Radiative relaxation time of quasi-normal optical modes in small dielectric particles

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Radiative relaxation times of optical states in small dielectric particles of arbitrary shape are calculated in the quasistatic limit up to the second order of perturbation theory, assuming that the polarization distribution for the optical states is known. The concept of antisymmetrical optical states, previously developed for a system of discrete dipoles, is generalized for the case of a bulk dielectric particle. We use the integral form of Maxwell's equations to obtain a general expansion of solutions for the polarization function inside a particle in terms of eigenfunctions of the integral interaction operator. Then we calculate imaginary parts of corresponding eigenvalues, which determine the radiative relaxation times of optical excitations, treating the non-Hermitian part of the interaction operator as a perturbation. The imaginary parts of eigenvalues are expanded in terms of total multipole momenta of corresponding eigenmodes. Particles with special properties of symmetry can possess polarization modes with very large radiative relaxation time. We also discuss a possibility of application of the eigenfunction decomposition to numerical calculations of optical cross-sections for some particles of non-spherical shape.

I.   INTRODUCTION

The problem of radiative relaxation time of optical excitations in bulk dielectric particles or microcavities received much attention in the recent few years (Ching, Leung and Young 1996; Brorson and Skovgaard 1996; Leung, Liu, Tong and Young 1993a-c). Relaxation of optical excitation in dielectric particles has two major reasons. First, energy dissipation into heat can occur in the volume if the imaginary part of dielectric constant is positive. When the latter is very small (mathematically, it can be equal to zero), relaxation due to radiative reaction becomes important. In this paper, we consider only the radiative part of the relaxation time. As a result of the radiative reaction, any optical excitation in a dielectrical particle is inevitably "leaky" (Ching *et al.* 1996), and the corresponding interaction operator (an analog of Hamiltonian) is non-Hermitian. As a result, the excitation modes of a "leaky" particle do not form, in general, an orthonormal basis of states. Due to this reason, such excitation modes were referred to as "quasi-normal modes" (Ching, *et al.* 1996; Leung, *et al.* 1993a-c).

Leung *et al.* (1993) considered the quasi-normal modes for scalar waves in a one-dimensional leaky cavity. Ching *et al.* (1996) presented a perturbation technique to calculate frequency shifts and quality factors (proportional to inverse radiative relaxation times) of quasi-normal modes of a slightly distorted microsphere (the results for a perfect sphere are known from the exact Mie solution). But the general problem of radiative relaxation time of optical excitations in particles of arbitrary shape is very complicated and has not been solved completely, due to the fact that calculation of electromagnetic modes inside an irregular particle is a difficult problem itself.

However, if the linear size of a particle R is much smaller than the radiation wavelength in vacuum λ, corresponding to some specific frequency ω ($\lambda = 2\pi c/\omega$), the problem is somewhat simplified and separated into two independent parts. First, we can find the eigenmodes (in the zero approximation, in the frame of

pure electrostatics), e.g., numerically. Then we can calculate relaxation time for a given eigenmode treating the non-Hermitian part of interaction operator as a perturbation. In the present paper, the latter problem is solved up to the second order of the perturbation theory. Since the electromagnetic modes are supposed to be known, we do not consider any specific particle geometry. Our main goal is to calculate radiative relaxation time for an electromagnetic mode with a known distribution of electric field (or, equivalently, polarization) inside the particle. Note that in the zero approximation of the quasi-static limit the modes are ω-independent.

Intuitively, it is clear that an eigenmode with maximum possible total dipole moment would have the smallest relaxation time. On the other hand, eigenmodes with zero total dipole moment can have anomalously large relaxation times. The dependence of relaxation time on dipole configuration for quantum transitions between collective states of ensembles of particles (atoms) coupled by electromagnetic dipole-dipole interaction has been intensively studied (see, for example, Rehler and Eberly 1971; Bonifacio, Schwendimann and Haake 1971a-b; Zaitsev, Malyshev and Trifonov 1983; Avetisyan, Zaitsev and Malyshev 1985) since Dicke (1954) introduced the phenomenon of superradiance. One of the main results of the theory of superradiance is that the rate of spontaneous radiation of a collective state of N atoms can be, under certain conditions, N times larger than that of an isolated atom. If the radiating system is small compared to λ, the superradiant transitions are characterized by a huge total transitional dipole moment.

A phenomenon wherein the collective relaxation time is significantly increased compared to that of an isolated atom was first discussed by Sipe and Van Kranendonk (1974) for a pair of polarizable atoms separated by a distance much smaller than λ in and excited by a plane monochromatic wave propagating along the line connecting the atoms, and by Sipe and Van Kranendonk (1975) for a spatially dispersive slab of polarizable atoms. This phenomenon was referred to by Sipe and Van Kranendonk as antiresonance. A general solution for a pair of polarizable particles excited by a plane wave with arbitrary wavelength, polarization and direction of propagation was also obtain by Markel (1992); this solution demonstrated existence of antiresonances polarized both parallel and perpendicular to the line connecting the particles. Since the increase of relaxation time due to coherent dipole-dipole interaction of atoms is analogous to the superradiance effect with respect to its physical origin, but directly opposite to it with respect to the outcome, we will call this effect "antisuperradiance".

In a recent paper (Markel, 1995) the antisuperradiance effect was considered for ensembles of discrete polarizable particles; this system was assumed to be small compared to λ, but otherwise arbitrary. It was shown that the antisuperradiance can occur in ensembles with special properties of symmetry, and the radiative relaxation time was calculated in the first order of perturbation theory with respect to the small parameter R/λ, where R is the characteristic linear size of the system. It was also shown that the characteristic factor of increasing of the radiative relaxation time is $(\lambda/R)^2$ for resonances with zero total dipole moment, and can be, in principle, even larger for resonances with higher order of antisymmetricity. Note that the requirement $\lambda \gg R$ is not a principal one for observing the antisuperradiance. It allows, however, to obtain results which are not restricted to some specific geometry. The antisuperradiance, as well as the superradiance, can be observed in systems not small compared to the wavelength, such as an infinite slab (Sipe *et al.* 1975) and a finite (Freedhoff and Van Kranendonk 1967) or an infinite chain (Markel 1993) of polarizable atoms. But the parameter characterizing the

collective relaxation time is different in this case from $(\lambda/R)^2$.

The theory developed in (Markel 1995) was based on analysis of the coupled-dipole equation which was first proposed by Purcell and Pennypacker (1973) and extensively used in different contexts after that (see, for instance, Singham and Salzman 1986; Singham and Bohren 1988; Draine 1988; Taubenblatt and Tran 1993; Markel, Shalaev, Stechel, Kim and Armstrong 1996; Shalaev, Poliakov, Markel 1996). This equation couples linearly transitional dipole momenta of all the particles to each other and to the external field. It can be viewed as a linear operator equation of the form

$$|\mathtt{d}\rangle = \chi[|\mathtt{E}\rangle + \mathtt{W}|\mathtt{d}\rangle] \ , \tag{1}$$

where $|\mathtt{d}\rangle$ is the vector of dipole momenta, $|\mathtt{E}\rangle$ is the vector of the incident field, $\mathtt{W}$ is a non-Hermitian interaction operator and χ is the polarizability of an individual particle. The non-Hermitian part of $\mathtt{W}$ can be considered as a perturbation if $R \ll \lambda$. In (Markel 1995) the perturbation theory was built to the first order. This allowed to relate the radiative relaxation time of an excitation to its total dipole moment.

It is important, that equation (1) is essentially analogous to the Maxwell equations (written in the integral form) for the excitation of a bulk particle with a scalar and uniform dielectric permittivity ϵ. The specific form of the interaction operator is, of course, different in these two cases, but the structure of the equations, and some properties of eigenfunctions and eigenvalues which allow us to build the perturbation theory and to relate imaginary parts of eigenvalues to the multipole momenta of excitations stay the same.

Based on the above observation, we show in this paper that the antisymmetrical optical states and the antisuperradiance are not exclusive properties of discrete systems; such states can be adequately introduced for optical excitations of bulk dielectric particles. Moreover, the continuous description developed below allows to identify the physical origin of the higher-order corrections to the eigenvalues, and is somewhat simpler and more straightforward.

In Section II we review the integral form of Maxwell equations and the expressions for optical cross-sections. In Section III we derive the eigenfunction expansion of solutions for the polarization function and for optical cross-sections. In this Section we also discuss a possibility of application of the eigenfunction expansion to numerical calculations of optical cross-sections for light scattering from some non-spherical particles. In Section IV we discuss time evolution in order to relate the relaxation time of excitations to the eigenvalues introduced in the previous Section. In Section V we build the perturbation theory for eigenvalues considering the non-Hermitian part of the interaction operator as a small perturbation. In this Section we obtain our main results concerning the collective relaxation time of optical excitations and their relation to multipole momenta and symmetry properties of excitations. Finally, Section VI contains concluding remarks.

II.   BASIC EQUATIONS

Let us consider the general problem of interaction of an incident monochromatic plane wave,

$$\mathbf{E}_{\mathtt{inc}}(\mathbf{r}, t) = \mathbf{E}_0 \exp(\mathrm{i}\mathbf{k} \cdot \mathbf{r} - \mathrm{i}\omega t) \tag{2}$$

with a material (dielectric) particle occupying some fixed volume V in space and surrounded by vacuum. We do not make any assumptions regarding V at this point except that it is finite; in particular, V can be discontinuous. The dielectric permittivity of the particle, $\epsilon = \epsilon(\omega)$, is assumed to be scalar and uniform in V and equal to unity outside V. The time dependence factor, $\exp(-\mathrm{i}\omega t)$, will be omitted everywhere below, except Section IV, where we consider time evolution.

The integral form of Maxwell equations for polarization function $\mathbf{P}(\mathbf{r})$ in the frequency domain is (see, for example, Keller and Bustmante 1986):

$$\mathbf{P}(\mathbf{r}) = \kappa \left[\mathbf{E}_{\texttt{inc}}(\mathbf{r}) + \int_V \hat{G}(\mathbf{r} - \mathbf{r}')\mathbf{P}(\mathbf{r}')\mathrm{d}\mathbf{r}' \right] \ , \ \ \mathbf{r} \in V \ , \tag{3}$$

$$\kappa = (3/4\pi)[(\epsilon - 1)/(\epsilon + 2)] \ , \tag{4}$$

where $d\mathbf{r}$ is an element of volume and $\mathbf{P}(\mathbf{r}) = 0$ outside the region V. The tensor $\hat{G}$ in (3) is the regular part of the Green's function of the vector wave equation. It is a tensor of second rank defined by the general relations for dipole radiation (see, for example, Jackson 1975):

$$G_{\alpha\beta} = k^3[A(kr)\delta_{\alpha\beta} + B(kr)r_\alpha r_\beta/r^2] \ , \tag{5}$$

$$A(x) = [x^{-1} + \mathrm{i}x^{-2} - x^{-3}]\exp(\mathrm{i}x) \ , \tag{6}$$

$$B(x) = [-x^{-1} - 3\mathrm{i}x^{-2} + 3x^{-3}]\exp(\mathrm{i}x) \ , \tag{7}$$

where the Greek indices denote the Cartesian components and $k = \omega/c$.

Equation (3) is an integral analog of the coupled-dipole equation, studied in (Markel 1995), except for the fact that the polarizability constant has been changed for the coupling constant κ defined by (4). Note that although the polarizability of a particle should be always complex, even for an absolutely nonabsorbing particle (Van Kranendonk and Sipe 1977; Draine 1988; Draine and Goodman 1993), there is no such a requirement for κ. A purely real κ corresponds to the case of no absorption, which we will be mostly concerned with.

Given the polarization function $\mathbf{P}(\mathbf{r})$, the scattering amplitude $\mathbf{f}(\mathbf{s})$ is expressed as

$$\mathbf{f}(\mathbf{s}) = k^2 \int_V [\mathbf{P}(\mathbf{r}) - (\mathbf{P}(\mathbf{r}) \cdot \mathbf{s})\mathbf{s}]\exp(-\mathrm{i}k\mathbf{s} \cdot \mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{8}$$

$\mathbf{s}$ being a unit vector in the direction of scattering.

The extinction, scattering, and absorption cross sections, σ_e, σ_s, and σ_a respectively, can be found from the optical theorem:

$$\sigma_e = \frac{4\pi\mathrm{Im}[\mathbf{f}(\mathbf{k}/k) \cdot \mathbf{E}_0]}{k|\mathbf{E}_0|^2} \ , \tag{9}$$

$$\sigma_s = \frac{1}{|\mathbf{E}_0|^2} \int_V |\mathbf{f}(\mathbf{s})|^2 \mathrm{d}\Omega \ , \tag{10}$$

$$\sigma_a = \sigma_e - \sigma_s \ , \tag{11}$$

where we have assumed excitation by the plane wave of the form (2) and $\mathrm{d}\Omega$ is an element of solid angle in the direction of scattering $\mathbf{s}$.

The expression for the extinction cross-section follows readily from (9) and (8):

$$\sigma_e = \frac{4\pi k}{|\mathbf{E}_0|^2}\mathrm{Im} \int_V \mathbf{P}(\mathbf{r}) \cdot \mathbf{E}_{\texttt{inc}}^*(\mathbf{r})\mathrm{d}\mathbf{r} \ . \tag{12}$$

For the scattering cross-section we have from (10,8):

$$\sigma_s = \frac{k^4}{|\mathbf{E}_0|^2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_{4\pi} d\Omega \ [\mathbf{P}(\mathbf{r}) - (\mathbf{P}(\mathbf{r}) \cdot \mathbf{s})\mathbf{s}] \cdot [\mathbf{P}(\mathbf{r}') - (\mathbf{P}(\mathbf{r}') \cdot \mathbf{s})\mathbf{s}]^*$$
$$\times \exp(-i k \mathbf{s} \cdot (\mathbf{r} - \mathbf{r}')) \ . \tag{13}$$

The integration over Ω can be performed directly (see Markel 1995 for the details) and yields

$$\sigma_s = \frac{4\pi k}{|\mathbf{E}_0|^2} \mathrm{Im} \int_V d\mathbf{r} \int_V d\mathbf{r}' \ \mathbf{P}^*(\mathbf{r}) \cdot \hat{G}(\mathbf{r} - \mathbf{r}') \mathbf{P}(\mathbf{r}') \ , \tag{14}$$

where $\hat{G}$ is the operator defined by (5-7) and we have moved the sign of complex conjugation from $\mathbf{P}(\mathbf{r}')$ to $\mathbf{P}(\mathbf{r})$ (which is valid because $\hat{G}(\mathbf{r}-\mathbf{r}') = \hat{G}(\mathbf{r}'-\mathbf{r})$.) The integral over $d\mathbf{r}'$ in (14) can be expressed in terms of the incident field $\mathbf{E}_{\mathrm{inc}}$ and the polarization function $\mathbf{P}$ through equation (3). The final result for the scattering cross-section follows readily from (14) and (3), but it is more convenient to adduce the final result for the absorption cross-section, instead of the scattering, using expressions (11) and (12):

$$\sigma_a = \frac{4\pi k y_a^{(c)}}{|\mathbf{E}_0|^2} \int_V \mathbf{P}^*(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}) d\mathbf{r} \ , \tag{15}$$

$$y_a^{(c)} = -\mathrm{Im}(1/\kappa) \equiv \frac{4\pi \mathrm{Im}\epsilon}{|\epsilon - 1|^2} \ . \tag{16}$$

The constant $y_a^{(c)}$ appearing in (15) is a positively defined quantity for any physically reasonable permittivity ϵ (that is, if $\mathrm{Im}\epsilon > 0$.) Following (Markel 1995), we can call $y_a^{(c)}$ the absorption strength parameter. The superscript (c) relates this constant to the continuous medium and distinguishes it from the absorption strength parameter for a discrete system defined in (Markel 1995) as $y_a = -\mathrm{Im}(1/\chi) - 2k^3/3$, where χ is the polarizability of a point-like particle. Expression (15) for the absorption is equivalent to its counterpart in the discrete case with y_a being replaced by $y_a^{(c)}$ and summation by integration. The parameter $y_a^{(c)}$ is dimensionless, while y_a has the dimension of inverse volume. This is explained by the fact that the integration according to (15), compared to the summation of the form $\sum \mathbf{P}_i^* \cdot \mathbf{P}_i$, contains the additional factor $d\mathbf{r}$ which has the dimensionality of volume.

III. EIGENFUNCTION EXPANSION

Let us rewrite integral equation (3) in the operator form. First, we introduce an infinite-dimensional Hilbert space $L_2(V)$ of vector functions, which are square-integrable in the (finite) region V. All physically reasonable polarization functions $\mathbf{P}(\mathbf{r})$ must be elements of this space (according to (15), divergence of the integral of $|\mathbf{P}(\mathbf{r})|^2$ would mean an infinite rate of absorption.) We denote the element of $L_2(V)$ that corresponds to $\mathbf{P}(\mathbf{r})$ as $|\mathsf{P}\rangle$ and the element of $L_2(V)$ that corresponds to $\mathbf{E}_{\mathrm{inc}}(\mathbf{r})$ as $|\mathsf{E}\rangle$. Also we define a linear integral operator H, which maps $L_2(V)$ onto itself according to the rule

$$\mathsf{H}|\mathsf{f}\rangle = \int_V \hat{G}(\mathbf{r} - \mathbf{r}')\mathbf{f}(\mathbf{r}')d\mathbf{r}' \ , \quad \mathbf{r} \in V \ . \tag{17}$$

We can easily verify that if $|\mathtt{f}\rangle$ is an element of $L_2(V)$, then $\mathtt{H}|\mathtt{f}\rangle$ is also an element of $L_2(V)$ by considering the convergence of the integral of $|\mathbf{f}|^2$ and using the slowest-decaying term in the definition (5-7) of $\hat{G}$.

Further, we can define a scalar product of two vectors $|\mathtt{f}\rangle$ and $|\mathtt{g}\rangle$ and a norm in $L_2(V)$ as

$$\langle \mathtt{g}|\mathtt{f}\rangle = \int_V \mathbf{g}^*(\mathbf{r}) \cdot \mathbf{f}(\mathbf{r})\mathrm{d}\mathbf{r} \ , \tag{18}$$

$$||\mathtt{f}|| = [\langle \mathtt{f}|\mathtt{f}\rangle]^{1/2} \ , \tag{19}$$

respectively.

Using the above notations, we can rewrite (3) as

$$|\mathtt{P}\rangle = \kappa[|\mathtt{E}\rangle + \mathtt{H}|\mathtt{P}\rangle] \ . \tag{20}$$

The expressions for the optical cross-sections take the following forms:

$$\sigma_e = \frac{4\pi k}{|\mathbf{E}_0|^2}\mathtt{Im}\langle \mathtt{E}|\mathtt{P}\rangle \ , \quad \sigma_a = \frac{4\pi k y_a^{(c)}}{|\mathbf{E}_0|^2}\langle \mathtt{P}|\mathtt{P}\rangle \ . \tag{21}$$

The operator $\mathtt{H}$ is an infinite-dimensional symmetrical operator. It is a "mixed" operator in the sense that it is both tensorial and integral. The symmetricity of $\mathtt{H}$ should be understood as the following property of the kernel $\hat{G}$:

$$\hat{G}(\mathbf{r}) = \hat{G}(-\mathbf{r}), \quad G_{\alpha\beta}(\mathbf{r}) = G_{\beta\alpha}(\mathbf{r}) \ . \tag{22}$$

These two equalities provide that for two arbitrary elements of $L_2(V)$, $|\mathtt{f}\rangle$ and $|\mathtt{g}\rangle$,

$$\langle \mathtt{f}^*|\mathtt{H}|\mathtt{g}\rangle = \langle \mathtt{g}^*|\mathtt{H}|\mathtt{f}\rangle \ , \tag{23}$$

where the star denotes complex conjugation of the corresponding function [1]. Equation (23) can be viewed as a generalized symmetricity condition for $\mathtt{H}$. It can be used to prove that if $|\mathtt{f}\rangle$ and $|\mathtt{g}\rangle$ are two different (linear independent) eigenfunctions of $\mathtt{H}$, they obey $\langle \mathtt{f}^*|\mathtt{g}\rangle = 0$ (Markel 1995), which is an analog of the orthogonality condition for eigenfunctions of Hermitian operators (which is $\langle \mathtt{f}|\mathtt{g}\rangle = 0$.) This property, in turn, will be used below to expand the solution of equation (20) in terms of eigenfunctions of the operator $\mathtt{H}$.

Let us denote the infinite set of eigenfunctions of $\mathtt{H}$ as $|\mathtt{P}_n\rangle, n = 1, 2...$, and the corresponding eigenvalues as h_n:

$$\mathtt{H}|\mathtt{P}_n\rangle = h_n|\mathtt{P}_n\rangle \ , \tag{24}$$

$$\langle \mathtt{P}_n^*|\mathtt{P}_m\rangle = 0 \ \ \text{if} \ \ n \neq m \ . \tag{25}$$

It is natural to assume that the set of $|\mathtt{P}_n\rangle$ covers the whole space $L_2(V)$ and constitutes its basis. This can be not so only if $\mathtt{H}$ has defective eigenvalue(s) (i.e., the geometrical multiplicity of an eigenvalue is less than its algebraic multiplicity (Chatelin 1993).) However, if we make a physically reasonable assumption, that the only possible source of degeneracy is spatial symmetry of the volume V, the

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[1] In our notations the symbol $\langle \mathtt{f}|$ stands for the complex conjugate of the function $\mathbf{f}$, and hence, $\langle \mathtt{f}^*|$ is, in fact, the function $\mathbf{f}$ itself. This system of notations may seem to be artificial, but we have decided to follow the standard Dirac notations, though they are more appropriate for Hermitian operators, while the operator $\mathtt{H}$ defined by (17),(5-7) is not Hermitian in general.

eigenvalues of H can not be defective. In the latter case all the eigenfunctions associated with a degenerate eigenvalue can be obtained one from another by different rotations and reflections in space, and, evidently, are linear independent. Note that the orthogonality condition (25) can be satisfied even if both $|P_m\rangle$ and $|P_n\rangle$ belong to the same degenerate eigenvalue but are linearly independent.

In order to define the eigenfunctions completely, one must specify some normalization rule. We will use here the following normalization:

$$\langle P_n|P_n\rangle = \langle E|E\rangle = |\mathbf{E}_0|^2 V \ . \tag{26}$$

We emphasize, that $\langle P_n^*|P_n\rangle \neq \langle P_n|P_n\rangle$, and the former value can be, in general, complex. Normalization (26) provides the correct dimensionality of the function $\mathbf{P}_n(\mathbf{r})$ (the counterpart of $|P_n\rangle$), which is the dimensionality of polarization, or, equivalently, of the electric field.

Now we can use the general decomposition of $|P\rangle$ in terms of the eigenfunctions $|P_n\rangle$, which, with the account of the orthogonality rule (25), takes the form

$$|P\rangle = \sum_{n=1}^{\infty} \frac{|P_n\rangle\langle P_n^*|P\rangle}{\langle P_n^*|P_n\rangle} \ , \tag{27}$$

and substitute it into the main equation (20) to obtain

$$|P\rangle = \sum_{n=1}^{\infty} \frac{|P_n\rangle\langle P_n^*|E\rangle}{\langle P_n^*|P_n\rangle[1/\kappa - h_n]} \ . \tag{28}$$

Finally, the expressions for the optical cross-sections, which follow from (28) and (21), are quite similar to those obtained in (Markel 1995) for the discrete case:

$$\sigma_e = \frac{4\pi k}{|\mathbf{E}_0|^2}\mathrm{Im}\sum_{n=1}^{\infty} \frac{\langle E|P_n\rangle\langle P_n^*|E\rangle}{\langle P_n^*|P_n\rangle[1/\kappa - h_n]} \ , \tag{29}$$

$$\sigma_a = \frac{4\pi k y_a^{(c)}}{|\mathbf{E}_0|^2}\sum_{m \neq n}^{\infty} \frac{\langle E|P_m^*\rangle\langle P_m|P_n\rangle\langle P_n^*|E\rangle}{\langle P_m|P_m^*\rangle\langle P_n^*|P_n\rangle[1/\kappa - h_n][1/\kappa - h_m]^*} \ . \tag{30}$$

In conclusion of this Section let us consider a possibility of employing the decomposition (28) for numerical calculations. In many cases (especially, if the volume V is "geometrically regular", i.e., it can be described by one of many well-known geometrical 3-dimensional figures) some orthonormal basis of functions $|\xi_n\rangle$ is known or can be easily found. Of course, these functions would be different for different shapes of V, because the orthonormality condition $\langle\xi_m|\xi_n\rangle = \delta_{mn}$ involves an integration over the volume V. Note also, that the basis of $|\xi_n\rangle$ can be chosen to be orthonormal in the usual sense, unlike the basis of eigenfunctions of H.

In some approximation one can assume that the first N basis functions are enough to expand the actual polarization function $|P\rangle$ with a sufficient precision. For example, the basis functions of higher order can oscillate too fast, while the space derivatives of polarization are anticipated to be limited. Then one can build a square matrix $\langle\xi_m|H|\xi_n\rangle$ of the order $N \times N$. The elements of this matrix can be obtained by analytical or, if that is not possible, by numerical integration. Now, that we have a matrix representation of the operator H, the problem of finding its eigenvalues and eigenfunctions is reduced to diagonalization of the square matrix $\langle\xi_m|H|\xi_n\rangle$, which can be done by the methods of linear algebra.

After that, the polarization function can be found according to (28) and any physically measurable quantity can be found from the polarization function.

The virtue of this method is that the matrix elements $\langle \xi_m | \mathtt{H} | \xi_n \rangle$ depend, in general, only on the shape of the particle and the frequency of the incident light, but do not depend on polarization of the incident light and the value of dielectric permittivity ϵ. Therefore, once the matrix $\langle \xi_m | \mathtt{H} | \xi_n \rangle$ is found and diagonalized (this is the most computationally intensive part), the solution can be found for different materials (different values of ϵ) and different polarizations of the incident light by a simple summation. Moreover, in the quasi-static case, when the wavelength of the incident light is much larger than the size of the particle, the elements of this matrix do not depend on the frequency ω as well. They also become real [2], which, in addition, simplifies the numerical procedure for diagonalization.

IV.   TIME DEPENDENCE

In order to establish the relation between the radiative relaxation time of an excitation and the imaginary parts of eigenvalues h_n of the operator $\mathtt{H}$, let us consider the time evolution of the polarization function in the case when the incident field is turned off abruptly at some moment of time. Namely, consider the incident wave of the form

$$\mathbf{E}_{\mathtt{inc}}(x,t) = \begin{cases} \mathbf{E}_0 \exp(\mathrm{i} k_0 x - \mathrm{i} \omega_0 t + \alpha t) & \text{if } t < x/c \\ 0 & \text{if } t \geq x/c \end{cases} . \tag{31}$$

Here we have assumed that the incident beam propagates along the x direction, α is some small positive constant, which indicates that the field has been "turned on" sometimes in the past (and later it was "turned off"), and $k_0 = \omega_0/c$.

The Fourier transformation of (31) gives

$$\mathbf{E}_{\mathtt{inc}}(x,\omega) = \frac{-\mathrm{i}\,\mathbf{E}_0}{\sqrt{2\pi}} \frac{\exp(\mathrm{i}\omega x/c + \alpha x/c)}{\omega - (\omega_0 + \mathrm{i}\alpha)} . \tag{32}$$

Note that the positive value of α allows to make the inverse Fourier transformation correctly. The pole $\omega = \omega_0 + \mathrm{i}\alpha$ lies in the upper complex semi-plane, and for $t > x/c$ we must close the integration contour of the inverse transformation in the lower semi-plane, so that the integration gives zero, in accordance with (31). Analogously, for $t < x/c$ we must close the integration contour in the upper semi-plane, which returns us the original function (31).

The solution (28) is, in fact, the ω-dependent Fourier component of the time-dependent polarization function. The dependence of the free term $|\mathtt{E}\rangle$ on ω is defined by the Fourier transformation of the time-dependent incident field (in our case, by formula (32)), so that we can write

$$|\mathtt{E}(\omega)\rangle = \frac{-\mathrm{i}\,|\mathtt{E}_0(\omega)\rangle}{\sqrt{2\pi}} \frac{1}{\omega - (\omega_0 + \mathrm{i}\alpha)} , \tag{33}$$

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[2] As we will see in Section V (equation (59)), the scattering cross-section is determined by the imaginary parts of eigenvalues and, eventually, by the imaginary parts of the elements of the matrix $\langle \xi_m | \mathtt{H} | \xi_n \rangle$. The latter are non-zero and depend on ω even in the quasi-static approximation. However, this dependence is trivial (see expressions (48),(54) for the matrix elements below) and does not require actual diagonalization of the ω-dependent matrix. Instead, one can use only the real parts of $\langle \xi_m | \mathtt{H} | \xi_n \rangle$ (which are ω-independent in the quasi-static case) for the diagonalization procedure, and then use the calculated eigenvectors and the relations quoted above to obtain the imaginary parts of the eigenvalues.

where $|E_0(\omega)\rangle$ has no singularities in the complex ω-plane. Now the time-dependent solution can be obtained by the inverse Fourier transformation:

$$|P(t)\rangle = \frac{-i}{2\pi} \sum_{n=1}^{\infty} \int_{-\infty}^{\infty} \frac{|P_n(\omega)\rangle\langle P_n^*(\omega)|E_0(\omega)\rangle}{\langle P_n^*(\omega)|P_n(\omega)\rangle} \frac{\exp(-i\omega t)d\omega}{[\omega - (\omega_0 + i\alpha)][\frac{1}{\kappa(\omega)} - h_n(\omega)]} . \quad (34)$$

Note that the eigenfunctions $|P_n(\omega)\rangle$ depend on ω, since the operator H depends on ω itself. However, it is reasonable to assume that the factor

$$\frac{|P_n(\omega)\rangle\langle P_n^*(\omega)|E_0(\omega)\rangle}{\langle P_n^*(\omega)|P_n(\omega)\rangle}$$

has no singularities because $\langle P_n^*(\omega)|P_n(\omega)\rangle$ never turns to zero [3].

Further, we can conclude that the factor $[1/\kappa(\omega) - h_n(\omega)]^{-1}$ can not have singularities in the upper complex semi-plane. Otherwise, it would mean that the turn-off of the excitation at the moment $t = x_l/c$ (let x_l be the x coordinate of the "most left" point of the particle) affects the polarization at $t < x_l/c$. On the other hand, the polarization must have some "inertia" and can not become zero exactly at the moment $t = x_l/c$. This means that the above factor must have at least one pole in the lower semi-plane.

Strictly speaking, the concept of the relaxation time is valid only if the excitation decays slowly compared to the characteristic time scale of its oscillations. Therefore, we will adopt at this point the resonance approximation. Namely, we will assume, that $\kappa(\omega)$ is purely real (since we do not want to consider the relaxation time related to the absorption in the volume, but only its radiative part) and define the shifted resonance frequency ω_n of the nth eigenmode as a solution of the equation

$$1/\kappa(\omega_n) - \text{Re}(h_n(\omega_n)) = 0 . \quad (35)$$

For simplicity, we assume that this equation has a unique solution for every n. Further, the prevailing contributions to the integrals in (34) are given by the intervals of ω that are close to the corresponding resonance frequency ω_n, so that we can use the first term of the Taylor expansion of the resonance denominator to obtain $1/\kappa(\omega) - h_n(\omega) \cong \beta(\omega_n - \omega) - i\,\text{Im}(h_n(\omega_n))$, where β is some positive constant. Now the integrated functions in (34) possess poles at $\omega = \omega_n - i\,\text{Im}(h_n(\omega_n))/\beta$. The value of $\text{Im}(h_n(\omega_n))/\beta$ must be small compared to ω_n in order the relaxation to be slow. Therefore, we can use only the real part of the poles everywhere, except for the exponent and the denominator, as shown below:

$$\frac{-i}{2\pi} \int_{-\infty}^{\infty} \frac{|P_n(\omega)\rangle\langle P_n^*(\omega)|E_0(\omega)\rangle}{\langle P_n^*(\omega)|P_n(\omega)\rangle} \frac{\exp(-i\omega t)d\omega}{[\omega - (\omega_0 + i\alpha)][\beta(\omega_n - \omega) - i\,\text{Im}(h_n(\omega_n))]}$$

$$= \frac{|P_n(\omega_n)\rangle\langle P_n^*(\omega_n)|E_0(\omega_n)\rangle}{\langle P_n^*(\omega_n)|P_n(\omega_n)\rangle} \frac{\exp[-i\omega_n t - \text{Im}(h_n(\omega_n))\,t/\beta]}{\beta(\omega_0 - \omega_n) + i\,\text{Im}(h_n(\omega_n))} . \quad (36)$$

The value of α was set to zero in the right-hand part of this equation, since it has no significance except the indication of the direction of bypassing the poles. The

---

[3] There is a special case of the so-called isotropic eigenfunction, i.e. $|P_n\rangle \neq 0$ and $\langle P_n^*(\omega)|P_n(\omega)\rangle = 0$. However, as is known from the theory of linear operators, an eigenfunction can not be isotropic if it is not degenerate.

factor $i\mathrm{Im}h_n(\omega_n)$ ensures that the denominator in the right-hand part does not turn to zero if ω_0 coincides with one of the resonance frequencies ω_n.

By analyzing the exponential factor in (36), we find that the relaxation time of nth eigenmode can be defined as

$$\tau_n = \frac{\beta}{\mathrm{Im}\,(h_n(\omega_n))} \ . \tag{37}$$

The constant β is common for all the eigenmodes, and can be found if the specific form of $\epsilon(\omega)$ is known. The relaxation time depends on the nth resonance frequency ω_n, but not on ω_0. In our simplified consideration we assumed, that there is only one (unshifted) resonance frequency, but in practice there might be several of them.

In this Section we have made an attempt to make the derivation as general as possible. One can always employ some theoretical model for molecular polarizability and obtain some specific form of $\epsilon(\omega)$ and $\kappa(\omega)$ (or use experimental data for $\epsilon(\omega)$). However, it is important to keep in mind that the famous Clausius-Mossotti relation in its usual form does not take into account the radiative reaction and will lead to incorrect results. For example, it follows from $\chi_{\mathtt{mol}} = (3/4\pi\rho)(\epsilon-1)/(\epsilon+2)$, that, if ϵ is purely real, the molecular polarizability $\chi_{\mathtt{mol}}$ is also purely real. But it is clear, that an isolated molecule will always scatter light and, therefore, $\chi_{\mathtt{mol}}$ must have a nonzero imaginary part. In order to overcome this difficulty, one can use the modified Clausius-Mossotti relation which reads (Van Kranendonk *et al.* 1977; Draine 1988; Draine *et al.* 1993):

$$\frac{3}{4\pi\rho}\frac{\epsilon-1}{\epsilon+2} = \frac{1}{1/\chi_{\mathtt{mol}} + \mathrm{i}2k^3/3} \ . \tag{38}$$

The last relation is self-consistent, because the case of no absorption corresponds to $\mathrm{Im}(1/\chi_{\mathtt{mol}}) = -2k^3/3$ and $\mathtt{Im}\epsilon = 0$.

V. PERTURBATION OF EIGENVALUES

If the wavelength of the incident radiation is much larger than the linear dimensions of region V we can treat the imaginary part of the operator $\mathtt{H}$ as a perturbation and expand $\mathtt{H}$ according to

$$\mathtt{H} = \mathtt{H}_R + \mathrm{i}\,\mathtt{H}_I \ , \tag{39}$$

$$\mathtt{H}_I = \mathtt{H}_I^{(1)} + \mathtt{H}_I^{(2)} + \mathtt{H}_I^{(3)} + ... \ , \tag{40}$$

where $\mathtt{H}_R$ and $\mathtt{H}_I$ are real symmetrical (and, hence, Hermitian) operators, and $\mathtt{H}_I^{(l)}$ is the lth term in the Taylor expansion of $\mathtt{H}_I$. The first two terms of this expansion are defined by the following relations, which can be derived from (5-7) and (17):

$$\mathtt{H}_I^{(1)}|f\rangle = \frac{2k^3}{3} \int_V \mathbf{f}(\mathbf{r}')\mathrm{d}\mathbf{r}' \ , \tag{41}$$

$$\mathtt{H}_I^{(2)}|f\rangle = \frac{2k^3}{3} \int_V \frac{(k|\mathbf{r} - \mathbf{r}'|)^2}{10} \left[-2\mathbf{f}(\mathbf{r}') + \frac{(\mathbf{r} - \mathbf{r}')[(\mathbf{r} - \mathbf{r}') \cdot \mathbf{f}(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|^2} \right] \mathrm{d}\mathbf{r}' \ . \tag{42}$$

Now we can build the usual perturbation theory, starting from the orthonormal basis $|\mathtt{P}_n^{(0)}\rangle$ of the (unperturbed) eigenfunctions of $\mathtt{H}_R$ and expanding the eigenfunctions and eigenvalues of $\mathtt{H}$ in the usual manner:

$$|\mathtt{P}_n\rangle = |\mathtt{P}_n^{(0)}\rangle + |\mathtt{P}_n^{(1)}\rangle + |\mathtt{P}_n^{(2)}\rangle + ... \ , \tag{43}$$

$$h_n = h_n^{(0)} + h_n^{(1)} + h_n^{(2)} + ... \ , \tag{44}$$

where $h_n^{(0)}$ are the purely real eigenvalues of the Hermitian operator $\mathtt{H}_R$ ($\mathtt{H}_R|\mathtt{P}_n^{(0)}\rangle = h_n^{(0)}|\mathtt{P}_n^{(0)}\rangle$), and the upper indices indicate the order of correction.

Since we are interested in the imaginary parts of eigenvalues, which govern the relaxation times according to (37), we do not need to know the values of $h_n^{(0)}$. The higher corrections follow from the perturbation theory [4], with the account of the normalization rule (26):

$$h_n^{(1)} = \mathrm{i}\frac{\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(1)}|\mathtt{P}_n^{(0)}\rangle}{|\mathbf{E}_0|^2 V} \ , \tag{45}$$

$$h_n^{(2)} = \frac{1}{|\mathbf{E}_0|^2 V}\left[-\sum_{m\neq n}^{\infty}\frac{|\langle \mathtt{P}_m^{(0)}|\mathtt{H}_I^{(1)}|\mathtt{P}_n^{(0)}\rangle|^2}{h_n^{(0)} - h_m^{(0)}} + \mathrm{i}\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle\right] \ , \tag{46}$$

so that

$$\mathrm{Im}h_n = \frac{1}{|\mathbf{E}_0|^2 V}[\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(1)}|\mathtt{P}_n^{(0)}\rangle + \langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle + ...] \ . \tag{47}$$

In order to identify physical meaning of these matrix elements, let us consider polarization function $\mathbf{P}_n^{(0)}(\mathbf{r})$ corresponding to the nth unperturbed eigenvector $|\mathtt{P}_n^{(0)}\rangle$. From the definition of $\mathtt{H}_I^{(1)}$ (41) we have

$$\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(1)}|\mathtt{P}_n\rangle = \frac{2k^3}{3}\int_V \mathrm{d}\mathbf{r}\int_V \mathrm{d}\mathbf{r}' \ \mathbf{P}_n^{(0)*}(\mathbf{r})\cdot\mathbf{P}_n^{(0)}(\mathbf{r}') \equiv \frac{2k^3}{3}|\mathbf{D}_n|^2 \ , \tag{48}$$

where we have introduced the total dipole moment of the nth eigenmode $\mathbf{D}_n$, according to the rule

$$\mathbf{D}_n = \int_V \mathbf{P}_n^{(0)}(\mathbf{r})\mathrm{d}\mathbf{r} \ . \tag{49}$$

An antisymmetrical state by its definition, is the state with $\mathbf{D}_n = 0$. If such a state exists, we must calculate the second-order correction to h_n in order to find the relaxation time. It is clear, that the second-order correction is much smaller, than the first order one. The parameter which is characteristic to the ratio of the second-order and the first-order corrections can be easily seen from comparison of (41) and (42) and is equal to $(R/\lambda)^2$, where R is the characteristic linear dimension of the particle. Thus the relaxation time in an antisymmetrical state can be $(\lambda/R)^2$ times larger than in a typical state with nonzero dipole moment.

---

[4] For simplicity we consider only the non-degenerate perturbation theory. However, as was shown in (Markel 1995), degeneracy does not change the results for the antisymmetrical states.

We can assert that a particle with special properties of symmetry must always possess antisymmetrical eigenstate(s) (see footnote 1).

It should be noted, that the matrix element (48) depends on frequency. In order to obtain the relaxation time according to (37) one needs to set $\omega = \omega_n$. If we use the quasi-static expression for $\mathtt{H}_R$ (by omitting the terms proportional to x^{-1} and x^{-2} and setting $\exp(\mathrm{i}x) = 1$ in (6,7)), $\mathbf{D}_n$ is frequency independent, so that the relaxation time becomes proportional to ω_n^{-3}.

Since the first order correction to $\mathrm{Im}h_n$ is determined by the total dipole moment of the eigenmode, it is natural to anticipate that the second order correction should be governed by quadrupole and magneto-dipole momenta. In order to verify this assumption we analyze the expression for the matrix element $\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle$,

$$
\begin{aligned}
\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle = \frac{2k^3}{3} \int_V \mathrm{d}\mathbf{r} \int_V \mathrm{d}\mathbf{r}' \, \frac{(k|\mathbf{r}-\mathbf{r}'|)^2}{10} \\
\times \left[-2\mathbf{P}_n^{(0)*}(\mathbf{r}) \cdot \mathbf{P}_n^{(0)}(\mathbf{r}') + \frac{[(\mathbf{r}-\mathbf{r}') \cdot \mathbf{P}_n^{(0)*}(\mathbf{r})][(\mathbf{r}-\mathbf{r}') \cdot \mathbf{P}_n^{(0)}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|^2} \right] , \quad (50)
\end{aligned}
$$

and the expressions for quadrupole and magneto-dipole momenta of the nth eigenmode in terms of polarization function $\mathbf{P}_n^{(0)}(\mathbf{r})$. The components of the quadrupole moment tensor $Q_{n,\alpha\beta}$ are given by

$$
Q_{n,\alpha\beta} = -\int_V [\nabla \cdot \mathbf{P}_n^{(0)}(\mathbf{r})][3r_\alpha r_\beta - \delta_{\alpha\beta} r^2] \mathrm{d}\mathbf{r} . \quad (51)
$$

Integrating (51) by parts, we obtain:

$$
Q_{n,\alpha\beta} = -\int_V \left[3\left(r_\alpha P_{n,\beta}^{(0)}(\mathbf{r}) + r_\beta P_{n,\alpha}^{(0)}(\mathbf{r}) \right) - 2\delta_{\alpha\beta} \left(\mathbf{P}_n^{(0)}(\mathbf{r}) \cdot \mathbf{r} \right) \right] \mathrm{d}\mathbf{r} . \quad (52)
$$

The magneto-dipole moment $\mathbf{M}_n$ is expressed with the use of the continuity equation as

$$
\mathbf{M}_n = \frac{\mathrm{i}k}{2} \int_V [\mathbf{r} \times \mathbf{P}_n^{(0)}(\mathbf{r})] \mathrm{d}\mathbf{r} . \quad (53)
$$

Comparing (52,53) with (50), we find that the matrix element $\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle$ can be expressed as

$$
\langle \mathtt{P}_n^{(0)}|\mathtt{H}_I^{(2)}|\mathtt{P}_n^{(0)}\rangle = \frac{2k^3}{3} \left[|\mathbf{M}_n|^2 + (k^2/120)|\mathbf{Q}_n|^2 + (k^2/5)\mathrm{Re}\left[\mathbf{D}_n^* \cdot \mathbf{O}_n \right] \right] , \quad (54)
$$

where

$$
|\mathbf{M}_n|^2 = \sum_\alpha M_{n,\alpha} M_{n,\alpha}^* , \quad (55)
$$

$$
|\mathbf{Q}_n|^2 = \sum_{\alpha,\beta} Q_{n,\alpha\beta} Q_{n,\beta\alpha}^* , \quad (56)
$$

$$
\mathbf{O}_n = \int_V \left[\left(\mathbf{r} \cdot \mathbf{P}_n^{(0)}(\mathbf{r}) \right) \mathbf{r} - 2r^2 \mathbf{P}_n^{(0)}(\mathbf{r}) \right] \mathrm{d}\mathbf{r} . \quad (57)
$$

The first two terms in (54) are convolutions of the elements of the magneto-dipole and quadrupole momenta of the nth eigenmode. The third term is, in general, the

same order of magnitude as the first two, but it disappears in an antisymmetrical state. It would be logically to assume, that the value $\mathbf{O}_n$ is a convolution of the elements of the electrical octupole moment of the nth eigenmode.

As one can see from (50), the matrix element $\langle \mathrm{P}_n^{(0)}|\mathrm{H}_I^{(2)}|\mathrm{P}_n^{(0)}\rangle$ does not depend on the choice of the origin of the coordinate system, i.e., it is invariant with respect to the transformation $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{a}$ where $\mathbf{a}$ is a constant vector. The expression (54) is also invariant with respect to this transformation, but the individual terms in (54) can depend on $\mathbf{a}$. However, if $\mathbf{D}_n = 0$, both $\mathbf{Q}_n$ and $\mathbf{M}_n$ do not depend on $\mathbf{a}$, as it can be seen from their definitions (51-53). It corresponds to the well-known fact that quadrupole and magneto-dipole momenta of a system of charges do not depend on the choice of the origin of coordinates if the total dipole moment is equal to zero. The vector $\mathbf{O}_n$ still depends on $\mathbf{a}$, even if $\mathbf{D}_n = 0$. But, in this case, it does not influence the value of matrix element $\langle \mathrm{P}_n^{(0)}|\mathrm{H}_I^{(2)}|\mathrm{P}_n^{(0)}\rangle$. As one can expect, $\mathbf{O}_n$ becomes invariant if both $\mathbf{Q}_n$ and $\mathbf{M}_n$ are equal to zero.

If not only $\mathbf{D}_n$, but also $\mathbf{M}_n$ and $\mathbf{Q}_n$ are equal to zero, we have a state of a higher order of antisymmetricity. In this case one needs to calculate the third-order correction to h_n in order to find the relaxation time. Obviously, the third-order correction is proportional to the small factor $(R/\lambda)^4$, so that the relaxation time in such an eigenstate becomes proportional to $(\lambda/R)^4$. We can generalize this dependence and state that if an eigenstate is of lth order of antisymmetricity, which means that the electric $2l$-pole and magnetic $(2l-2)$-pole momenta of the eigenstate are equal to zero, the relaxation time is proportional to $(\lambda/R)^{2l}$.

Now let us turn to the situation, when the dipole moment of an excitation is large, contrary to the case of antisymmetrical states. As it can be easily seen from (49) and the normalization rule (26), the maximum possible value of $|\mathbf{D}_n|^2$ is $|\mathbf{E}_0|^2 V^2$ and, consequently, the maximum possible value of $\mathrm{Im}h_n$ is $2(k^3 V)/3$. The corresponding relaxation time becomes proportional to $1/V$. This is in agreement with the result of the theory of superradiance, which states that the relaxation time is proportional to the inverse number of atoms (if we assume that the number of atoms is proportional to the volume V.) Note that in order to achieve the maximum value of $|\mathbf{D}_n|^2$, the polarization inside the volume must be uniform. This is the analog of the requirement, that the density matrix of all atoms is the same, which is used in the quantum theory of superradiance (Zaitsev, Malyshev and Trifonov 1983).

Finally, the zero-order expressions for the absorption and scattering cross-sections follow from (29), (30), (11) and the orthogonality of the set of $|\mathrm{P}_n^{(0)}\rangle$ (the exact eigenvectors are not orthogonal in the usual sense, see equation (25).) These expressions are similar to their counterparts in the discrete case that are found in (Markel 1995):

$$\sigma_a^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{n=1}^{\infty} |\langle \mathrm{E}|\mathrm{P}_n^{(0)}\rangle|^2 \frac{y_a^{(c)}}{|1/\kappa - h_n|^2} \ , \tag{58}$$

$$\sigma_s^{(0)} = \frac{4\pi k}{|\mathbf{E}_0|^2} \sum_{n=1}^{\infty} |\langle \mathrm{E}|\mathrm{P}_n^{(0)}\rangle|^2 \frac{\mathrm{Im}h_n}{|1/\kappa - h_n|^2} \ . \tag{59}$$

In the stationary regime of excitation by the incident wave (2) all the quantities in the right-hand sides of these equations should be taken at the frequency ω. Note that we have left the *exact* eigenvalues in the zero-order expressions for the cross-sections. This was done because the terms in the expansion for the scattering cross-section are proportional to the imaginary parts of eigenvalues, $\mathrm{Im}h_n$. These

values are equal to zero in the zero order of the perturbation theory, and in the first order of the perturbation theory if the state is antisymmetrical.

VI.   DISCUSSION

The main result of this paper is expression for radiative relaxation time of an optical excitation in a bulk dielectric particle. The relaxation time is defined by the imaginary part of the corresponding eigenvalue h_n according to (37). The constant β appearing in (37) can be found for any specific geometry and material if the dielectric constant $\epsilon(\omega)$ and the resonance frequency ω_n for this excitation mode are known. The expressions for the imaginary parts of eigenvalues, h_n, are given in (47,48,54) with the multipole momenta defined in (49,55,56,57). We emphasize that the problem of calculation of ω_n, as well as multipole momenta of a specific eigenmode, can be solved numerically for any specific geometry and is not considered in this paper. An approach based on pure electrostatics can be used for such calculation. The electrostatic solution itself, however, carries no information about radiative relaxation.

We showed that the relaxation time of an optical excitation of a bulk dielectric particle is defined by its multipole momenta. This result is analogous in its nature to the well-known fact from the quantum theory of radiation. We know that an optical transition takes more time, if the transitional dipole moment is zero. However, the theory build here uses only classical language.

It is important, that the theoretical approach developed in this paper embraces both the superradiance (the relaxation time is proportional to the inverse number of particles, or, equivalently, the inverse occupied volume) and the antisuperradiance (the relaxation time is proportional to $(\lambda/R)^2$.) These two cases differ only in the symmetry properties of the polarization function. For the superradiance, the polarization function is uniform and the total dipole moment of the particle reaches its maximum possible value, while for the antisuperradiance the polarization function is antisymmetrical and the total dipole moment is equal to zero.

The approach based on the eigenfunction decomposition of solutions of the Maxwell equations can be useful for practical problem solving. In Section III we proposed a numerical algorithm based on an approximation of replacing the infinite-dimensional interaction operator by a finite-dimensional square matrix.

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