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Optical response of two interacting clusters in composites

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Abstract

We have investigated the optical response of two clusters in an infinite random conductance network by using our recently developed Green's-function formalism. The method allows analytic solutions of two centrally symmetric clusters embedded in a binary network. Our results show that both red and blue shifts of resonance occur in contrast to that of a well separated cluster. In a uniform applied field, only a red or blue shift of the optical response is found. Numerical calculations by the Drude model further confirm the above statements.

1. Introduction

Recently, the interaction among nanocrystals has attracted great interest [1–4]. It significantly modifies the optical absorption in metal–dielectric mixtures [5, 6], as well as the nonlinear optical response through the local-field and geometric-response effect in various resonant composites [7–11]. Between clusters having a simple geometry, the interaction has been investigated [1, 2, 12–15], but without a consideration of local-field distribution. It is known that the local field plays a central role in the optical properties of composites. However, using the spectral representation [3, 16] and traditional effective-medium approximation (EMA) [17], it is difficult to work out the local-field distribution. In this connection, the general Green's-function formalism (GFF) is developed to deal with the geometric resonance of arbitrary-shaped metallic clusters embedded in an infinite dielectric network and in the quasistatic limit [18, 19]. Using the formalism, the resonance spectrum and local-field distribution for each eigenmode are analytically obtained. Therefore the aim of this paper is to investigate the optical response of two interacting clusters in view of the local-field distribution.

In the following, two identical clusters with admittance ϵ_1 in each bond are placed in an otherwise homogeneous network with admittance ϵ_2 . The admittance of each bond is generally complex and frequency dependent. There exist many geometric resonances subject to an external field. Due to the interaction of two clusters, one resonance splits into two, one

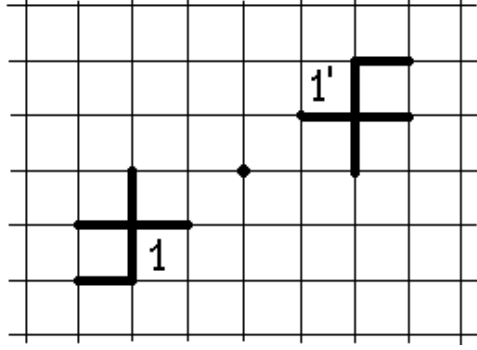


Figure 1. Schematic diagram of two clusters (shown in thick lines) embedded in an infinite conductance network.

of which is red shifted while the other is blue shifted with respect to that of the isolated cluster. When resonance occurs, the field localized around the clusters leads to a large enhancement in the effective linear and nonlinear optical responses. However, in a uniform applied field, we find only a red or blue shift of optical response for the different arrangements of two clusters. The simplest two-bond cluster can be used to represent the general case of two interacting clusters. For various two-bond clusters, the local-field distribution near resonance is illustrated by the symmetric and anti-symmetric arrangements of local field of a one-bond cluster subject to a point source. For uniform applied field, the symmetric local field is enhanced while the anti-symmetric is diminished, therefore only one of the shifts is observed.

In section 2, we derive the Green's function of two centrally symmetric clusters. The analytical results predict the shift of resonance of two interacting clusters. In section 3, we interpret the shift of optical response by means of the local-field distribution of two-bond clusters. In section 4, numerical calculations by the Drude model are performed to demonstrate the above statements. Finally, we conclude in section 5.

2. Analytic results of two interacting clusters

2.1. GFF of two centrally symmetric clusters

Two identical clusters (1 and 1') embedded in an infinite random conductance network are considered, as shown in figure 1. Clusters 1 and 1' construct the cluster subspace and they are centrally symmetric. Clusters 1 and 1' each possess n_s sites. Here we suppose a unit point source is placed at $\mathbf{0} = (0, 0)$ outside the clusters.

First, only cluster 1 is considered; namely, we remove cluster 1' temporarily. The electric potential satisfies the Kirchhoff equation

$$\sum_{\mathbf{y}(x)} \epsilon_{x,\mathbf{y}} (F_{x,\mathbf{0}} - F_{\mathbf{y},\mathbf{0}}) = \delta_{x,\mathbf{0}}, \quad (1)$$

where $\mathbf{x} = (x_1, x_2)$ and $\mathbf{y}(x)$ denote the four nearest-neighbouring sites of \mathbf{x} ; $F_{x,\mathbf{0}}$ is the electrostatic Green's function at \mathbf{x} due to the point source at $\mathbf{0}$ and $\epsilon_{x,\mathbf{y}} = \epsilon_{\mathbf{y},x}$ is the admittance of the bond joining the neighbouring sites \mathbf{x} and \mathbf{y} . Letting $\epsilon_1/\epsilon_2 = h$, equation (1) is rewritten as [18]

$$-\Delta F_{x,\mathbf{0}} = (1-h) \sum_{\mathbf{y} \in \mathcal{C}(x)} (F_{x,\mathbf{0}} - F_{\mathbf{y},\mathbf{0}}) + \frac{\delta_{x,\mathbf{0}}}{\epsilon_2}, \quad (2)$$

where $\mathbf{y} \in C(\mathbf{x})$ means that the bond (\mathbf{x}, \mathbf{y}) belongs to cluster 1, and Δ is the (finite-difference) Laplace operator defined on the square lattice for any arbitrary physical quantity Q_x , i.e. $-\Delta Q_x \equiv \sum_{\mathbf{y}(x)} (Q_x - Q_y)$. Then equation (1) admits a formal solution:

$$F_{x,0} = \frac{G_{x,0}}{\epsilon_2} + (1-h) \sum_{\mathbf{y} \in C} \sum_{\mathbf{z} \in C(\mathbf{y})} G_{x,y} (F_{y,0} - F_{z,0}), \quad (3)$$

written in terms of the Green's function $G_{x,y}$ of the Laplace operator in the infinite square lattice, i.e. $-\Delta G_{x,y} = \delta_{x,y}$ with $G_{x,x} = 0$. We simplify equation (3) by defining the matrix \mathbf{M}

$$M_{x,y} = \sum_{\mathbf{z} \in C(\mathbf{y})} (G_{x,y} - G_{x,z}), \quad (4)$$

so that

$$F_{x,0} = \frac{G_{x,0}}{\epsilon_2} + (1-h) \sum_{\mathbf{y} \in C} M_{x,y} F_{y,0}. \quad (5)$$

The first term on the right-hand side is the Green's function of a point source at site $\mathbf{0}$ without the clusters, while the second term represents the perturbation due to the existence of clusters. For an infinite network, \mathbf{M} is generally an $\infty \times n_s$ matrix, while \mathbf{F} and \mathbf{G} are column vectors of the Green's functions. In the cluster subspace, let $\tilde{\mathbf{M}}$, $\tilde{\mathbf{F}}$ and $\tilde{\mathbf{G}}$ denote the respective quantities; i.e., $\tilde{\mathbf{M}}$ is an $n_s \times n_s$ submatrix of \mathbf{M} , while $\tilde{\mathbf{F}}$ and $\tilde{\mathbf{G}}$ are restricted to the n_s cluster sites. Here the square matrix $\tilde{\mathbf{M}}$ is called the Green matrix. In the cluster subspace, we obtain a matrix form:

$$\tilde{\mathbf{F}} = \frac{\tilde{\mathbf{G}}}{\epsilon_2} + (1-h)\tilde{\mathbf{M}} \cdot \tilde{\mathbf{F}}, \quad (6)$$

which can readily be inverted to yield $\tilde{\mathbf{F}}$, by solving a set of n_s linear simultaneous equations.

Then, considering the existence of cluster $1'$ and defining $\tilde{\mathbf{F}}_1$ and $\tilde{\mathbf{F}}_{1'}$ as the potentials of cluster 1 and cluster $1'$, we have

$$\begin{pmatrix} \tilde{\mathbf{F}}_1 \\ \tilde{\mathbf{F}}_{1'} \end{pmatrix} = \frac{1}{\epsilon_2} \begin{pmatrix} \tilde{\mathbf{G}}_1 \\ \tilde{\mathbf{G}}_{1'} \end{pmatrix} + (1-h) \begin{pmatrix} \tilde{\mathbf{M}}_{1,1} & \tilde{\mathbf{M}}_{1,1'} \\ \tilde{\mathbf{M}}_{1',1} & \tilde{\mathbf{M}}_{1',1'} \end{pmatrix} \begin{pmatrix} \tilde{\mathbf{F}}_1 \\ \tilde{\mathbf{F}}_{1'} \end{pmatrix} \quad (7)$$

with $\tilde{\mathbf{M}}_{1,1} = \tilde{\mathbf{M}}_{1',1'}$ and $\tilde{\mathbf{M}}_{1,1'} = \tilde{\mathbf{M}}_{1',1}$ due to the central symmetry of two clusters. By defining $\tilde{\mathbf{F}}_{\pm} = \tilde{\mathbf{F}}_1 \pm \tilde{\mathbf{F}}_{1'}$, $\tilde{\mathbf{G}}_{\pm} = \tilde{\mathbf{G}}_1 \pm \tilde{\mathbf{G}}_{1'}$ and $\tilde{\mathbf{M}}_{\pm} = \tilde{\mathbf{M}}_{1,1} \pm \tilde{\mathbf{M}}_{1',1}$, equation (7) is simplified as

$$\tilde{\mathbf{F}}_{\pm} = \frac{\tilde{\mathbf{G}}_{\pm}}{\epsilon_2} + (1-h)\tilde{\mathbf{M}}_{\pm} \cdot \tilde{\mathbf{F}}_{\pm}. \quad (8)$$

The same form as equation (6) is found, so the two-cluster problem is reduced to one similar to a single-cluster problem. As discussed in [18], the resonance spectrum and local-field distribution near resonance can be analytically obtained.

In the cluster subspace, if only cluster 1 exists, the eigenvalues of Green matrix $\tilde{\mathbf{M}}_{1,1}$ form the resonance spectrum. However, when cluster $1'$ is placed in a centrally symmetric position with cluster 1, $\tilde{\mathbf{M}}_{1,1}$ is replaced by the above matrices $\tilde{\mathbf{M}}_{\pm}$. One of its eigenvalues s_n splits into two, s_{n+} , s_{n-} , which satisfy the conditions

$$s_{n+} < s_n < s_{n-} \quad (9)$$

or

$$s_{n-} < s_n < s_{n+}, \quad (10)$$

and

$$s_{n+} + s_{n-} = 2s_n. \quad (11)$$

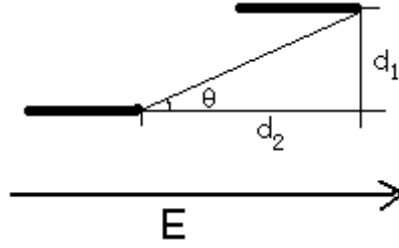


Figure 2. Schematic diagram of a two-bond cluster in an infinite network. A unit uniform field is applied along the bonds.

Therefore one of s_{n_1} and s_{n_2} is red shifted while the other is blue shifted. We note a similar solution in a two-component granular composite [14], which, however, did not clearly exhibit the local-field distribution.

Instead of the right eigenvector \tilde{R}_n and left eigenvector \tilde{L}_n solved by $\tilde{M}_{1,1}$ if only a single cluster exists, we introduce $\tilde{R}_{n\pm}$ and $\tilde{L}_{n\pm}$ related to \tilde{M}_{\pm} to express the solution of equation (8). For $x \in C_{\pm}$, which is a kind of combination of clusters 1 and 1', we have a similar form to that found in [18],

$$\tilde{F}_{\pm} = \sum_{n_{\pm}=1}^{n_R} \frac{s}{\epsilon_2(s - s_{n_{\pm}})} \left(\sum_{y \in C_{\pm}} \tilde{L}_{n_{\pm},y} \tilde{G}_{\pm,y,o} \right) \tilde{R}_{n_{\pm}}. \quad (12)$$

For $x \notin C_{\pm}$, we obtain the Green's function F_{\pm} at the position x ,

$$F_{\pm,x,o} = \frac{G_{x,0}}{\epsilon_2} + \frac{1}{\epsilon_2} \sum_{n_{\pm}=1}^{n_R} \frac{1}{s - s_{n_{\pm}}} \left(\sum_{y \in C_{\pm}} \tilde{L}_{n_{\pm},y} \tilde{G}_{\pm,y,o} \right) \left(\sum_{z \in C_{\pm}} M_{x,z} \tilde{R}_{n_{\pm},z} \right) \quad (13)$$

with $M_{x,y} = \sum_{z \in C_{\pm}} (G_{x,y} - G_{x,z})$. It is remarked that equations (12) and (13) describe a generalized image problem in electrostatics. When the point of observation is inside the cluster, there is only one term, i.e. the contribution from the screened source. However, when the point of observation x is outside the clusters, there are two contributions to the Green's function. One arises from the point source as described by the first term of equation (13), whereas the other term describes the image contribution of the polarization of the clusters. When s is very close to $s_{n_{\pm}}$, the local fields around the clusters diverge, leading to a large enhancement in the effective linear and nonlinear optical responses. In the cluster subspace, \tilde{F}_1 and $\tilde{F}_{1'}$ can be expressed by \tilde{F}_{\pm} as

$$\tilde{F}_1 = \frac{(\tilde{F}_+ + \tilde{F}_-)}{2}, \quad (14)$$

and

$$\tilde{F}_{1'} = \frac{(\tilde{F}_+ - \tilde{F}_-)}{2}. \quad (15)$$

So when resonance occurs, for the above Green's functions \tilde{F}_1 and $\tilde{F}_{1'}$ it is found that only $\frac{\tilde{F}_+}{2}$ (or $\frac{\tilde{F}_-}{2}$) is a product term.

2.2. Two simple examples

Example 1. A two-bond cluster is shown in figure 2 as $\theta = 3\pi/4$, in which one bond is from $1(-0.5, -0.5)$ to $2(0.5, -0.5)$ and the other is from $2'(-0.5, 0.5)$ to $1'(0.5, 0.5)$ (note that

they are centrally symmetric). Here a unit uniform field is applied along the bonds. The above matrices $\tilde{M}_{1,1}$ and $\tilde{M}_{1,1'}$ become

$$\tilde{M}_{1,1} = \begin{pmatrix} G_{0,0} - G_{1,0} & G_{1,0} - G_{0,0} \\ G_{1,0} - G_{0,0} & G_{0,0} - G_{1,0} \end{pmatrix} \quad (16)$$

and

$$\tilde{M}_{1,1'} = \begin{pmatrix} G_{1,1} - G_{1,0} & G_{1,0} - G_{1,1} \\ G_{1,0} - G_{1,1} & G_{1,1} - G_{1,0} \end{pmatrix}. \quad (17)$$

The corresponding \tilde{M}_+ reads

$$\begin{pmatrix} G_{1,1} - 2G_{1,0} & 2G_{1,0} - G_{1,1} \\ 2G_{1,0} - G_{1,1} & G_{1,1} - 2G_{1,0} \end{pmatrix}. \quad (18)$$

We obtain its eigenvalue $s_1 = 1 - \frac{2}{\pi} < 0.5$. According to equations (14) and (15), the local potentials of \tilde{F}_1 and $\tilde{F}_{1'}$ are contributed only by $\tilde{F}_+/2$. Because $\tilde{G}_1 = \begin{pmatrix} -0.5 \\ 0.5 \end{pmatrix}$ and $\tilde{G}_{1'} = \begin{pmatrix} 0.5 \\ -0.5 \end{pmatrix}$, in the calculation of \tilde{F}_+ the source term $\tilde{G}_1 + \tilde{G}_{1'}$ becomes $\begin{pmatrix} 0 \\ 0 \end{pmatrix}$, so the local fields are diminished. It is known that the eigenvalue s is monotonically increased with the frequency in the general Drude model and Lorentz model. Hence the red shift of optical response does not appear.

Then, \tilde{M}_- can be written as

$$\begin{pmatrix} -G_{1,1} & G_{1,1} \\ G_{1,1} & -G_{1,1} \end{pmatrix}. \quad (19)$$

Its eigenvalue is $s_2 = \frac{2}{\pi} > 0.5$. Similar to the situation of \tilde{M}_+ , after the calculation of \tilde{F}_1 and $\tilde{F}_{1'}$, the local potential is contributed only by $\tilde{F}_-/2$. However, the source term $\tilde{G}_1 - \tilde{G}_{1'}$ in \tilde{F}_- is $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$, so the local field is enhanced and leads to the effective linear and nonlinear optical responses. Since $s_2 > 0.5$, a blue shift of optical response occurs.

Example 2. Another two-bond cluster is shown as figure 2 for $\theta = 0$, which means that one bond is from 1(-1.5, 0) to 2(-0.5, 0) and the other bond is from 2'(0.5, 0) to 1'(1.5, 0) (again the two bonds are centrally symmetric). The applied field is also along the bonds. The matrices $\tilde{M}_{1,1}$ and $\tilde{M}_{1,1'}$ read

$$\tilde{M}_{1,1} = \begin{pmatrix} G_{0,0} - G_{1,0} & G_{1,0} - G_{0,0} \\ G_{1,0} - G_{0,0} & G_{0,0} - G_{1,0} \end{pmatrix}, \quad \tilde{M}_{1,1'} = \begin{pmatrix} G_{3,0} - G_{2,0} & G_{2,0} - G_{3,0} \\ G_{2,0} - G_{1,0} & G_{1,0} - G_{2,0} \end{pmatrix}. \quad (20)$$

We obtain that

$$\tilde{M}_+ = \begin{pmatrix} G_{3,0} - G_{2,0} - G_{1,0} & -G_{3,0} + G_{2,0} + G_{1,0} \\ G_{2,0} & -G_{2,0} \end{pmatrix}, \quad (21)$$

$$\tilde{M}_- = \begin{pmatrix} -G_{1,0} + G_{2,0} - G_{3,0} & G_{1,0} - G_{2,0} + G_{3,0} \\ 2G_{1,0} - G_{2,0} & -2G_{1,0} + G_{2,0} \end{pmatrix}. \quad (22)$$

Two splitting eigenvalues are $s_1 = -2 + \frac{8}{\pi} > 0.5$ and $s_2 = 3 - \frac{8}{\pi} < 0.5$. The same as the discussion in example 1, the source term $\tilde{G}_1 + \tilde{G}_{1'}$ in \tilde{F}_+ disappears and the source term $\tilde{G}_1 - \tilde{G}_{1'}$ in \tilde{F}_- exists. Thus, near s_2 , the field is localized around two bonds. Only a red shift of optical response is found. In the case of two identically shaped clusters, the result of the blue shifted versus red shifted split resonance has been discussed [14].

In a uniform applied field, only a blue shift or a red shift of optical response for two interacting bonds is predicted. It is also shown that for two centrally symmetric clusters the shift of optical response is dominated by the above matrix \tilde{M}_- .

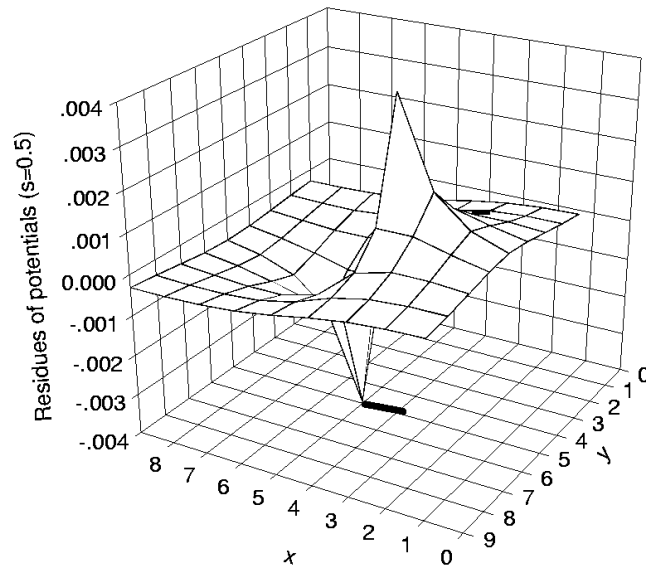


Figure 3. The three-dimensional plot of the residue of the Green's function of a single bond cluster subject to a positive point source $\mathbf{0} = (0, 0)$.

3. Local-field distribution of two interacting bonds

In order to investigate the spectral shift of optical responses, local-field distributions for various two-bond clusters are illustrated. For comparison with that of the two-bond clusters, the Green's function of a single bond is shown by a three-dimensional plot in figure 3 [18]. In this case, only one resonance exists, i.e. $s = 0.5$. It is found that the potentials are very localized and the effect of one isolated bond subject to a point source is similar to a 'dipole'. This polarization is closely related to the effective optical response, so the resonant frequency corresponds to the absorption peak and the third-order nonlinear enhancement peak. If there exist two bonds subject to a point source, due to the coupling between 'dipoles', one resonant frequency splits into two and the local fields are re-arranged. If two 'dipoles' are ordered along the same direction this is called the symmetric arrangement, while we name the other arrangement the anti-symmetric arrangement.

Figures 4–7 display the three-dimensional plots of residues of Green's functions for various pairs of bonds shown as the thick lines subject to a unit positive point source $(0, 0)$ [18]. The configurations of two bonds in these figures can also be represented by d_1 and d_2 as shown in figure 2. Figures 4(a) and 5(a) illustrate the local-field distributions of anti-symmetric arrangements. The eigenvalue s_1 ($=0.3633$ or 0.4933) is less than the value of a single bond s ($=0.5$) and is solved by the matrix \tilde{M}_+ . Figures 4(b) and 5(b) describe the local-field distributions of symmetric arrangements. Different from the anti-symmetric case, the eigenvalue s_2 ($=0.6366$ or 0.5067) is greater than s ($=0.5$) and originates from \tilde{M}_- . A uniform field can be reproduced by placing a positive source and a negative source concomitantly on both sides of the cluster and in the limit of an infinite separation between the sources. Considering the action of a negative source, for an anti-symmetric arrangement, or s_1 , the local field is diminished, while for a symmetric arrangement, or s_2 , the local field is enhanced and a blue shift of optical response occurs. In figure 4, due to a strong interaction of two bonds with $d = \sqrt{d_1^2 + d_2^2} = 1$, s_1 and s_2 have a large deviation from the value s , but in figure 5 the

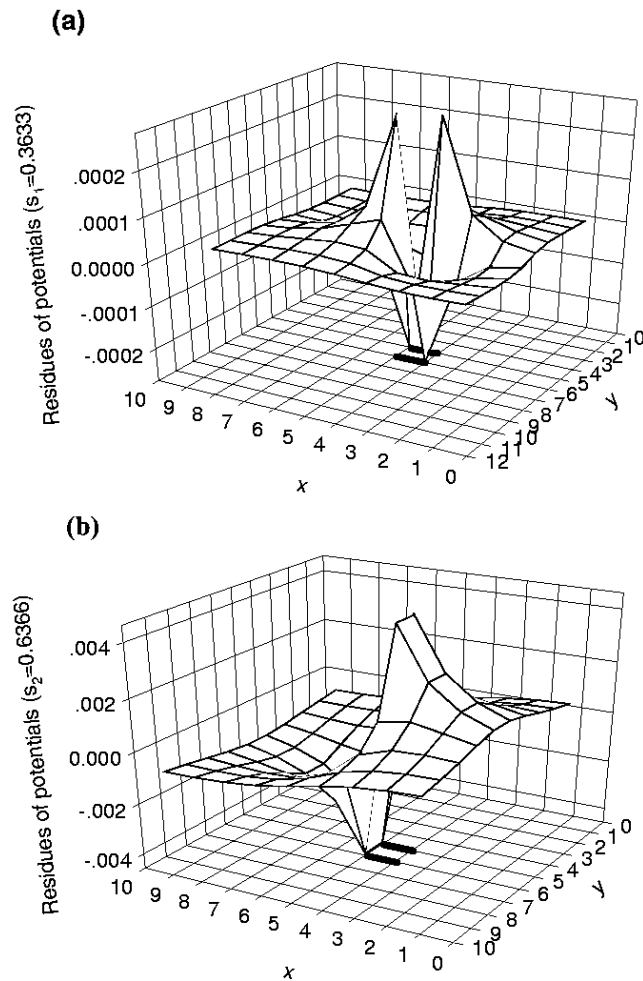


Figure 4. The three-dimensional plots of the residue of the Green's function of two perpendicular bonds (thick lines) subject to a positive point source $(0, 0)$. Two bonds are placed as $d_1 = 1$ and $d_2 = 0$ shown in figure 2. Graph (b) describes the symmetric arrangement of local field and the eigenvalue $s_2 = 0.6366$ (>0.5) originates from M_1 .

distance between the bonds is increased, i.e. $d = 5$, and the interaction becomes weaker, so a small deviation of s_1 and s_2 , and a small blue shift are observed. In this figure, it is also noted that the intensity of local field corresponding to s_2 is one or two orders higher than that corresponding to s_1 . In figures 6(a) and 7(a), the local-field distributions of anti-symmetric arrangements are illustrated. The eigenvalue s_1 ($=0.5465$ or 0.5067) is greater than s ($=0.5$) and is solved by the matrix \tilde{M}_+ . Figures 6(b) and 7(b) show the local-field distributions of symmetric arrangements. The eigenvalue s_2 ($=0.4535$ or 0.4933) is less than s ($=0.5$) and originates from M_- . Similarly the diminishment and enhancement appear due to the existence of a negative source, namely, for a symmetric arrangement the local field is enhanced and a red shift occurs. We also observe the same deviation of eigenvalues at a different distance. Finally, due to the coupling between two 'dipoles' and superposition of two sources, the symmetric arrangement of local field (or \tilde{M}_-) always corresponds to the shift of optical response.

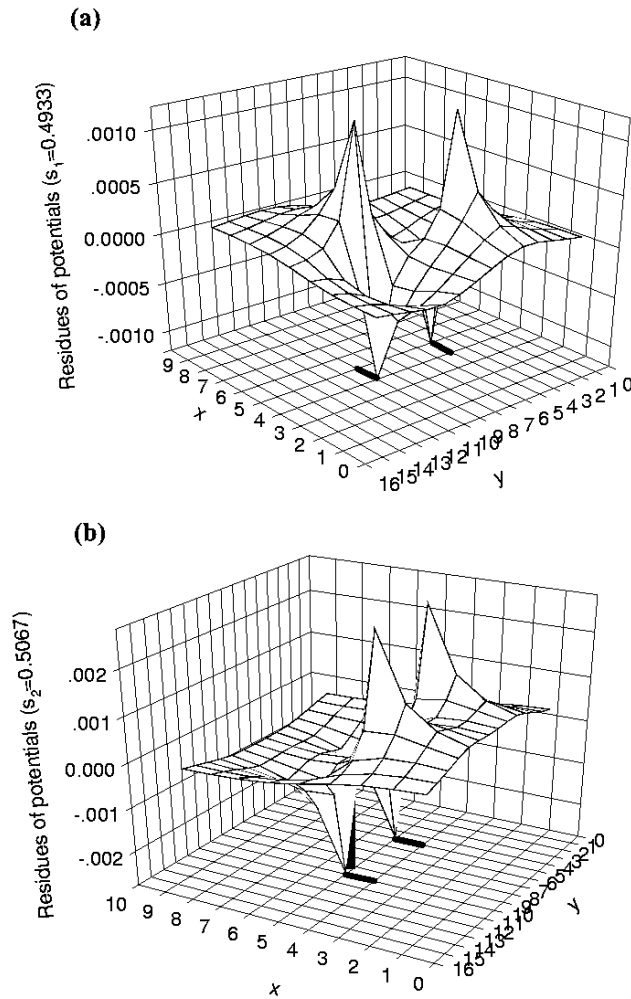


Figure 5. The three-dimensional plots of the residue of the Green's function of two perpendicular bonds (thick lines) subject to a positive point source $(0, 0)$. Different from figure 4, two bonds are placed as $d_1 = 5, d_2 = 0$ shown in figure 2. Graph (b) describes the symmetric arrangement of local field and the eigenvalue $s_2 = 0.5067 (>0.5)$ originates from M_1 .

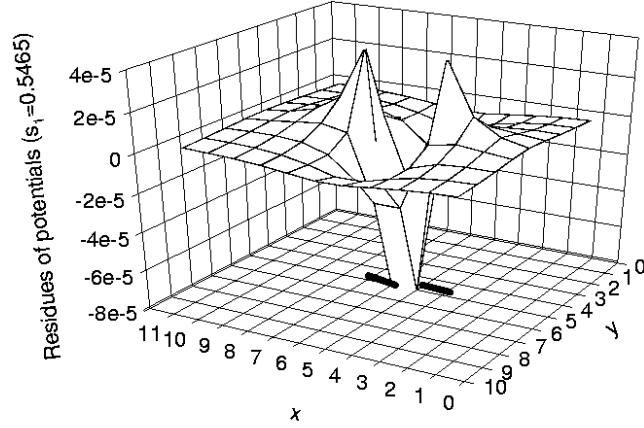
4. Numerical calculations by the Drude model

In this section, the Drude free electric model is employed to demonstrate the shift of effective linear and nonlinear optical responses. The admittance of the impurity metallic bonds is

$$\epsilon_1 = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}, \quad (23)$$

where ω is a plasma frequency, and γ a damping constant. For metal, the plasma frequency $\omega_p = 10^{16}$, being in the ultraviolet. We choose $\gamma = 0.1\omega_p$, which is a typical value of a metal, and $\epsilon_2 = 1.77$, which is the dielectric constant of water for model calculations. The range of optical responses is $\omega/\omega_p \in (0, 1)$. A schematic diagram of two bonds in an infinite random conductance network is shown as figure 2. By the finite-difference transformation, the imaginary part of the effective linear response function along the applied field reads [20]

(a)



(b)

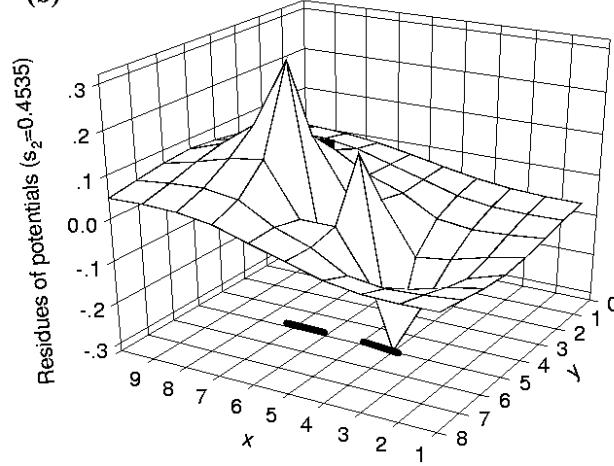


Figure 6. The three-dimensional plots of the residue of the Green's function of two parallel bonds (thick lines) subject to a positive point source $(0, 0)$. Two bonds are expressed as $d_1 = 0, d_2 = 1$ shown in figure 2. Graph (b) describes the symmetric arrangement of local field and the eigenvalue $s_2 = 0.4535$ (< 0.5) originates from M_1 .

$$-\text{Im}(\epsilon_e) = \text{Im} \sum_{n=1}^{n_c} \frac{\gamma_n}{\epsilon_2(s - s_n)} \quad (24)$$

with $\gamma_n = L_{\hat{n}} R_{\hat{n}}$, where $L_{\hat{n}} = \sum_{y \in C} \tilde{L}_{n,y} y_1$ and $R_{\hat{n}} = \sum_{x,y \in C} (x_1 - y_1)(\tilde{R}_{n,x} - \tilde{R}_{n,y})$. When resonance occurs, the local field V_x is determined completely, so our formulae can be extended to the calculation of the nonlinear response. When only the bonds within the cluster have a nonlinear term, i.e. $\chi_2 = 0$ and $\chi_1 = 1$, the effective nonlinear response function is written as [20]

$$\chi_e = \sum_{(x,y) \in C} |F_x - F_y|^2 (F_x - F_y)^2. \quad (25)$$

Based on the above formulae, the effective optical responses for various two-bond clusters are computed.

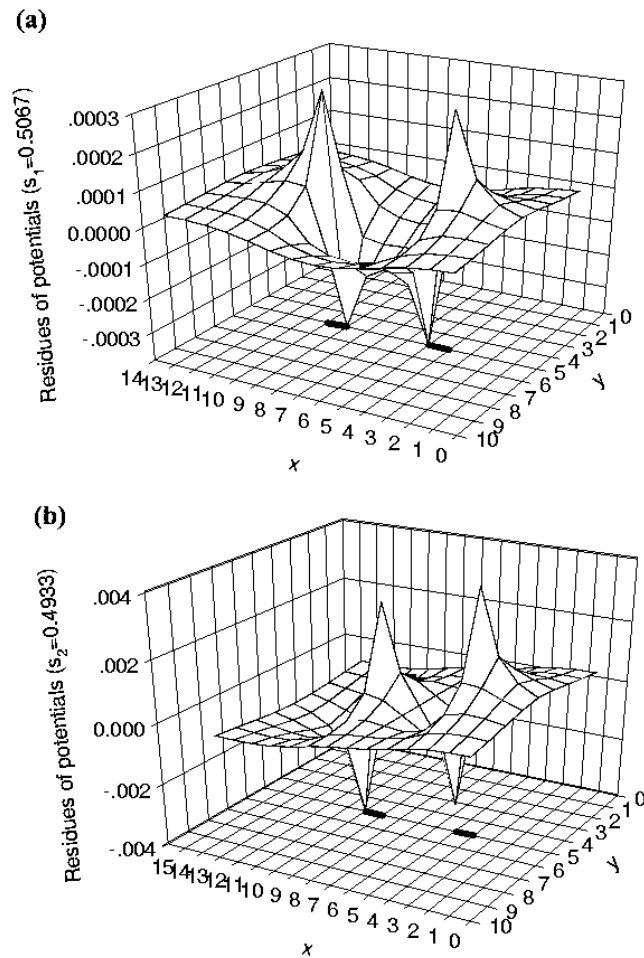


Figure 7. The three-dimensional plots of the residue of the Green's function of two parallel bonds (thick lines) subject to a positive point source $(0, 0)$. Two bonds are expressed as $d_1 = 0, d_2 = 5$ shown in figure 2. Graph (b) describes the symmetric arrangement of local field and the eigenvalue $s_2 = 0.4933$ (< 0.5) originates from M_1 .

Figures 8 and 9 display respectively the shift of effective linear and nonlinear optical responses for various two-bond clusters. In these figures, the dotted curves are used to represent the optical response of a single-bond cluster. For comparison with two-bond clusters, the absorption term $-\text{Im}(\epsilon_e)$ and the third-order nonlinear response χ_e are normalized by N_b , the number of total bonds in the cluster subspace. Here N_b is unity for a single-bond cluster and two for various two-bond clusters. When the angle θ increases from zero to $\pi/2$, the spectrum changes from red shift to blue shift. We observe a red shift in figures 8(a) and (b) and 9(a) and (b), while in figures 8(d) and (e) and 9(d) and (e) a blue shift is exhibited. In these figures, we note that there is no shift when $\theta = \pi/4$, i.e. figure 8(c) or 9(c), which is an intermediate case. Because of the smaller distance between bonds as shown in figures 8(a) and (e) and 9(a) and (e), there is a stronger interaction, so we observed a larger shift than found in figures 8(b) and (d) and 9(b) and (d). Finally, at a large distance, the interaction between bonds becomes weak and the results of a single cluster appear as shown in figures 8(f) and 9(f). For two interacting

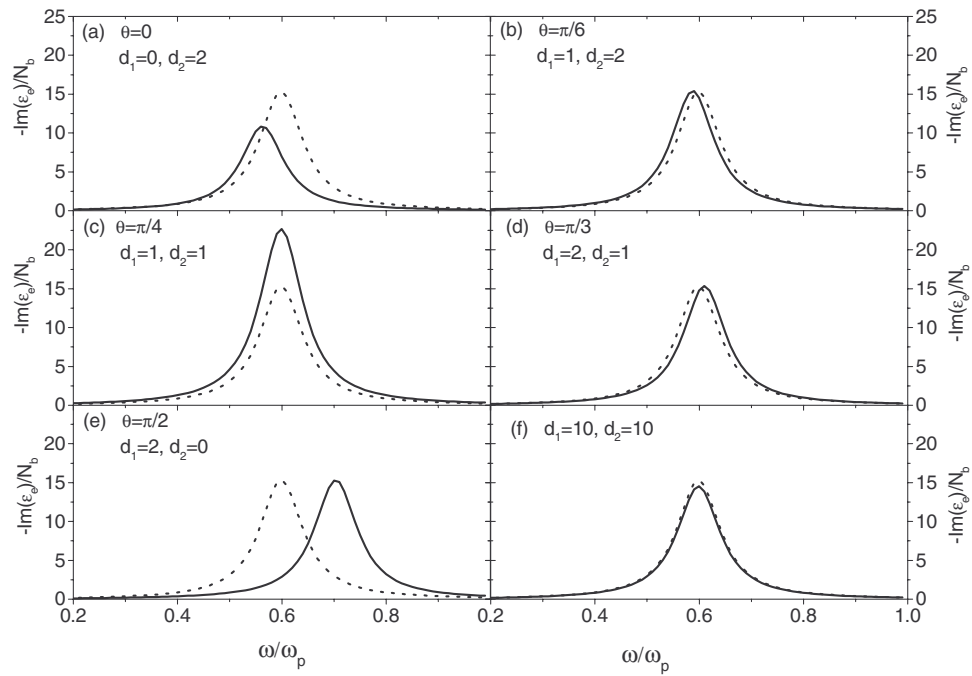


Figure 8. Effective linear optical responses of various two-bond clusters by the Drude model. The dotted curve represents the results of a single bond.

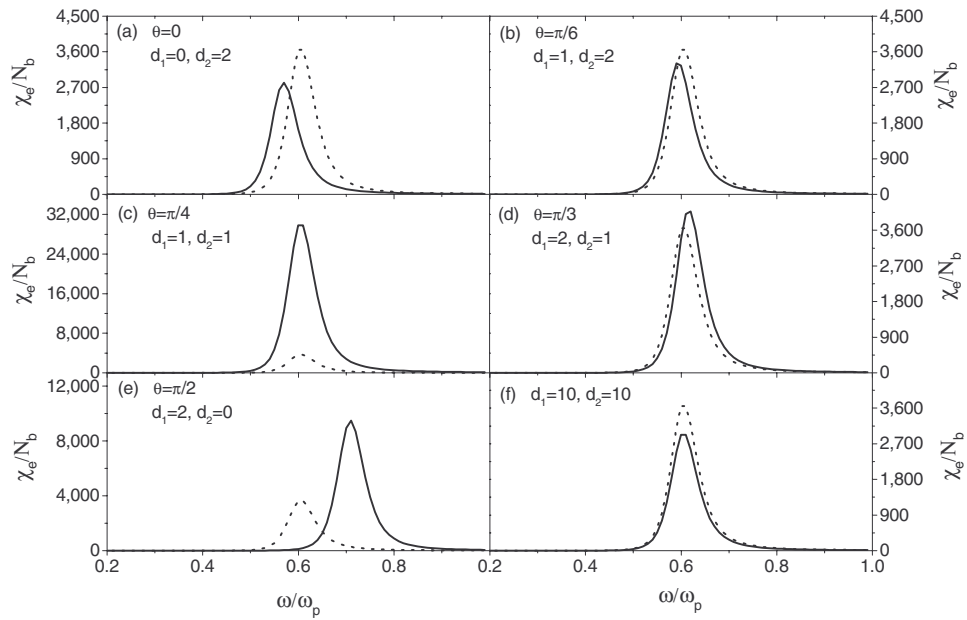


Figure 9. Effective nonlinear optical responses of various two-bond clusters by the Drude model. The dotted curve represents the results of a single bond.

multi-bond clusters, which are not strictly centrally symmetric, we also find a blue shift and red shift of optical responses [19].

5. Conclusion

We have investigated the optical response of two interacting clusters in the resonant composites. First, the GFF of two centrally symmetric clusters is derived. Based on this formalism, we find the split of resonance due to the interaction between two clusters. In a uniform applied field, we predict that only a red shift or blue shift of optical response occurs for the different arrangements of two clusters. We also observe a transition from red to blue shifts with respect to the arrangement of two clusters. We discuss these shifts by the symmetric and anti-symmetric local-field distribution. Due to the coupling between two ‘dipoles’ and superposition of two sources, it is found that the symmetric arrangement of local field (or \tilde{M}_-) always corresponds to the shift of optical responses. Finally, the numerical calculations by the Drude model are performed to demonstrate the spectral shifts in the effective linear and nonlinear optical responses.

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