes of PL are analyzed in detail. The identical MNPs case shows that the mode blue shifts as the coupling strength increases, which is opposite to the parallel polarized excitation (the mode red shifts as the coupling strength increases) that has been investigated in our previous work [18]. The non-resonant MNPs case shows that the two original modes behave differently. As the coupling strength increases, the peak of Mode 1 blue shifts while the peak of Mode 2 red shifts, and the intensity ratio of Mode 1 to Mode 2 becomes larger in PL and scattering spectra but smaller in absorption spectra. Furthermore, the relative PL efficiency is about the order of $10^{-2}$. This work would be helpful to understanding the coupling properties of MNPs more deeply.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request. All data that support the findings of this study are included within the article (and any supplementary files).

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Conflicts of interest

The authors declare no conflicts of interest.

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References

[1] Lu G, Hou L, Zhang T, Liu J, Shen H, Luo C and Gong Q 2012 J. Phys. Chem. C 116 25509
[2] Wu L, You Q, Shan Y, Gan S, Zhao Y, Dai X and Xiang Y 2018 Sens. Actuators B 277 210
[3] Qiu G, Ng S P and Wu C-M L 2018 Sens. Actuators B 265 459
[4] Rahman B M A, Viphavakit C, Chitaree R, Ghosh S, Pathak A K, Verma S and Sakda N 2022 Biosensors 12 42
[5] Lan X, Zhou X, McCarthy L A, Govorov A O, Liu Y and Link S 2019 J. Am. Chem. Soc. 141 19336
[6] George J, Kar S, Anupriya E S, Somasundaran S M, Das A D, Sissa C, Painelli A and Thomas K G 2019 ACS Nano 13 4392
[7] Chen H, Feng L, Ma J, Liang C, Lin Z and Zheng H 2022 Phys. Rev. B 106 054301
[8] Bhuyan P D, Gupta S K, Kumar A, Sonvane Y and Gajjar P N 2018 Phys. Chem. Chem. Phys. 20 11109
[9] Atabaki A H et al 2018 Nature 556 349
[10] Cheben P, Halir R, Schmid J H, Atwater H A and Smith D R 2018 Nature 560 565
[11] Xi X, Wang Y, Li R, Sun M, Zhang Z and Zheng H 2019 Nanophotonics 8 487
[12] Wuritz G A, Pollard R, Hendren W, Wiederrecht G P, Gosztola D J, Podolskiy V A and Zayats A V 2011 Nan. Nanotechnol. 6 107
[13] Kauranen M and Zayats A V 2012 Nat. Photon. 6 377
[14] Joe Y S, Satarin A M and Kim C S 2006 Phys. Scr. 74 259
[15] Fan S, Suh W and Joannopoulos J D 2003 J. Opt. Soc. Am. A 20 569
[16] Yang Y, Kravchenko I I, Briggs D P and Valentine J 2014 Nat. Commun. 5 5753
[17] Griffiths D J 2013 Introduction to Electrodynamics 4th edn (New York: Pearson)
[18] Cheng Y and Sun M 2022 New J. Phys. 24 033026
[19] Cheng Y, Zhang W, Zhao J, Wen T, Hu A, Gong Q and Lu G 2018 Nanotechnology 29 315201
[20] Pasquale A J, Reinhard B M and Dal Negro L 2011 ACS Nano 5 6578
[21] Varnavski O P, Mohamed M B, El-Sayed M A and Goodson T 2003 J. Phys. Chem. B 107 3101
[22] Dulkeith E, Niedereichholz T, Klar T A, Feldmann J, von Plessen G, Gittins D I, Mayya K S and Caruso F 2004 Phys. Rev. B 70 205424
[23] Varnavski O P, Goodson T, Mohamed M B and El-Sayed M A 2005 Phys. Rev. B 72 235405