Antisymmetrical optical states

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The general properties of antisymmetrical solutions of the coupled-dipole equation are studied. This equation is used to describe the interaction of a cluster of small particles acting as elementary dipoles with an external electromagnetic wave. It is shown that antisymmetrical (with zero total dipole moment) eigenstates can be excited even in clusters that are much smaller in size than the wavelength of the incident radiation. In this case the quality of the collective optical resonance may be enhanced by the large parameter $(\lambda/R_c)^2$ (R_c is the characteristic size of the cluster). This phenomenon, in contrast to superradiance, leads to an increased [by the factor $(\lambda/R_c)^2$] lifetime of the system in the excited state and can be called antisuperradiance. © 1995 Optical Society of America

1. INTRODUCTION

Scattering and absorption of light by a cluster is a problem of general interest in optics and classical electrodynamics. One usually refers to a cluster as a set of small particles fixed in space and acting as elementary dipoles. This simple model was extensively studied during the past 20 years. It was used to describe interaction of light with improperly shaped particles,[1–8] fractal clusters,[9–16] molecular clusters,[17] and in many other applications. The theoretical point of departure in these publications was the coupled-dipole equation (CDE, also known as the discrete-dipole equation or the discrete-dipole approximation), which couples the dipole moments of particles to each other and to the incident wave through classical dipole radiation fields. The CDE can be derived from the Maxwell equations provided that the local electrical field varies slightly in the size of each particle.[18–20]

In this paper the general properties of eigenstates of the CDE with zero total dipole moment (antisymmetrical states) are investigated. It turns out that under certain circumstances such eigenstates can be excited in clusters even by incident radiation with the wavelength λ much larger than the size of cluster R_c. The quasi-static approximation is not valid in this case, no matter how large the ratio λ/R_c is.

The quasi-static approximation (i.e., restricted to the near-zone term in the formula for dipole radiation and neglecting the phase shift of the effect of the incident wave on the size of the cluster) was used extensively (see, for example, Refs. 10–13). In many cases, especially if there is strong absorption, this approximation is absolutely justified. However, if absorption is weak and the system possesses antisymmetrical states, the quasi-static approximation fails dramatically.

The antisymmetrical states, if they exist, possess remarkable properties. Probably the most important of these are mutual compensation of the radiation reaction and high quality of optical resonance.

In Section 2 the basic equations and expressions for optical cross sections of clusters are reviewed. In Section 3 general expressions for optical cross sections are obtained by integration of the scattering amplitude. In Section 4 a general eigenstate formalism for the complex symmetrical interaction matrix is developed, and expressions for the optical cross sections in terms of dipole eigenstates are obtained. Section 5 is devoted to the long-wave limit, when the non-Hermitian part of the interaction matrix may be treated as a perturbation. In this section the antisymmetrical states are introduced, and it is shown that even for an asymptotically infinite wavelength of the incident light one must take into account the second-order corrections to the eigenvalues to describe scattering and absorption in an antisymmetrical state correctly. (If a state is not antisymmetrical, one still needs to keep the first-order correction to describe scattering.) In Section 6 the properties of the antisymmetrical states are discussed in more detail. In Section 7 some examples of the antisymmetrical state are given, and Section 8 is devoted to a final discussion.

2. BASIC EQUATIONS

Let us consider scattering of a plane wave of the form

$$\mathbf{E}_{\mathrm{inc}}(\mathbf{r}, t) = \mathbf{E}_0 \exp(i\mathbf{k}\mathbf{r} - i\omega t) \tag{1}$$

from a set of N small spherically symmetrical particles located at points $\mathbf{r}_1, \ldots, \mathbf{r}_N$. Each particle obeys linear dipole polarizability χ so that its dipole moment $\mathbf{d}_i$ is proportional to the local field at the point $\mathbf{r}_i$, which is the superposition of the incident wave and all the secondary waves scattered by other dipoles. Therefore the dipole moments are coupled to each other and to the incident field (1) by

$$\mathbf{d}_i = \chi[\mathbf{E}_0 \exp(i\mathbf{k}\mathbf{r}_i) + \sum_{j=1}^{N}{}' \hat{W}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{d}_j], \tag{2}$$

where the time dependence $\exp(-i\omega t)$ is omitted, $\sum'$ denotes the sum over all values of the index j except $j = i$, and the 3×3 interaction tensor $\hat{W}$ acts on a three-dimensional vector of the dipole moment and is defined by the general formulas for dipole radiation:

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$$W_{\alpha\beta}(r) = k^3\left[A(kr)\delta_{\alpha\beta} + B(kr)\frac{r_\alpha r_\beta}{r^2} \right], \tag{3}$$

$$A(x) = (x^{-1} + ix^{-2} - x^{-3})\exp(ix), \tag{4}$$

$$B(x) = (-x^{-1} - 3ix^{-2} + 3x^{-3})\exp(ix). \tag{5}$$

Here Greek indexes stand for Cartesian components of vectors and A and B are complex functions of a real scalar argument.

The dipole moments defined by Eq. (2) may be used to find the scattering amplitude and all the cross sections. The scattered field $\mathbf{E}_s$ at some point $\mathbf{R}$ in the far zone ($R \gg |\mathbf{r}_i - \mathbf{r}_j|, \lambda$) is given by

$$\mathbf{E}_s = k^2 \sum_{i=1}^{N} \frac{\mathbf{d}_i - (\mathbf{d}_i\mathbf{s})\mathbf{s}}{|\mathbf{r}_i - \mathbf{R}|} \exp(ik|\mathbf{r}_i - \mathbf{R}|). \tag{6}$$

With the usual decomposition $|\mathbf{r}_i - \mathbf{R}| \approx R - \mathbf{s}\mathbf{r}_i$, where $\mathbf{s} = \mathbf{R}/R$ is the unit vector in the direction of scattering, one gets the expression for the scattering amplitude $\mathbf{f}(\mathbf{s})$:

$$\mathbf{f}(\mathbf{s}) = k^2 \sum_{i=1}^{N} [\mathbf{d}_i - (\mathbf{d}_i\mathbf{s})\mathbf{s}]\exp(-ik\mathbf{s}\mathbf{r}_i). \tag{7}$$

The cross sections of extinction, scattering, and absorption, σ_e, σ_s, and σ_α, respectively, are expressed through the scattering amplitude:

$$\sigma_e = \frac{4\pi}{k} \frac{\mathrm{Im}[\mathbf{f}(\mathbf{k}/k)\mathbf{E}_0{}^*]}{|\mathbf{E}_0|^2}, \tag{8}$$

$$\sigma_s = \frac{1}{|\mathbf{E}_0|^2} \int |\mathbf{f}(\mathbf{s})|^2 \mathrm{d}\Omega, \tag{9}$$

$$\sigma_\alpha = \sigma_e - \sigma_s. \tag{10}$$

Here $\mathbf{k}/k$ is the unit vector in the forward direction and $\mathrm{d}\Omega$ is an element of the solid angle in the direction of scattering $\mathbf{s}$.

The straightforward application of the optical theorem [Eq. (8)] to the scattering amplitude [Eq. (7)] leads to the simple and well-known result for the extinction cross section:

$$\sigma_e = \frac{4\pi k}{|\mathbf{E}_0|^2} \mathrm{Im} \sum_{i=1}^{N} \mathbf{d}_i\mathbf{E}_0{}^* \exp(-i\mathbf{k}\mathbf{r}_i), \tag{11}$$

The expression for the scattering cross section, which follows from Eqs. (7) and (9), is

$$\sigma_s = \frac{k^4}{|\mathbf{E}_0|^2} \sum_{i,j=1}^{N} \int [\mathbf{d}_i\mathbf{d}_j{}^* - (\mathbf{d}_i\mathbf{s})(\mathbf{d}_j{}^*\mathbf{s})] \times \exp[ik\mathbf{s}(\mathbf{r}_i - \mathbf{r}_j)]\mathrm{d}\Omega. \tag{12}$$

Unlike the extinction cross section, the scattering cross section is given by the double summation and contains all the relative distances $\mathbf{r}_i - \mathbf{r}_j$ in the cluster. In Section 3 it is shown that Eq. (2) may be used to reduce the double summation to a single summation and to eliminate the relative distances from the expression for the scattering cross section.

3. INTEGRATION OF THE SCATTERING AMPLITUDE

It is convenient to represent Eq. (12) for σ_s as a sum of diagonal and off-diagonal terms:

$$\sigma_s = \sum_{i=1}^{N} \sigma_{s,ij} + \sum_{i\neq j}^{N} \sigma_{s,ij}, \tag{13}$$

where $\sum_{i\neq j}^{N}$ denotes double summation over i from 1 to N and over j not equal to i from 1 to N. Integration according to Eq. (12) gives us, for the diagonal terms,

$$\sigma_{s,ii} = \frac{8\pi k^4}{3} \frac{|\mathbf{d}_i|^2}{|\mathbf{E}_0|^2}, \tag{14}$$

and for the off-diagonal terms,

$$\sigma_{s,ij} = \frac{4\pi k^4}{|\mathbf{E}_0|^2}\left\{ \left[\frac{\sin(kr_{ij})}{kr_{ij}} + \frac{\cos(kr_{ij})}{(kr_{ij})^2} - \frac{\sin(kr_{ij})}{(kr_{ij})^3} \right] \mathbf{d}_i\mathbf{d}_j{}^* + \left[-\frac{\sin(kr_{ij})}{kr_{ij}} - 3\frac{\cos(kr_{ij})}{(kr_{ij})^2} + 3\frac{\sin(kr_{ij})}{(kr_{ij})^3} \right] \times (\mathbf{d}_i\mathbf{n}_{ij})(\mathbf{d}_j{}^*\mathbf{n}_{ij}) \right\}, \tag{15}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{n}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$. Obviously $\sigma_{s,ii}$ is equal to the scattering cross section of an isolated dipole $\mathbf{d}_i$ (i.e., without interference), and $\sigma_{s,ij}$ are the interference terms.

At this point we make use of the properties given in Eqs. (3)–(5) of the interaction tensor $\hat{W}$ and the coupled-dipole equation (2). First we notice that the terms in square brackets in Eq. (15) are equal to Im $A(kr_{ij})$ and Im $B(kr_{ij})$, where A and B are defined by Eqs. (4) and (5), so that $\sigma_{s,ij}$ may be rewritten as

$$\sigma_{s,ij} = \frac{4\pi k^4}{|\mathbf{E}_0|^2}[\mathbf{d}_i\mathbf{d}_j{}^* \ \mathrm{Im}\ A(kr_{ij}) + (\mathbf{d}_i\mathbf{n}_{ij})(\mathbf{d}_j{}^*\mathbf{n}_{ij}) \times \mathrm{Im}\ B(kr_{ij})]. \tag{16}$$

After summing $\sigma_{s,ij}$ and $\sigma_{s,ji}$ ($i \neq j$), one obtains purely real coefficients in front of Im A and Im B, and therefore for the sum of the off-diagonal elements [Eq. (16)] over all i and $j \neq i$ it is possible to put the symbol for the imaginary part in front:

$$\sum_{i\neq j}^{N} \sigma_{s,ij} = \frac{4\pi k^4}{|\mathbf{E}_0|^2} \mathrm{Im} \sum_{i\neq j}^{N} [\mathbf{d}_i\mathbf{d}_j{}^* A(kr_{ij}) + (\mathbf{d}_i\mathbf{n}_{ij})(\mathbf{d}_j{}^*\mathbf{n}_{ij})B(kr_{ij})]. \tag{17}$$

Notice that the term in the brackets is exactly equal to the interaction tensor $\hat{W}$ [Eq. (3)] that acts on $\mathbf{d}_j{}^*$ and is multiplied by $\mathbf{d}_i$, so that

$$\sum_{i\neq j}^{N} \sigma_{s,ij} = \frac{4\pi k}{|\mathbf{E}_0|^2} \mathrm{Im} \sum_{i\neq j}^{N} \sum_{\substack{j=1 \\ j\neq i}}^{N} [\mathbf{d}_i{}^* \cdot \hat{W}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{d}_j]. \tag{18}$$

The summation over the i and j indices is written explicitly in the right-hand part of Eq. (18), and the sign of complex conjugation is moved from $\mathbf{d}_j$ to $\mathbf{d}_i$ (this is valid because $\hat{W}$ is a symmetrical operator). Now the summation over j can be done with Eq. (2), which states that

$$\sum_{j=1}^{N}{}' \hat{W}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{d}_j = \frac{1}{\chi}\mathbf{d}_i - \mathbf{E}_0 \exp(i\mathbf{k}\mathbf{r}_i). \tag{19}$$

Combining Eqs. (13), (14), (18), and (19), one obtains the final expression for the scattering cross section:

$$\sigma_s = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{i=j}^{N} \{\mathrm{Im}[\mathbf{d}_i\mathbf{E}_0{}^*\exp(-i\mathbf{k}\mathbf{r}_i)] - y_\alpha|\mathbf{d}_i|^2\}, \tag{20}$$

where y_α is a nonnegative constant defined by

$$y_\alpha = -\mathrm{Im}(\chi^{-1}) - 2k^3/3\,. \tag{21}$$

The fact that y_α is nonnegatively defined follows from the condition that the absorption cross section of a single isolated monomer is not negative.[21] Actually, y_α is the constant that characterizes the strength of absorption. From comparing Eqs. (11) for the extinction cross section and (20) for the scattering cross section, one can easily obtain the absorption cross section, which turns out to be

$$\sigma_\alpha = \frac{4\pi k}{|\mathbf{E}_0|^2}\, y_\alpha \sum_{i=1}^{N} |\mathbf{d}_i|^2\,. \tag{22}$$

Equations (20) and (22) give the desired cross sections. Both of them are given by single summation, and the expression for σ_s, Eq. (20), contains only the coordinates of particles [by means of the factor $\exp(-i\mathbf{k}\mathbf{r}_i)$] instead of the set of $N(N-1)/2$ relative distances $\mathbf{r}_i - \mathbf{r}_j$ in the Eq. (12).

The expressions for optical cross sections were obtained here by the use of straightforward integration of the scattering amplitude. It is also possible to obtain these expressions from simple physical arguments based on energy conservation.[7,21] One can associate extinction with the work exerted by the external field (produced by some source external to the cluster) and absorption with the work of the total local field, which includes the field of radiation reaction and all secondarily scattered waves. Application of this principle leads immediately to Eqs. (8) and (22). The derivation in this section is basically more strict and shows that the above principle is valid only if the system obeys the CDE.

4. EIGENSTATE ANALYSIS

The formulas for the optical cross section acquire an elegant form if the dipole moments are expressed in terms of the eigenstates of Eq. (2). First we rewrite Eq. (2) in matrix form:

$$|\mathrm{d}\rangle = \chi(|\mathrm{E}\rangle + \mathrm{W}|\mathrm{d}\rangle)\,. \tag{23}$$

Here $|\mathrm{d}\rangle \in \mathbb{C}^{3N}$ is a $3N$-dimensional column vector built from usual three-dimensional dipole moments $\mathbf{d}_i$. Analogously $|\mathrm{E}\rangle$ is the $3N$-dimensional column-vector of the right-hand part and W is $3N \times 3N$ interaction matrix built from 3×3 blocks $\hat{W}(\mathbf{r}_i - \mathbf{r}_j)$. We also use the orthonormal basis $|i\alpha\rangle$ in $\mathbb{C}^{3N}$ with the unit on the $3(i-1)+\alpha$ place and zeros on all others. The Cartesian components of the 3-dimensional vectors $\mathbf{d}_i$ are expressed as $d_{i\alpha} = \langle i\alpha\,|\,\mathrm{d}\rangle$.

The interaction matrix W appearing in Eq. (23) is in the general case a complex symmetrical matrix and therefore is not Hermitian. A complex symmetrical matrix possesses a complete set of eigenvectors that covers the $\mathbb{C}^{3N}$ space, provided that the matrix is not defective (i.e., geometric multiplicity of each eigenvalue is not less than its algebraic multiplicity). The sufficient condition of nondefectiveness is nondegeneracy of the matrix. Basically we can restrict consideration to only nondegenerate matrices because one can always think of a small perturbation of vectors $\mathbf{r}_i$ that breaks degeneracy but leaves optical properties almost unchanged.[22] But even this is not necessary, because the most important reason for degeneracy of W is some kind of geometric symmetry of the cluster; in this case the degenerate eigenstates correspond to spatial symmetry transformations of some given eigenstate (i.e., rotations or reflections), and therefore geometric and algebraic multiplicities of the corresponding eigenvalues are equal. Another possibility is random degeneracy, which is not related to spatial symmetry of a cluster, but the probability of such an event is asymptotically zero.[23] Based on the above arguments, consider the full set of eigenstates $|\mathrm{n}\rangle$ and corresponding eigenvalues w_n:

$$\mathrm{W}|\mathrm{n}\rangle = w_n|\mathrm{n}\rangle\,. \tag{24}$$

Here n runs from 1 to $3N$, as the dimension of the system is $3N$ and $|\mathrm{n}\rangle$ is a $3N$-dimensional column vector with elements that are probably complex. We denote the Hermitian conjugate of $|\mathrm{n}\rangle$ as $\langle\mathrm{n}|$, the latter being a $3N$-dimensional row vector with entries obtained by complex conjugation of the corresponding entries of $|\mathrm{n}\rangle$.

Unlike in the case of Hermitian matrix, the eigenvectors $|\mathrm{n}\rangle$ are not orthogonal, which means that $\langle\mathrm{m}\,|\,\mathrm{n}\rangle \neq \delta_{mn}$. Instead, for symmetrical matrices one can prove (see Appendix A) that

$$\langle\overline{\mathrm{m}}\,|\,\mathrm{n}\rangle = 0 \quad \text{if} \quad m \neq n\,, \tag{25}$$

where the bar denotes complex conjugation of all entries. Thus $\langle\overline{\mathrm{m}}|$ actually denotes a row vector with the same entries as $|\mathrm{m}\rangle$. We assume the usual normalization of eigenvectors, so that $\langle\mathrm{n}\,|\,\mathrm{n}\rangle = 1$, whereas $\langle\overline{\mathrm{n}}\,|\,\mathrm{n}\rangle$ is not equal to the unit (and actually may be a complex number[24]).

The representation of the unit matrix in this basis is

$$\mathrm{I} = \sum \frac{|\overline{\mathrm{n}}\rangle\langle\mathrm{n}|}{\langle\overline{\mathrm{n}}\,|\,\mathrm{n}\rangle}\,. \tag{26}$$

Provided that the basis [Eq. (24)] exists, one can decompose the solution of Eq. (23) in terms of $|\mathrm{n}\rangle$:

$$|\mathrm{d}\rangle = \sum_{n=1}^{3N} \frac{|\mathrm{n}\rangle\langle\overline{\mathrm{n}}\,|\,\mathrm{E}\rangle}{\langle\overline{\mathrm{n}}\,|\,\mathrm{n}\rangle(1/\chi - w_n)}\,. \tag{27}$$

Clearly the sums in Eqs. (11), (20), and (22) for the cross sections may be represented as

$$\sum_{i=1}^{N} \mathbf{d}_i\mathbf{E}_0 \exp(-i\mathbf{k}\mathbf{r}_i) = \langle\mathrm{E}\,|\,\mathrm{d}\rangle\,, \qquad \sum_{i=1}^{N} |\mathbf{d}_i|^2 = \langle\mathrm{d}\,|\,\mathrm{d}\rangle\,, \tag{28}$$

and therefore

$$\sigma_e = \frac{4\pi k}{|\mathbf{E}_0|^2}\ \mathrm{Im} \sum_{n=1}^{3N} \frac{\langle\mathrm{E}\,|\,\mathrm{n}\rangle\langle\overline{\mathrm{n}}\,|\,\mathrm{E}\rangle}{\langle\overline{\mathrm{n}}\,|\,\mathrm{n}\rangle(1/\chi - w_n)}\,, \tag{29}$$

$$\sigma_\alpha = \frac{4\pi k y_a}{|\mathbf{E}_0|^2} \times \sum_{m\neq n}^{3N} \frac{\langle\mathrm{E}\,|\,\overline{\mathrm{m}}\rangle\langle\mathrm{m}\,|\,\mathrm{n}\rangle\langle\overline{\mathrm{n}}\,|\,\mathrm{E}\rangle}{\langle\mathrm{m}\,|\,\overline{\mathrm{m}}\rangle\langle\overline{\mathrm{n}}\,|\,\mathrm{n}\rangle(1/\chi - w_n)(1/\chi - w_m)^*}\,. \tag{30}$$

Equations (29) and (30) give the general form of dependence of the cross sections on χ. They may be used

to deduce some general properties of imaginary parts of eigenvalues.

First we notice that the vector $|\mathrm{E}\rangle$ in Eqs. (29) and (30) is just the right-hand part of Eq. (20) and may be, in principle, arbitrary. This means that one may consider excitation of the system by an incident field of an arbitrary configuration, not necessarily by a plane wave. Still the inequality $\sigma_e \geq \sigma_\alpha$ must hold for any $|\mathrm{E}\rangle$.[25] Let us assume for a moment that $|\mathrm{E}\rangle$ coincides with one of the eigenvectors, say, $E_0|\mathrm{M}\rangle$. Then the expressions for the cross sections are simplified as

$$\sigma_e = 4\pi k \frac{\mathrm{Im}(1/\chi - w_M)^*}{|1/\chi - w_M|^2}, \qquad \sigma_\alpha = 4\pi k \frac{y_\alpha}{|1/\chi - w_M|^2}. \tag{31}$$

Using the definition (21) of y_α and the inequality $\sigma_e \geq \sigma_\alpha$, we can derive the exact property of the eigenvalues:

$$\mathrm{Im}\ w_n \geq -2k^3/3\ \forall\ n. \tag{32}$$

Because the trace of the W matrix is zero, its eigenvalues obey the sum rule,

$$\sum_{n=1}^{3N} w_n = 0, \tag{33}$$

which when combined with inequality (32) leads to

$$\mathrm{Im}\ w_n \leq (3N-1)2k^3/3\ \forall\ n. \tag{34}$$

As we show below, imaginary parts of the eigenvalues never can be exactly equal to the margins defined by inequalities (32) and (34) but may approach them asymptotically. This ensures that the resonance denominators in Eqs. (29) and (30) are never exactly zero, even for absolutely nonabsorbing particles with $y_\alpha = 0$.

Note that the margins for the imaginary parts of eigenvalues do not depend on the geometry of the cluster but only on the frequency and the number of particles. On the contrary, the margins for real parts of eigenvalues should clearly depend on the geometry. The simplest example is a couple of particles.[21]

For a cluster lying in a two-dimensional plane, inequality (34) may be replaced by a stronger one. Indeed, in the two-dimensional case the space of eigenvectors can be split into two nonintersecting subspaces: one corresponds to the polarization orthogonal to the plane with dimensionality N, and the other corresponds to the parallel polarization with dimensionality $2N$. Clearly one can write the following instead of inequality (34):

$$\mathrm{Im}\ w_n \leq (N-1)2k^3/3, \quad n \in [1, N]\ \text{(orthogonal polarization)},$$
$$\mathrm{Im}\ w_n \leq (2N-1)2k^3/3, \quad n \in [N+1, 3N]\ \text{(parallel polarization)}.$$

5. LONG-WAVE LIMIT

If the wavelength of the incident radiation λ is much larger than the cluster size, one can consider the imaginary part of the W matrix as a perturbation:

$$\mathrm{W} = \mathrm{W}_r + i\mathrm{W}_i, \tag{35}$$

$$\mathrm{W}_i = \mathrm{V}_1 + \mathrm{V}_2 + \mathrm{V}_3 + \dots. \tag{36}$$

Here W_r and W_i are purely real symmetrical (and therefore Hermitian) matrices and V_l are the corresponding terms in the Taylor expansion of W_i. The matrix elements of the first two terms in the decomposition of W_i are as follows:

$$\langle i\alpha|\mathrm{V}_1|j\beta\rangle = \frac{2k^3}{3}(1-\delta_{ij})\delta_{\alpha\beta}, \tag{37}$$

$$\langle i\alpha|\mathrm{V}_2|j\beta\rangle = \frac{2k^3}{3}\,\frac{(kr_{ij})^2}{10}\left(-2\delta_{\alpha\beta} + \frac{r_{ij\alpha}r_{ij\beta}}{{r_{ij}}^2}\right). \tag{38}$$

We can build the usual perturbation theory starting with the orthonormal basis $|\mathrm{n}^{(0)}\rangle$ of the eigenvectors of W_r. The corresponding unperturbed eigenvalues are $w_n^{(0)}$. We consider first the nondegenerate case [$w_n^{(0)} \neq w_m^{(0)}$ if $n \neq m$] and decompose the eigenvectors and eigenvalues of W in the usual manner:

$$|\mathrm{n}\rangle = |\mathrm{n}^{(0)}\rangle + |\mathrm{n}^{(1)}\rangle + |\mathrm{n}^{(2)}\rangle + \dots, \tag{39}$$

$$w_n = w_n^{(0)} + w_n^{(1)} + w_n^{(2)} + \dots. \tag{40}$$

As we show below, although the zero-order approximation is sufficient for the eigenvectors in the limit of infinite λ, it may be necessary to take into account higher approximations for the eigenvalues.

A. Zero-Order Approximation

We understand the zero-order approximation here as limiting us to the first term in the expansion [Eq. (39)] for eigenvectors, assuming that $|\mathrm{n}\rangle = |\mathrm{n}^{(0)}\rangle$. We do not make any approximations at this point regarding eigenvalues, and we use exact eigenvalues w_n here. Below we show which terms in the expansion [Eq. (40)] for w_n should be left. Analogously, we use the exact right-hand part vector $|\mathrm{E}\rangle$.

Because the $|\mathrm{n}^{(0)}\rangle$ basis is orthonormal and real, the expressions for optical cross sections acquire the following form:

$$\sigma_e^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{n=1}^{3N} |\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle|^2 \frac{(y_\alpha + 2k^3/3 + \mathrm{Im}\ w_n)}{|1/\chi - w_n|^2}, \tag{41}$$

$$\sigma_\alpha^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{n=1}^{3N} |\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle|^2 \frac{y_\alpha}{|1/\chi - w_n|^2}, \tag{42}$$

$$\sigma_s^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{n=1}^{3N} |\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle|^2 \frac{2k^3/3 + \mathrm{Im}\ w_n}{|1/\chi - w_n|^2}. \tag{43}$$

The superscript (0) denotes the order of approximation.

As follows from Eq. (43), the imaginary parts of the eigenvalues are always important for the scattering cross section. But $w_n^{(0)}$ are eigenvalues of the Hermitian matrix W_r and therefore are real. This means that even in the zero-order approximation we cannot neglect higher corrections to $w_n^{(0)}$. As we have shown above, the left margin for $\mathrm{Im}\ w_n$ is $-2k^3/3$. If it turns out that $\mathrm{Im}\ w_n^{(1)}$ can reach this margin, it would mean that the next term with a nonzero imaginary part in the expansion [Eq. (40)] should be kept in Eq. (43).

In the case of small absorption (small y_α), and if some resonance conditions are fulfilled, the imaginary parts of eigenvalues become important for the absorption cross section as well. Note that by small absorption we mean

small absorption by an individual particle. The absorption by cluster given by Eq. (42) is not necessarily small. Indeed, let us consider the resonance denominator $|1/\chi - w_n|^2$ and assume that the resonance condition $\mathrm{Re}(1/\chi - w_n) = 0$ is fulfilled (for some resonance frequency of the incident light). Then $|1/\chi - w_n|^2 = (y_\alpha + 2k^3/3 + \mathrm{Im}\ w_n)^2$. Let us also assume that $2k^3/3$ and $\mathrm{Im}\ w_n$ nearly compensate each other, so that $2k^3/3 + \mathrm{Im}\ w_n = \xi$ (small ξ). Then the absorption cross section would be of the order of $y_\alpha/[\max(y_\alpha, \xi)]^2$. If it happens that ξ is smaller than y_α, the absorption cross section becomes proportional to $1/y_\alpha$ instead of y_α.

We also note that the perturbation matrix V_1 has the order of k^3, and the first two terms in decomposition of $|\mathrm{E}\rangle$ are of the order of k and k^2, respectively. This justifies the use of the exact right-hand part vector $|\mathrm{E}\rangle$ in the zero-order approximation.

B. Perturbation of Eigenvalues

The expressions for $w_n^{(1)}$ and $w_n^{(2)}$ follow from the usual perturbation theory:

$$w_n^{(1)} = i\langle \mathrm{n}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle, \tag{44}$$

$$w_n^{(2)} = -\sum_{m\neq n} \frac{|\langle \mathrm{m}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle|^2}{w_n^{(0)} - w_m^{(0)}} + i\langle \mathrm{n}^{(0)}|\mathrm{V}_2|\mathrm{n}^{(0)}\rangle. \tag{45}$$

It can be easily shown from Eq. (37) for V_1 that

$$\mathrm{V}_1 = \frac{2k^3}{3}\left(\sum_{\alpha=1}^{3} |0_\alpha\rangle\langle 0_\alpha| - \mathrm{I}\right), \tag{46}$$

where $|0_\alpha\rangle = \sum_i |i\alpha\rangle$ ($\alpha = 1, 2, 3$) are the homogeneous vectors with components defined by $\langle i\beta\,|\,0_\alpha\rangle = \delta_{\alpha\beta}$ and I is the unit matrix. Therefore the matrix elements $\langle \mathrm{m}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle$ are expressed as

$$\langle \mathrm{m}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle = \frac{2k^3}{3}\sum_{\alpha=1}^{3} \langle \mathrm{m}^{(0)}\,|\,0_\alpha\rangle\langle 0_\alpha\,|\,\mathrm{n}^{(0)}\rangle, \quad \text{for} \quad m \neq n, \tag{47}$$

$$\langle \mathrm{n}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle = \frac{2k^3}{3}\left(\sum_{\alpha=1}^{3} |\langle \mathrm{n}^{(0)}\,|\,0_\alpha\rangle|^2 - 1\right). \tag{48}$$

It is natural to introduce three-dimensional vectors of the total dipole moment of the nth eigenmode $\mathbf{D}_n$ with Cartesian components $D_{n\alpha} = \langle 0_\alpha\,|\,\mathrm{n}^{(0)}\rangle$. Then Eqs. (44) and (45) may be rewritten as

$$w_n^{(1)} = i\,\frac{2k^3}{3}\,(|\mathbf{D}_n|^2 - 1), \tag{49}$$

$$w_n^{(2)} = -\left(\frac{2k^3}{3}\right)^2 \sum_{m\neq n} \frac{|\mathbf{D}_m\mathbf{D}_n|^2}{w_n^{(0)} - w_m^{(0)}} + i\langle \mathrm{n}^{(0)}|\mathrm{V}_2|\mathrm{n}^{(0)}\rangle. \tag{50}$$

One can see that $w_n^{(1)}$ is purely imaginary and $w_n^{(2)}$ has both real and imaginary parts.

It may occur that there exists an eigenmode with zero total dipole moment, i.e., $\mathbf{D}_n = 0$. We call this eigenstate antisymmetrical. In this case one has

$$w_n^{(1)} = -i(2k^3/3), \qquad w_n^{(2)} = i\langle \mathrm{n}^{(0)}|\mathrm{V}_2|\mathrm{n}^{(0)}\rangle. \tag{51}$$

Thus we show that if the antisymmetrical eigenstate exists, $\mathrm{Im}\ w_n^{(1)}$ reaches the left margin of $\mathrm{Im}\ w_n$. As follows from the above discussion, this means that the scattering cross section in the zero-order approximation is determined by the second-order correction $w_n^{(2)}$. If it turns out that y_α is much smaller than $\mathrm{Im}\ w_n^{(2)} = \langle \mathrm{n}^{(0)}|\mathrm{V}_2|\mathrm{n}^{(0)}\rangle$, the resonance absorption is also governed by $w_n^{(2)}$.

One can also consider the case of a symmetrical eigenstate, i.e., with maximum possible $|\mathbf{D}_n|^2$. Given the normalization rule $\langle \mathrm{n}^{(0)}\,|\,\mathrm{n}^{(0)}\rangle = 1$, it can be easily verified that the maximum possible value of $|\mathbf{D}_n|^2$ is N and the corresponding $\mathrm{Im}\ w_n^{(1)} = (2k^3/3)(N - 1)$ does not reach the right margin for $\mathrm{Im}\ \omega$ defined by inequality (34). The latter may be explained by the fact that if a symmetrical eigenstate exists in an essentially three-dimensional system, it must be triple degenerate. Also it is apparent from Eq. (33) that, if such a triple-degenerate symmetrical eigenstate exists, all other eigenstates must be antisymmetrical.

If a cluster has no antisymmetrical eigenstates, Eq. (43) for the scattering cross section can be written as

$$\sigma_s^{(0)} = \frac{8\pi k^4}{3|\mathbf{E}_0|^2} \sum_{n=1}^{3N} |\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle|^2 \frac{|\mathbf{D}_n|^2}{|1/\chi - w_n|^2}. \tag{52}$$

If the external field can effectively excite only the symmetrical mode (as in the case of a small dielectric sphere), the scattering cross section becomes proportional to N^2 according to the classical conception. Indeed, in this case $|\mathbf{D}_n|^2 = N$, $|\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle|^2 = N|\mathbf{E}_0|^2$, and only one term is left in the above summation [Eq. (52)]. Note that this is always the case if the interaction between monomers is weak and may be neglected.

In the general case, however, the scattering cross section is not proportional to N^2, nor can it be expressed through the squared total dipole moment of the cluster, $\mathbf{D}^{\mathrm{tot}}$, with Cartesian components $D_\alpha{}^{\mathrm{tot}} = \langle 0_\alpha\,|\,\mathrm{d}\rangle$. Indeed, in the zero-order approximation one has, from Eq. (27) and the above definition of D^{tot},

$$|\mathbf{D}^{\mathrm{tot}}|^2 = \sum_{n,m=1}^{3N} \langle \mathrm{n}^{(0)}\,|\,\mathrm{E}\rangle\langle \mathrm{E}\,|\,\mathrm{m}^{(0)}\rangle \frac{\mathbf{D}_n\mathbf{D}_m}{(1/\chi - w_n)(1/\chi - w_m)^*}. \tag{53}$$

One can see from comparison of Eqs. (52) and (53) that if we leave only diagonal terms (with $n = m$) in Eq. (53), the cluster would scatter as one particle and the classical relation $\sigma_s = 8\pi k^4|\mathbf{D}^{\mathrm{tot}}|^2/3|\mathbf{E}_0|^2$ will hold. However, the sum of the off-diagonal terms in Eq. (53) is typically not equal to zero. This means that even if the size of a cluster is much smaller than the wavelength, it cannot be replaced by a single effective particle with the total dipole moment $\mathbf{D}^{\mathrm{tot}}$. Instead, as follows from Eq. (52), different eigenmodes scatter independently, without mutual interference.

C. First-Order Approximation

Although the zero-order approximation [Eqs. (41)–(43)] together with the expansion of eigenvalues [Eqs. (49) and (50)] is sufficient for analysis of antisymmetrical eigenstates, in this section we report the first-order corrections to the optical cross sections.

The expression for $|\mathrm{n}^{(1)}\rangle$ that follows from the perturbation theory is

$$|\mathrm{n}^{(1)}\rangle = \sum_{m=1}^{3N}{}' \frac{|\mathrm{m}^{(0)}\rangle\langle\mathrm{m}^{(0)}|\mathrm{V}_1|\mathrm{n}^{(0)}\rangle}{w_n^{(0)} - w_m^{(0)}} = \frac{2k^3}{3} \sum_{m=1}^{3N}{}' \frac{|\mathrm{m}^{(0)}\rangle\mathbf{D}_m\mathbf{D}_n}{w_n^{(0)} - w_m^{(0)}}. \tag{54}$$

The first-order approximations for the scalar products $\langle \mathrm{m}\,|\,\mathrm{n}\rangle$ and $\langle \overline{\mathrm{n}}\,|\,\mathrm{n}\rangle$ are

$$\langle \mathrm{m}\,|\,\mathrm{n}\rangle = \delta_{mn} + i\frac{4k^3}{3}(1-\delta_{mn})\frac{\mathbf{D}_m\mathbf{D}_n}{w_n^{(0)} - w_m^{(0)}}, \qquad \langle \overline{\mathrm{n}}\,|\,\mathrm{n}\rangle = \langle \mathrm{n}\,|\,\overline{\mathrm{n}}\rangle = 1. \tag{55}$$

Note that in the first-order approximation $\langle \mathrm{m}\,|\,\mathrm{n}\rangle = -\langle \mathrm{n}\,|\,\mathrm{m}\rangle$ for $m \neq n$.

Using Eqs. (54) and (55), we can find the first-order corrections to the optical cross sections. We start with the correction for the extinction, $\sigma_e^{(1)}$. By substitution of Eq. (54) into Eq. (29), with the use of Eq. (47), we obtain

$$\sigma_e^{(1)} = \frac{16\pi k^4}{3|\mathbf{E}_0|^2} \sum_{m\neq n} \frac{(\mathbf{D}_n\mathbf{D}_m)\mathrm{Re}[\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle\langle \mathrm{m}^{(0)}\,|\,\mathrm{E}\rangle]}{w_n^{(0)} - w_m^{(0)}} \times \mathrm{Re}\left(\frac{1}{1/\chi - w_n}\right), \tag{56}$$

where again we used the definition of the total dipole moment of the nth eigenmode $\mathbf{D}_n$. Because the second-order correction to σ_e is proportional to k^6, it is natural to keep the exact right-hand part $|\mathrm{E}\rangle$ in Eq. (56). It is worthwhile to note that the decomposition of the cross sections according to the perturbation theory does not coincide with the Taylor expansion with respect to the powers of k. Indeed, the zero-order approximation [Eq. (41)] for σ_e contains all powers of k starting from 1. The first-order correction [Eq. (56)] contains powers of k starting from 4. Thus the terms of different order actually differ in the lowest power of k in their Taylor expansion.

Analogously, the first-order correction to the absorption cross section is

$$\sigma_\alpha^{(1)} = \frac{16\pi k^4 y_\alpha}{3|\mathbf{E}_0|^2}\,\mathrm{Im} \sum_{m\neq n} \frac{\mathbf{D}_n\mathbf{D}_m\langle \mathrm{E}\,|\,\mathrm{n}^{(0)}\rangle\langle \mathrm{m}^{(0)}\,|\,\mathrm{E}\rangle}{[w_n^{(0)} - w_m^{(0)}](1/\chi - w_n)} \times \left(\frac{1}{1/\chi - w_n} - \frac{1}{1/\chi - w_m}\right)^*. \tag{57}$$

The first-order correction for the scattering cross section may be obtained by $\sigma_s^{(1)} = \sigma_e^{(1)} - \sigma_\alpha^{(1)}$.

D. Case of Degeneracy of W_r

Above, we used the nondegenerate perturbation theory. In the case of degeneracy of W_r this is invalid. Although the zero-order expressions for the cross sections [Eqs. (41)–(43)] and the first-order correction for eigenvalues [Eqs. (44) and (49)] hold despite degeneracy, the higher corrections [Eqs. (45), (50), and (54)–(57)] must be modified.

However, there are two important cases when no corrections to the nondegenerate perturbation theory are necessary. The first is if one of the degenerate eigenstates, say the nth, is antisymmetrical. In this case the terms in sums [Eqs. (45), (50), and (54)–(57)] with denominators $w_n^{(0)} - w_m^{(0)}$ corresponding to degenerate eigenvalues $[w_n^{(0)} = w_m^{(0)}]$ may be omitted because of the fact that $\mathbf{D}_n = 0$.

The second case is when the degeneracy occurs because of some spatial symmetry of the cluster and the degenerate eigenvectors correspond to orthogonal polarizations in space. Then, for these eigenstates $\mathbf{D}_n\mathbf{D}_m = 0$ and corresponding terms are also canceled. Note that spatial symmetry may result in a kind of degeneracy when the degenerate eigenstates have the same polarization (see the example in Subsection 6.B).

6. ANTISYMMETRICAL STATES

In this section we examine in more detail properties of the antisymmetrical states introduced in Subsection 5.B. We use the zero-order approximation [Eqs. (41)–(43)] for optical cross sections. We also assume that the Mth eigenstate is antisymmetrical ($\mathbf{D}_M = 0$) and consider only one term in Eqs. (41)–(43) with $n = M$. If all other terms in Eqs. (41)–(43) are off resonance and the distance between modes is large enough, this term is prevalent (resonance approximation).

Note that in this section we assume that the antisymmetrical state exists *a priori*. In Section 7 we give some examples of antisymmetrical states.

For convenience we introduce notations for the real and imaginary parts of $1/\chi$:

$$1/\chi = -x - iy, \qquad y = 2k^3/3 + y_\alpha \tag{58}$$

A. Scattering

From Eqs. (43), (44), (45), and (47), the resonance scattering cross section in an antisymmetrical state is given by

$$\sigma_s^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \frac{|\langle \mathrm{E}\,|\,\mathrm{M}^{(0)}\rangle|^2\langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle}{(x + w_M^{(0)})^2 + [y_\alpha + \langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle]^2}, \tag{59}$$

with V_2 given by Eq. (38).

Let us assume that the resonance condition $x + w_M^{(0)} = 0$ is fulfilled and that the absorption is very small ($y_\alpha \ll \langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle$). Then the resonance scattering cross section is given by

$$\sigma_s^{(0)}(x = -w_M^{(0)}) = \frac{4\pi k}{|\mathbf{E}_0|^2} \frac{|\langle \mathrm{E}\,|\,\mathrm{M}^{(0)}\rangle|^2}{\langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle}. \tag{60}$$

We can decompose the $|\mathrm{E}\rangle$ vector as $|\mathrm{E}\rangle = |\mathrm{E}^{(0)}\rangle + |\mathrm{E}^{(1)}\rangle + \ldots$, $\langle i\alpha\,|\,\mathrm{E}^{(0)}\rangle = E_{0\alpha}$ and $\langle i\alpha\,|\,\mathrm{E}^{(1)}\rangle = E_{0\alpha} i\mathbf{k}\mathbf{r}_i$, where $\mathbf{E}_0$ is the amplitude of the incident wave. Because $|\mathrm{M}^{(0)}\rangle$ is an antisymmetrical state, one has $\langle \mathrm{E}^{(0)}\,|\,\mathrm{M}^{(0)}\rangle = 0$, and therefore $|\langle \mathrm{E}\,|\,\mathrm{M}^{(0)}\rangle|^2 \sim |\mathbf{E}_0|^2(kR_c)^2$, where R_c is the characteristic size of the cluster. On the other hand $\mathrm{V}_2 \sim k^5 R_c{}^2$, and finally

$$\sigma_s^{(0)}(x = -w_M^{(0)}) \sim k^{-2} \sim \lambda^2. \tag{61}$$

Thus one can see that the antisymmetrical state produce resonance scattering cross section of the order of λ^2, as in the well-known case of symmetrical states. But the width of antisymmetrical resonance is smaller than that of an isolated particle by the factor $(kR_c)^{-2}$.

Let us make an estimate of the possible linewidth of an antisymmetrical resonance in a cluster of nonabsorbing two-level atoms with transition dipole moment $\mathbf{d}_{12}$. The polarizability of a two-level atom near resonance can be written as $\chi = -|\mathbf{d}_{12}|^2/\hbar(\Omega + i\Gamma)$, where Ω is

the detuning from resonance frequency. Because we assume no absorption, we can find from Eq. (21) that $\Gamma = (2k^3/3)|\mathbf{d}_{12}|^2/\hbar$. For our estimate we assume that $|\mathbf{d}_{12}| \sim ea_B$, where e is the electron charge and a_B is the Bohr radius, and that the transition frequency is $\omega_0 = 4.71 \times 10^{15}$ ($\lambda_0 = 400$ nm). This gives us $\Gamma \approx 1.7 \times 10^7$ rad/s, which is a realistic value for atomic dipole transitions. Now we use Eq. (59) with $x = \hbar\Omega/|\mathbf{d}_{12}|^2$ and $y_\alpha = 0$ to calculate the linewidth of an antisymmetrical resonance Γ'. This gives us $\Gamma' = |\mathbf{d}_{12}|^2\langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle/\hbar$. As we already have mentioned, $\mathrm{V}_2 \sim k^5 {R_c}^2$, and therefore $\Gamma' \sim (kR_c)^2\Gamma$. Because the value of kR_c can, in principle, be as small as 10^{-2}, we can obtain Γ' of the order of 10^3 (corresponding lifetime 10^{-3} s).

The phenomenon discussed above can be referred to as the antisuperradiance effect. The superradiance, introduced in Dicke's classic paper[26] and discussed later by a number of authors,[27–30] is essentially a phenomenon in which an ensemble of N interacting atoms emits radiation at a rate that is N times greater than those for isolated atoms; i.e., the (radiation) lifetime of the system is N times smaller. As was shown above (see the discussion in Subsection 5.B), this situation takes place for symmetrical eigenstates when the linewidth is determined by $2k^3/3 + \mathrm{Im}\ \omega_n^{(1)}$ and $\mathrm{Im}\ w_n^{(1)} = (2k^3/3)(N-1)$. But for an antisymmetrical state the situation is quite the opposite: the radiation linewidth is determined by $\mathrm{Im}\ w_n^{(2)} \sim (2k^3/3)(kR_c)^2$, where kR_c is a small parameter.

Theoretically one can think of an eigenstate of even higher order of antisymmetry, in which not only $\mathbf{D}_M = 0$ but also $\langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle = 0$. For such an eigenstate the width of the resonance would be of the order of $(2k^3/3)(kR_c)^4$. An example of such an eigenstate is given in the next section.

B. Absorption

In Subsection 4.A we used the limit of small absorption by formally putting $y_\alpha = 0$. However, for the absorption cross section this will yield $\sigma_\alpha = 0$, so we need to consider some nonzero y_α. The resonance absorption cross section [analogous to Eq. (60) for scattering] is

$$\sigma_\alpha^{(0)}(x = -w_M^{(0)}) = \frac{4\pi k}{|\mathbf{E}_0|^2}\,\frac{|\langle \mathrm{E}\,|\,\mathrm{M}^{(0)}\rangle|^2 y_\alpha}{[y_\alpha + \langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle]^2}. \quad (62)$$

Considering y_α as an independent variable, we can find that maximum resonance absorption can be reached if $y_\alpha = \langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle$. In this case, although $y_\alpha \ll 2k^3/3$ and absorption by an individual monomer would be very small, the resonance absorption cross section is proportional to λ^2, as we had it in the case of scattering.

Note that if $y_\alpha = \langle \mathrm{M}^{(0)}|\mathrm{V}_2|\mathrm{M}^{(0)}\rangle$, both the absorption and the scattering resonance cross sections are equal to 1/4 the value of Eq. (60).

7. EXAMPLES OF ANTISYMMETRICAL EIGENSTATES

Antisymmetrical eigenstates may occur either because of spatial symmetry of the cluster or randomly. In the latter case the antisymmetry is unlikely to be exact, in the sense that $\mathbf{D}_n$ may be small but not exactly zero. Below we consider some examples of exactly antisymmetrical eigenstates.

A. Two Particles

The case of two particles separated by a distance a was considered in detail in Ref. 21. Here we adduce the results concerning the antisymmetrical states. The system has two antisymmetrical states, as shown schematically below:

1) ⊗———⊙ 2) ←⊙———⊙→

The first eigenstate is double degenerate because of the axial symmetry. The corresponding eigenvalues are

$$w_1 = -k^3 A(ka), \qquad w_2 = -k^3[A(ka) + B(ka)], \quad (63)$$

where A and B are defined by Eqs. (4) and (5), respectively.

Taylor expansion of Eqs. (63) gives us

$$\mathrm{Im}\ w_1^{(1)} = -2k^3/3, \qquad \mathrm{Im}\ w_1^{(2)} = (2k^3/15)(ka)^2, \quad (64)$$

$$\mathrm{Im}\ w_2^{(1)} = -2k^3/3, \qquad \mathrm{Im}\ w_2^{(2)} = (k^3/15)(ka)^2. \quad (65)$$

Note that the same expressions can be obtained with perturbation Eqs. (49) and (50), although the first eigenvalue is double degenerate.

B. Four Particles

Let us consider four particles forming a square with size a. We consider here only eigenstates normal to the plane of the square. There are two antisymmetrical eigenstates in this system, as schematically shown below:

(A) ⊙———⊗ (B) ⊗———⊙
⊙———⊗ ⊙———⊗

The corresponding eigenvalues are

$$w_1 = -k^3 A(\sqrt{2}\,ka), \qquad w_2 = k^3[A(\sqrt{2}\,ka) - 2A(ka)]. \quad (66)$$

Note that the first eigenstate is double degenerate. The degenerate eigenstates have the same polarization, but we can use the degenerate perturbation theory because they are antisymmetrical. Also the geometric multiplicity is clearly equal to the algebraic multiplicity in this case, and therefore the expansion in Eq. (27) is correct.

The Taylor expansion of Eqs. (66) gives us

$$\mathrm{Im}\ w_1^{(1)} = -2k^3/3, \qquad \mathrm{Im}\ w_1^{(2)} = (4k^3/15)(ka)^2, \quad (67)$$

$$\mathrm{Im}\ w_2^{(1)} = -2k^3/3, \qquad \mathrm{Im}\ w_2^{(2)} = 0,$$

$$\mathrm{Im}\ w_2^{(3)} = (k^3/70)(ka)^4. \quad (68)$$

The same results can be obtained with perturbation theory Eqs. (49) and (50).

Note that the second eigenstate possesses even higher-order antisymmetry than the first one, which results in $\mathrm{Im}\ w_2^{(2)} = 0$. Physically, this means that not only the total dipole moment of this eigenstate but also the quadrupole and magneto-dipole moments are zero. As a result the linewidth of this resonance is determined by $\mathrm{Im}\ w_2^{(3)}$ instead of $\mathrm{Im}\ w_2^{(2)}$. However, the resonance value of the scattering cross section is still of the order of λ^2 (instead of λ^4/a^2 as one could expect). The reason for this is that the projection of this eigenstate on $|\mathrm{E}^{(1)}\rangle$ is always zero, and one needs to use higher decomposi-

tion of $|\mathrm{E}\rangle$. The resulting resonance value of the scattering cross section is (with $y_a = 0$) $\sigma_s^{(0)}$ $(x = -w_M^{(0)}) = (35\lambda^2/2\pi)\cos^2\phi\,\sin^2\phi$, where ϕ is the angle between the wave vector of the incident wave and one of the sides of the square.

8. DISCUSSION

In the paper it has been shown that if the absorption parameter y_α is small enough the resonance optical cross section (both absorption and scattering) may be of the order of λ^2 and that quasi-static approximation in this case gives the wrong results no matter how small the size of the cluster under consideration. Actually, it was shown that the smaller the size of the cluster, the smaller the resonance linewidth $[\sim(kR_c)^2]$.

The antisymmetrical states considered here are actually resonances of the total quadrupole moment (in contrast to symmetrical eigenstates, which are resonances of the total dipole moment). The second eigenstate considered as an example in Subsection 7.B has not only zero total dipole moment but also zero quadrupole and magneto-dipole moments. This state may be considered an octupole resonance. However, the resonance cross sections in this state are still of the order of λ^2, as they are in the case of quadrupole resonance and in the well-known case of dipolar resonance (the latter is the only resonance if only one particle is present).

One can make a generalization for the case of l-polar resonances in clusters of weakly absorbing particles. The resonance value of the optical cross sections for any l is $\sim\lambda^2$, but the linewidth, being proportional to $k^3(kR_c)^{l-1}$, depends strongly on the order of multipole l. The condition on y_α also varies with l and may be approximately written as $y_\alpha \le (2k^3/3)(kR_c)^{l-1}$.

Theoretically, by using higher l, one can obtain resonances of extremely high quality. The physical limit is the value of y_α, which can never be exactly zero. However, it can be very small. For example, in the systems of atoms in vacuum (without collisions) there are no evident sources of absorption except light pressure (dispersion forces) exerted by atoms on each other.

APPENDIX A

Let us consider a symmetrical matrix W of the order q ($q = 3N$ in our case, where N is the number of particles) with complex entries. We assume that its eigenvectors $|\mathrm{n}\rangle \in \mathbb{C}^q$ $(n = 1, \ldots, q)$ form a (normalized) basis in the $\mathbb{C}^q$ space. This is always true if $\hat{W}$ is nondegenerate (see, for example, Ref. 31). We also use here a basis of unit vectors $|e_i\rangle$ $(i = 1, \ldots, q)$, which are vectors with the unit in the ith place and zeros in all other places. The symmetry of W means that $\langle e_i|\mathrm{W}|e_j\rangle = \langle e_j|\mathrm{W}|e_i\rangle$ $\forall\ i, j$.

The eigenvectors for W are not orthogonal in the general case, which means that $\langle \mathrm{m}\,|\,\mathrm{n}\rangle \neq \delta_{mn}$. Instead we prove here that for a symmetrical matrix the orthogonality rule is replaced by

$$\langle \overline{\mathrm{m}}\,|\,\mathrm{n}\rangle = 0 \quad \text{if} \quad m \neq n\,, \tag{A1}$$

where we obtain $|\overline{\mathrm{n}}\rangle$ from $|\mathrm{n}\rangle$ by complex conjugation of all entries (but without transportation). Thus if $|\mathrm{n}\rangle$ is a column vector, $\langle\overline{\mathrm{n}}|$ is a row vector with the same entries as $|\mathrm{n}\rangle$.

To prove Eq. (A1) let us consider $\langle\overline{\mathrm{n}}|\mathrm{W}|\mathrm{m}\rangle$:

$$\langle\overline{\mathrm{n}}|\mathrm{W}|\mathrm{m}\rangle = \sum_{i,j}\langle\overline{\mathrm{n}}\,|\,e_i\rangle\langle e_i|\mathrm{W}|e_j\rangle\langle e_j\,|\,\mathrm{m}\rangle\,. \tag{A2}$$

Noting that $\langle\overline{\mathrm{n}}\,|\,e_i\rangle = \langle e_i\,|\,\mathrm{n}\rangle$, $\langle e_j\,|\,\mathrm{m}\rangle = \langle\overline{\mathrm{m}}\,|\,e_j\rangle$ and $\langle e_i|\mathrm{W}|e_j\rangle = \langle e_j|\mathrm{W}|e_i\rangle$, we can write

$$\langle\overline{\mathrm{n}}|\mathrm{W}|\mathrm{m}\rangle = \sum_{i,j}\langle\overline{\mathrm{m}}\,|\,e_j\rangle\langle e_j|\mathrm{W}|e_i\rangle\langle e_j\,|\,\mathrm{n}\rangle = \langle\overline{\mathrm{m}}|\mathrm{W}|\mathrm{n}\rangle\,. \tag{A3}$$

On the other hand $\langle\overline{\mathrm{n}}|\mathrm{W}|\mathrm{m}\rangle = w_m\langle\overline{\mathrm{n}}\,|\,\mathrm{m}\rangle$ and $\langle\overline{\mathrm{m}}|\mathrm{W}|\mathrm{n}\rangle = w_n\langle\overline{\mathrm{m}}\,|\,\mathrm{n}\rangle$, where w_m and w_n are the corresponding eigenvalues of W. Because $w_m \neq w_n$, Eq. (A3) can hold only if $\langle\overline{\mathrm{n}}\,|\,\mathrm{m}\rangle = \langle\overline{\mathrm{m}}\,|\,\mathrm{n}\rangle = 0$, which proves Eq. (A1).

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22. Except in the $N = 2$ case, when degeneracy can be broken by introducing slightly different polarizabilities χ_1 and χ_2.
23. The author has diagonalized a lot of matrices for random clusters with N up to 1000 but never encountered random degeneracy.
24. There is a special case of the so-called isotropic eigenvector, i.e., $|\mathrm{n}\rangle \neq 0$ and $\langle \overline{\mathrm{n}} | \mathrm{n}\rangle = 0$. This case requires special consideration; however, $|\mathrm{n}\rangle$ cannot be isotropic for a nondegenerate eigenstate. Besides, as it is shown in Section 4, this case cannot be isotropic if the size of the system is less than the wavelength. Therefore this case is not considered.
25. The derivations of cross sections in Section 2 stay valid if one substitutes external fields $\mathbf{E}_0 \exp(i\mathbf{k}\mathbf{r}_i)$ by some arbitrary fields $\mathbf{E}_i$, but the amplitude $\mathbf{E}_0$ appears to be undefined. However, one can always find the electromagnetic energy flux for the arbitrary distribution of the incident field and redefine $\mathbf{E}_0$ in an appropriate way.
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