Quantum optics of metallic particle

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The S-matrix approach and the Green's-functions technique are used to analyze the interaction of an electromagnetic field with a metallic particle. A diagram technique is developed for the description of electrodynamic phenomena in inhomogeneous media. The results of the classical Mie theory of light scattering and absorption by a sphere are duplicated. It is shown that the photon–photon interaction (term quadratic in the field in the Hamiltonian of the metallic specimen + electromagnetic field system) increases anomalously near the frequencies of the surface plasmons in the particle. This leads to renormalization of the wave functions of the photons interacting with the particle, transforming them into excitations of the polariton type with poles as functions of the frequency. As a result: a) the cross sections for three-photon processes on the surfaces of small particles (e.g., second-harmonic generation) are anomalously large even in weak electromagnetic fields, b) the cross section for inelastic scattering of light by a small particle is of the same order as the elastic-scattering cross section.

1. INTRODUCTION

The interaction of an electromagnetic field with macroscopic particles of a dispersed phase are usually described by classical electrodynamics. In some situations, however, this approach cannot be used. These include the calculation of the cross sections of a number of inelastic electromagnetic processes, such as Raman scattering of light, where one must resort to quantum-mechanical relations of the "golden rule" type. A quantum-mechanical approach is needed essentially also in the calculation of the photoeffect in small particles.

There are also less known cases when the use of the classical approach can lead to errors. Thus, in the simplest multiphoton processes on the surfaces of small metallic particles, the photon–photon interaction, which can certainly be neglected in a uniform medium, becomes extremely substantial at frequencies close to those of the surface plasmons of a particle. This leads to a strong renormalization of the wave functions of the photons participating in the process: the plane electromagnetic wave indicative of the photon is transformed in the particle into an entirely different function having a pole dependence on the frequency. This gives rise to additional poles in the cross sections of many multiphoton processes. Similar phenomena are observed in certain two-photon processes—for example in inelastic scattering of light by a metallic particle.

There exists in addition one more curious phenomenon, not accounted for at all in classical electrodynamics, and similarly connected with multiphoton processes. Even the simplest three-photon processes on the surface of a particle can be realized via different channels that are experimentally undistinguishable. Allowance for the interference of probability amplitudes corresponding to all channels of the process is absolutely indispensable. None is made in the classical approach.

We investigate in the present paper the interactions of an electromagnetic field with particles of a disperse phase by using the method of quantum Green's functions, which makes it possible to surmount the above difficulties. This method has by now given such good account of itself that it requires no promotion. We therefore skip the appropriate words and the tremendous bibliography devoted to its use for research into a great variety of physical phenomena. At the same time, we wish to point out that when the Green's function method is used to describe electrodynamic phenomena preference is given to the use of photon propagations via Maxwell's equations rather than an initial Hamiltonian followed by traditional construction of a diagram technique.[1] It seems to us that this is no accident but is connected with the fact that only the transverse part of the electromagnetic field is quantized, while the Coulomb forces, which are wholly responsible for the existence of a condensed medium, are introduced via an interaction potential. This circumstance does not raise serious difficulties in the study of processes in a homogenous medium, where the longitudinal and transverse effects are completely separated and the choice of a gauge for the photon propagator is not decisive. In homogeneous media, however, the dielectric-constant gradients make it possible to transform a transverse field into a longitudinal and vice versa, leading to the so-called retardation effects characterized by a parameter $\omega R/c$ (ω is the field frequency, R is the characteristic dimension of the inhomogeneity, and c the speed of light). This raises ultimately a number of difficulties in the development of a diagram technique. In the present paper we overcome these difficulties and show how to use a consistent quantum-mechanical S-matrix approach to describe the electrodynamics of a metallic particle of a disperse phase.

In the next section, starting from the known connection between the S-matrix and the Hamiltonian of the interaction of an electromagnetic field with a particle, we construct a diagram representation for the amplitude of elastic scattering of light by a particle. With this as an example, we shall show how to find the photon propagator, the polarization operator of the particle, and an expression relating the scattering amplitude with the photon propagator. Furthermore, using the technique of expansion in vector spherical harmonics, we solve an integral equation for the photon propagator and calculate the differential cross section of elastic scattering of an optical photon by a particle, reproducing thereby the classical results of the Mie theory.[2] In Sec. 3,

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using the technique of Lehmann expansions,[1] we show how to obtain a classical expression for the cross section of light absorption by a particle. We finally proceed then to solve problems in which quantum theory is indispensable: 1) calculate the probabilities of three-photon processes on the surface of a particle—Sec. 4, 2) calculate the cross section of the inelastic scattering of light by a particle—Sec. 5, 3) analyze the photoeffect in a small metal particle—Sec. 6.

In our entire discourse we use the jellium model to describe the behavior of the particle, i.e., we assume that the particle is metallic, but its electrodynamic properties are due to a gas of conduction electrons contained in a self-consistent well produced by a positive ion background. All the calculations of the irreducible polarization operators are made in higher-order perturbation theory in electron–electron interaction. The described limitations and the specific choice of the model simplify substantially and shorten the discourse, but are not of fundamental importance.

Except in the final results, we use everywhere a system of units with $\hbar = c = 1$.

2. ELASTIC SCATTERING OF LIGHT BY A PARTICLE

In this section we use the calculation of the differential cross section for light scattering by a particle as an example to show how to develop a diagram technique for the investigation of electromagnetic processes in an inhomogeneous metallic sample.

It is assumed that the electromagnetic properties of the sample are due to a conduction-electron gas that interacts via a Coulomb potential and is located in a field $u(\mathbf{r})$ produced by a uniform positive ion background. The electron density $n(\mathbf{r})$ of the sample is specified in the form $n(\mathbf{r}) = n_0\eta(\mathbf{r})$, where n_0 is the average conduction-electron density, $\eta(\mathbf{r}) = 1$ inside the sample and to zero outside.

We represent the total Hamiltonian of the sample + electromagnetic field system in the form

$$H = H_0 + H_I,$$

where the Hamiltonian

$$H_0 = \frac{1}{2m}\int \mathbf{p}^2(\mathbf{r})d\mathbf{r} - \int u(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \sum_{\mathbf{k},\lambda} \omega_k a^+_{\mathbf{k},\lambda} a_{\mathbf{k},\lambda}$$

describes the non-interacting conduction electrons contained in the field $u(\mathbf{r})$ and the free transverse electromagnetic field; $\rho(\mathbf{r}) + \psi^+(\mathbf{r})\psi(\mathbf{r})$ is the electron-density operator, $\mathbf{p}(\mathbf{r}) = i\psi^+(\mathbf{r})\nabla\psi(\mathbf{r})$, is the electron-momentum density operator, where $\psi^+(\mathbf{r})$, and $\psi(\mathbf{r})$ are the electron creation and annihilation operators; m is the electron mass; $a^+_{\mathbf{k},\lambda}$ and $a_{\mathbf{k},\lambda}$ are the creation and annihilation operators for a photon with a wave vector $\mathbf{k}$, a polarization λ ($\lambda = 1,2$), and a frequency $\omega = ck$. The Hamiltonian of the electron interaction with one another and with the electromagnetic field is

$$H_I = \frac{e^2}{2}\int \delta\rho(\mathbf{r})Q(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r}')d\mathbf{r}d\mathbf{r}' - \frac{e}{m}\int \mathbf{p}(\mathbf{r})\mathbf{A}(\mathbf{r})d\mathbf{r} + \frac{e^2}{2m}\int \rho(\mathbf{r})\mathbf{A}^2(\mathbf{r})d\mathbf{r}, \qquad (1)$$

where $Q(\mathbf{r}) = |\mathbf{r}|^{-1}$, $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - n(\mathbf{r})$, e is the electron charge, and $\mathbf{A}$ is the vector-potential operator

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{k},\lambda} \sqrt{\frac{2\pi}{\omega V}}\, \mathbf{e}_{k,\lambda}(a^+_{\mathbf{k},\lambda}e^{-i\mathbf{kr}} + a_{\mathbf{k},\lambda}e^{i\mathbf{kr}}),$$

V is the normalization volume, $\mathbf{e}_{k\lambda}$ is the polarization unit vector and satisfies the relations

$$\mathbf{k}\mathbf{e}_{k,\lambda} = 0,$$

$$\mathbf{e}_{k,\lambda}\mathbf{e}_{k,\lambda'} = \delta_{\lambda\lambda'}.$$

The connection between the photon elastic scattering amplitude $\mathcal{T}$, which determines the probability of the process

$$W = 2\pi|\mathcal{T}|^2\delta(\omega_i - \omega_f),$$

with the S matrix is

$$\langle a_i S a_f^+\rangle = \delta_{if} - 2\pi i\delta(\omega_i - \omega_f)\mathcal{T},$$

where i and f label the initial and final states, and the angle brackets denote averaging over the ground state of the Hamiltonian H_0. The S matrix is defined in the standard manner[1]

$$S = T\exp\{-i\int_{-\infty}^{\infty} H^I(\tau)d\tau\}$$

$$= \sum_{k=0}^{\infty}\frac{(-i)^k}{k!}\int_{-\infty}^{\infty}dt_1\int_{-\infty}^{\infty}dt_2\ldots\int_{-\infty}^{\infty}dt_k\, T\{H^I(t_1)H^I(t_2)\ldots H^I(t_k)\}, \qquad (2)$$

where T is the chronological-ordering operator and $H^I(\tau) = \exp(iH_0\tau)H_I\exp(-iH_0\tau)$.

To calculate $\mathcal{T}$ we expand the S matrix in a perturbation-theory (PT) series in terms of H_I. In first-order PT we have:

$$\mathcal{T}_1 = \frac{2\pi}{\omega V}\int e_{i\alpha}\exp(-i\mathbf{k}_i\mathbf{r})\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}')e_{f\beta}\exp(i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}', \qquad (3)$$

where $\omega = \omega_i = \omega_f$, and $\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$ is the potential of the photon–particle interaction

$$\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}') = -\frac{e^2}{m}\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')n(\mathbf{r})$$

$$= \frac{\varepsilon(\omega) - 1}{4\pi}\delta(\mathbf{r}-\mathbf{r}')\delta_{\alpha\beta}\eta(\mathbf{r}). \qquad (4)$$

We have used in (4) the relation

$$\varepsilon(\omega) = 1 + 4\pi\alpha(\omega) = 1 - \omega_0^2/\omega^2,$$

between the dielectric constant $\varepsilon(\omega)$ of the particle material and the polarizability $\alpha(\omega)$ with the classical plasma frequency $\omega_0 = 4(\pi n_0 e^2/m)^{1/2}$ of the electron gas.

We set Eq. (4) in correspondence with diagram a) of Fig. 1, which shows in graphic form the PT series for $\mathcal{T}$. In

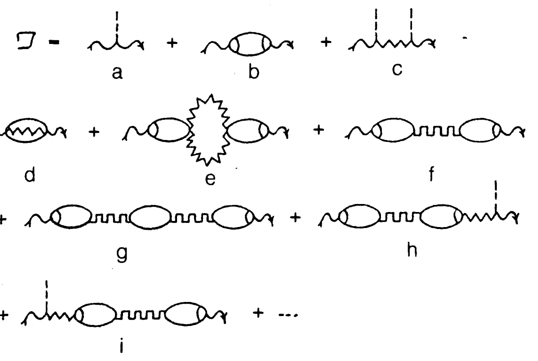

FIG. 1. Perturbation-theory series for elastic-scatterings amplitude.

second-order PT there appear two terms. The first of them is connected with diagram b). The corresponding analytic expression is:

$$\mathcal{T}_2 = -\frac{2\pi}{\omega V}\left(\frac{e}{m}\right)^2 \int_{-\infty}^{\infty} \langle T p_\alpha^I(\mathbf{r}_1, \tau) p_\beta^I(\mathbf{r}_2, 0)\rangle$$

$$\times \exp(-i\mathbf{k}_i\mathbf{r}_1)\exp(i\mathbf{k}_f\mathbf{r}_2)\exp(i\omega\tau)e_{i,\alpha}e_{f,\beta}d\mathbf{r}_1 d\mathbf{r}_2 d\tau.$$

Simple estimates show that the contribution of this diagram contains the small parameter $(r_0/R)(\omega_0/\omega)$ (r_0 is the Thomas–Fermi screening radius and R is the characteristic dimension of the sample) compared with the contribution of diagram a). We neglect hereafter the contribution made to the amplitude by diagrams containing a momentum–momentum correlator. In second-order PT, there appears on top the diagram b) one more component of $\mathcal{J}$:

$$\mathcal{T}_2 = -\left(\frac{e^2}{m}\right)^2 \frac{2\pi}{\omega V}\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}_1, \tau)\rho^I(\mathbf{r}_2, 0)\rangle$$

$$\times \langle T A_\alpha(\mathbf{r}_1, \tau)A_\beta(\mathbf{r}_2, 0)\rangle e_{i,\alpha}e_{f,\beta}\exp(-i\mathbf{k}_i\mathbf{r}_1)$$

$$\times \exp(i\mathbf{k}_f\mathbf{r}_2)\exp(i\omega\tau)d\mathbf{r}_1 d\mathbf{r}_2 d\tau.$$

Recognizing that $\rho(\mathbf{r}) = n(\mathbf{r}) + \delta\rho(\mathbf{r})$, we can represent it as a sum of two diagrams: c) and d). Diagram c) corresponds to a contribution

$$\mathcal{T}_2 = \frac{2\pi}{\omega V}\left(\frac{e^2}{m}\right)^2 \int n(\mathbf{r})n(\mathbf{r}')G^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$$

$$\times e_{i,\alpha}e_{f,\beta}\exp(-i\mathbf{k}_i\mathbf{r})\exp(i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}', \qquad (5)$$

where

$$G^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = i\int_{-\infty}^{\infty} \langle T A_\alpha(\mathbf{r}, \tau)A_\beta(\mathbf{r}', 0)\rangle e^{i\omega\tau}d\tau$$

is the free-photon propagator in a transverse gauge. Connected with the diagram d), which contains an integrated propagator line, is a small parameter e^2 which we shall omit. We shall also disregard analogous diagrams of higher orders of PT, of the type d) containing the small parameter λ_F/λ (λ is the wavelength of the incident radiation and λ_F is the Fermi wavelength of the electron).

A very interesting term appears in third-order PT in the amplitude $\mathcal{J}$ and is represented by diagram e). Its contribution to $\mathcal{J}$ is:

$$\mathcal{T}_3 = -\frac{2\pi}{\omega V}e^2\left(\frac{e}{m}\right)^2 \int_{-\infty}^{\infty} \langle T p_\alpha^I(\mathbf{r}, \tau)\rho^I(\mathbf{r}_1, 0)\rangle$$

$$\times e^{i\omega\tau}d\tau Q(\mathbf{r}_1, \mathbf{r}_2)\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}_2, \tau')p_\beta^I(\mathbf{r}', 0)\rangle$$

$$\times\ e^{i\omega\tau'}d\tau'\exp(-i\mathbf{k}_i\mathbf{r})\exp(i\mathbf{k}_f\mathbf{r}')e_{i\alpha}e_{f\beta}d\mathbf{r}_1 d\mathbf{r}_2.$$

The explicit forms of the irreducible polarization operators

$$\mathcal{P}_{\alpha 0}(\mathbf{r}, \mathbf{r}') = -i\int_{-\infty}^{\infty} \langle T p_\alpha^I(\mathbf{r}, \tau)\rho^I(\mathbf{r}', 0)\rangle e^{i\omega\tau}d\tau$$

$$= \frac{i}{\omega}\frac{\partial}{\partial r'_\alpha}[n(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')],$$

$$\mathcal{P}_{0\alpha}(\mathbf{r}, \mathbf{r}') = -i\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}, \tau)p_\alpha^I(\mathbf{r}', 0)\rangle e^{i\omega\tau}d\tau \qquad (6)$$

$$= \frac{i}{\omega}\frac{\partial}{\partial r_\alpha}[n(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')]$$

will be derived in Appendix A. These operators make nonzero contributions to $\mathcal{J}$ only in an inhomogeneous medium, and it is precisely they which describe the transformation of a longitudinal field into a transverse one and vice versa. Using (6) we can represent the diagrams f) of $\mathcal{J}$ in the form

$$-\frac{2\pi}{\omega V}\left(\frac{e^2}{m}\right)^2 \frac{e^2}{\omega^2}\int n(\mathbf{r})n(\mathbf{r}')\frac{\partial^2}{\partial r_\alpha \partial r'_\beta}Q(\mathbf{r}, \mathbf{r}')$$

$$\times\ e_{i\alpha}e_{f\beta}\exp(-i\mathbf{k}_i\mathbf{r})\exp(i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}'.$$

This term can be combined with (5) by introducing into the problem a new propagator

$$D^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = G^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}') - \frac{1}{\omega^2}\frac{\partial^2}{\partial r_\alpha \partial r'_\beta}Q(\mathbf{r}, \mathbf{r}')$$

$$= \left(\delta_{\alpha\beta} - \frac{1}{\omega^2}\nabla_\alpha\nabla'_\beta\right)$$

$$\times\frac{\exp(-i\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{(2\pi)^3}\int \frac{4\pi}{k^2 - \omega^2}$$

$$\times \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{\omega^2}\right)\exp[-i\mathbf{k}(\mathbf{r} - \mathbf{r}')]d\mathbf{k}, \qquad (7)$$

in which, with some experience, it is easy to recognize a free-photon propagation in a gauge with a zero scalar potential. It is just a propagator in this gauge which will play the principal role hereafter.

In higher orders of PT there appear, beside the elements already considered, also diagrams describing an added complication of the Coulomb line. In particular, in fourth order there appears the diagram h), which contains an irreducible density–density polarization operator

$$\mathcal{P}_{00}(\mathbf{r}, \mathbf{r}') = i\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}, \tau)\rho^I(\mathbf{r}', 0)\rangle e^{i\omega\tau}d\tau$$

$$= -\frac{1}{m\omega^2}\frac{\partial}{\partial r_\alpha}\left[n(\mathbf{r})\frac{\partial}{\partial r_\alpha}\delta(\mathbf{r} - \mathbf{r}')\right]. \qquad (8)$$

The explicit form of the correlator $\mathcal{P}_{00}$ will also be derived in Appendix A.

The rules for decoding the elements of the diagrams of Fig. 2 will help us with the now feasible summation of the PT series. It is easy to guess that to this end it suffices to replace

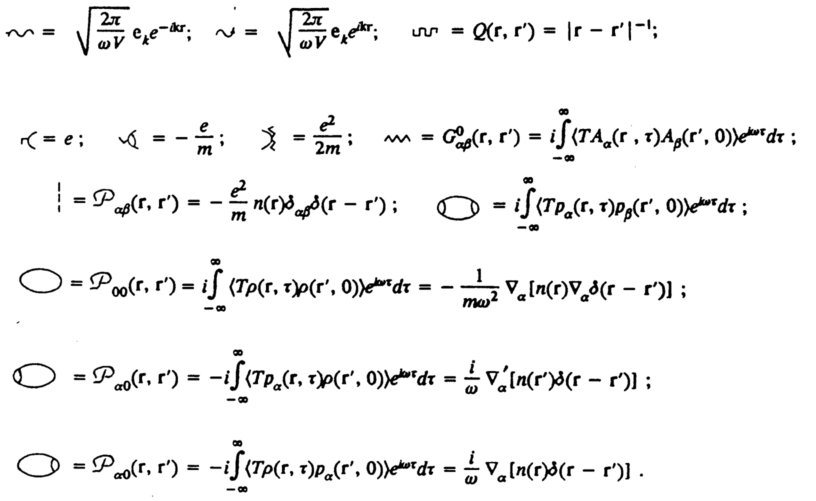

FIG. 2. Rules for interpreting the diagram elements.

the internal lines in diagrams (f), (c), (h), and (i) of Fig. 1, respectively, by the propagators G_{00}, $G_{\alpha\beta}$, $G_{0\alpha}$, and $G_{\alpha 0}$, defined in Fig. 3. It is easy also to obtain from Fig. 3 the system of four integral equations satisfied by these propagators (the parentheses denote integration over the internal coordinates)

$$G_{00} = Q + e^2(Q\mathcal{P}_{00}G_{00}) - \frac{e^2}{m}(Q\mathcal{P}_{0\alpha}G_{\alpha 0}),$$

$$G_{\alpha\beta} = G^0_{\alpha\beta} + (G^0_{\alpha\gamma}\mathcal{P}_{\gamma\mu}G_{\mu\beta}) - \frac{e^2}{m}(G^0_{\alpha\gamma}\mathcal{P}_{\gamma 0}G_{0\beta}),$$

$$G_{0\alpha} = -\frac{e^2}{m}(Q\mathcal{P}_{0\beta}G_{\beta\alpha}) + e^2(Q\mathcal{P}_{00}G_{0\alpha}),$$

$$G_{\alpha 0} = -\frac{e^2}{m}(G_{\alpha\beta}\mathcal{P}_{\beta 0}G_{00}) + (G^0_{\alpha\gamma}\mathcal{P}_{\gamma\nu}G_{\nu 0}).$$

The graphic forms of these equations are shown in Fig. 4.

A fundamental simplification of the procedure for summing the selected classes of diagrams is obtained by introducing a new propagator $D_{\alpha\beta}$, which is connected with $G_{0\alpha}$, G_{00}, $G_{\alpha\beta}$, and $G_{\alpha 0}$, by the relation

$$D_{\alpha\beta}(\mathbf{r},\mathbf{r}') = G_{\alpha\beta}(\mathbf{r},\mathbf{r}') - \frac{i}{\omega}\nabla_\alpha G_{0\beta}(\mathbf{r},\mathbf{r}') - \frac{i}{\omega}\nabla'_\beta G_{\alpha 0}(\mathbf{r},\mathbf{r}') - \frac{1}{\omega}\nabla_\alpha\nabla'_\beta G_{00}(\mathbf{r},\mathbf{r}'). \quad (9)$$

We establish first the identities

$$i\omega\mathcal{P}_{00}(\mathbf{r},\mathbf{r}') - \frac{1}{m}\nabla_\alpha\mathcal{P}_{\alpha 0}(\mathbf{r},\mathbf{r}') = 0,$$
$$-i\omega\mathcal{P}_{0\alpha}(\mathbf{r},\mathbf{r}') + \frac{m}{e^2}\nabla_\beta\mathcal{P}_{\beta\alpha}(\mathbf{r},\mathbf{r}') = 0, \quad (10)$$

which are obtained by using the continuity equation

$$\frac{\partial\rho}{\partial t} + \operatorname{div}\mathbf{j} = 0$$

and the relations

$$\rho(\mathbf{r}) = \int\mathcal{P}_{0\alpha}(\mathbf{r},\mathbf{r}_1)A_\alpha(\mathbf{r}_1)d\mathbf{r}_1 + \int\mathcal{P}_{00}(\mathbf{r},\mathbf{r}_1)V(\mathbf{r}_1)d\mathbf{r}_1,$$

$$j_\alpha(\mathbf{r}) = \frac{1}{m}\int\mathcal{P}_{\alpha 0}(\mathbf{r},\mathbf{r}_1)V(\mathbf{r}_1)d\mathbf{r}_1 + \int\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}_1)A_\beta(\mathbf{r}_1)d\mathbf{r}_1,$$

which connect the charges and currents induced in the sample with an electromagnetic field characterized by vector and scalar potentials $\mathbf{A}$ and V. Using (9) and (10) it is easy to show that the sum of the diagrams of interest has the form shown in Fig. 5, or:

$$\mathcal{T} = e_{i\alpha}\int\exp(-i\mathbf{k}_i\mathbf{r})\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}_1)\exp(i\mathbf{k}_f\mathbf{r}_1)e_{\beta f}\,d\mathbf{r}d\mathbf{r}_1$$
$$+ e_{i\alpha}\int\exp(-i\mathbf{k}_i\mathbf{r})\mathcal{P}_{\alpha\beta}(\mathbf{r},\mathbf{r}_1)D_{\beta\gamma}(\mathbf{r}_1,\mathbf{r}_2)$$
$$\times\mathcal{P}_{\gamma\nu}(\mathbf{r}_2,\mathbf{r}_3)e_{\nu f}\exp(i\mathbf{k}_f\mathbf{r}_3)d\mathbf{r}d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3, \quad (11)$$

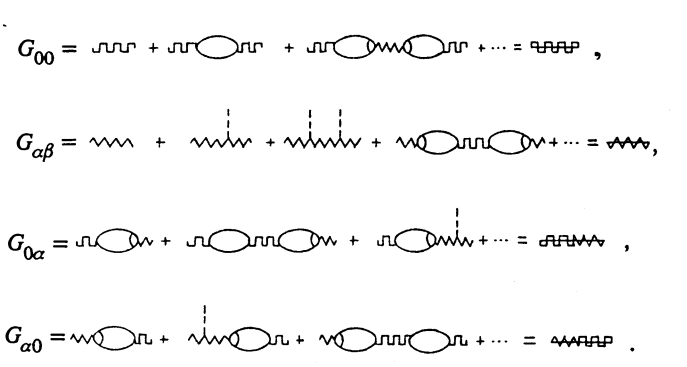

FIG. 3. Determination of four auxiliary propagators.

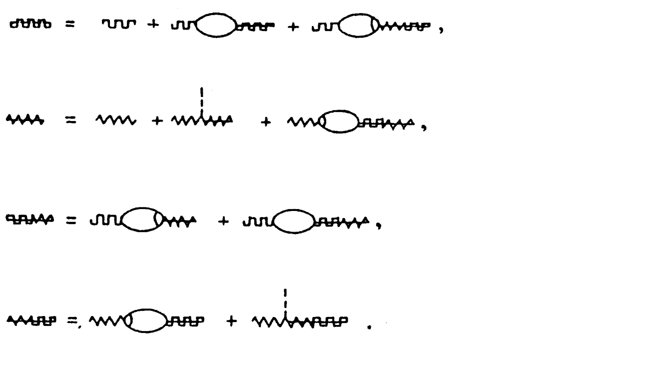

FIG. 4. System of equations for four auxiliary propagators.

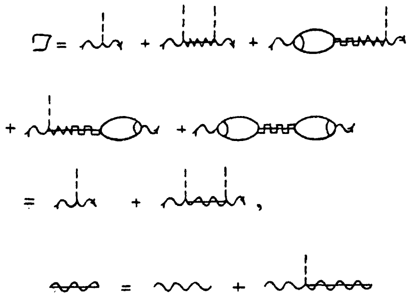

FIG. 5. Connection between the elastic-scattering amplitude and the propagator in a gauge with zero scalar potential and equation for this propagator.

where $\mathscr{P}_{\alpha\beta}$ is defined by expression (4), and D is the solution of the equation (see also the last line of Fig. 5):

$$D_{\alpha\beta} = D^0_{\alpha\beta} + (D^0_{\alpha\gamma}\mathscr{P}_{\gamma\nu}D_{\nu\beta}). \tag{12}$$

Equation (12) coincides with the well-known (see, e.g., Ref. 1) equation for the Green's function of the Maxwell equations in a gauge with a zero scalar potential. We were able to derive (11) and (12) without introducing potentials quantized in this gauge. Were it possible to introduce properly such operators and to express correctly the Hamiltonian in their terms, our exposition would be noticeably shortened. We have heard of no one able to do this distinctly. Our attempts in this direction also ended in failure.

Up to now, all the equations written by us depended in no way on the shape of the sample. Our task will now be to solve them for a spherical particle of radius a. We begin with Eq. (12). We use the technique of expanding in eigenfunctions a vector wave equation in a spherical coordinates—functions **L**, **M**, and **N**. These functions are introduced by the relations[3]

$$\mathbf{L}^z_{lm}(\omega, \mathbf{r}) = \frac{1}{\omega}\nabla[z_l(\omega r)Y_{lm}(\mathbf{n})]$$

$$= \mathbf{P}_{lm}(\mathbf{n})\frac{1}{\omega}\frac{d}{dr}z_l(\omega r) + \sqrt{l(l+1)}\frac{1}{\omega r}z_l(\omega r)\mathbf{B}_{lm}(\mathbf{n}),$$

$$\mathbf{M}^z_{lm}(\omega, \mathbf{r}) = \mathrm{rot}[\mathbf{r}z_l(\omega r)Y_{lm}(\mathbf{n})] = \sqrt{l(l+1)}z_l(\omega r)\mathbf{C}_{lm}(\mathbf{n})$$

$$= \frac{1}{\omega}\,\mathrm{rot}\,\mathbf{N}^z_{lm}(\omega, \mathbf{r}), \tag{13}$$

$$\mathbf{N}^z_{lm}(\omega, \mathbf{r}) = \frac{1}{\omega}\,\mathrm{rot}\,\mathbf{M}^z_{lm}(\omega, \mathbf{r})$$

$$= \frac{l(l+1)}{\omega r}z_l(\omega r)\mathbf{P}_{lm}(\mathbf{n}) + \sqrt{l(l+1)}\frac{1}{\omega r}\frac{d}{dr}[rz_l(\omega r)]\mathbf{B}_{lm}(\mathbf{n}),$$

where $\mathbf{n} = \mathbf{r}/r$ and $z_l(x)$ are spherical Bessel functions. The vector spherical harmonics **P**, **B**, and **C** are connected with the normalized scalar spherical harmonics $Y_{lm}(\mathbf{n})$ as follows:

$$\mathbf{P}_{lm}(\mathbf{n}) = \mathbf{n}Y_{lm}(\mathbf{n}),$$

$$\mathbf{B}_{lm}(\mathbf{n}) = \frac{r}{\sqrt{l(l+1)}}\nabla Y_{lm}(\mathbf{n}) = [\mathbf{n}\mathbf{C}_{lm}(\mathbf{n})],$$

$$\mathbf{C}_{lm}(\mathbf{n}) = \frac{1}{l(l+1)}\,\mathrm{rot}\,\mathbf{r}Y_{lm}(\mathbf{n}) = -[\mathbf{n}\mathbf{B}_{lm}(\mathbf{n})].$$

To start with, we obtain an expansion in the vector spherical harmonics for the free-photon propagator $D^0_{\alpha\beta}$ contained in Eq. (12) and having the explicit form (7). We use the well-known expansion[3]

$$\frac{\exp(i\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\delta_{\alpha\beta} = 4\pi i\omega\sum_{lm}\frac{1}{l(l+1)}$$

$$\times[M^j_{lm,\alpha}(\omega,\mathbf{r})\overline{M}^h_{lm,\beta}(\omega,\mathbf{r}')$$

$$+ N^j_{lm,\alpha}(\omega,\mathbf{r})\overline{N}^h_{lm,\beta}(\omega,\mathbf{r}')$$

$$+ l(l+1)L^j_{lm,\alpha}(\omega,\mathbf{r})\overline{L}^h_{lm,\beta}(\omega,\mathbf{r}')] \qquad (r < r'), \tag{14}$$

$$\frac{\exp(i\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}$$

$$= 4\pi i\omega\sum_{lm}Y_{lm}(\mathbf{n})Y^*_{lm}(\mathbf{n}')[j_l(\omega r)h_l(\omega r')\theta(r'-r)$$

$$+ j_l(\omega r')h_l(\omega r)\theta(r-r')], \tag{15}$$

where a superior bar denotes that the corresponding function is one of the complex-conjugate spherical harmonic Y^*_{lm}, j_l is a spherical Bessel function, h_l is a spherical Hankel function of the first kind, and $\theta(x)$ is the Heaviside unit step function. To make the mathematics clearer and more lucid, we omit some of the arguments and indices in the intermediate calculations and restore them in the final results.

Differentiating (15) we obtain

$$\frac{\partial^2}{\partial r_\alpha\partial r'_\beta}\frac{\exp(i\omega|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} = 4\pi i\omega^3\sum[L^j_\alpha(\mathbf{r})\overline{L}^h_\beta(\mathbf{r}')\theta(r'-r)$$

$$+ L^h_\alpha(\mathbf{r})\overline{L}^j_\beta(\mathbf{r}')\theta(r-r')]$$

$$- 4\pi i\omega^2\sum[L^h_\alpha(\mathbf{r})j_l(\omega r)Y^*(\mathbf{n}') - L^j_\alpha(\mathbf{r})h_l(\omega r)Y^*(\mathbf{n}')]n_\beta\delta(r-r'). \tag{16}$$

Substituting (16) in (7) and taking (14) into account, we see that the terms containing the products $L_\alpha\overline{L}_\beta$ in (16) are canceled out in analogy with the terms in (14). The remaining terms in (16) can be simplified by using the relations

$$h_l(x)j_l'(x) - h_l'(x)j_l(x) = -i/x^2 \tag{17}$$

and (13):

$$\sum[L^h_\alpha(\mathbf{r})j_l(\omega r) - L^j_\alpha(\mathbf{r})h_l(\omega r)]Y^*(\mathbf{n}')$$

$$= \sum P_\alpha(\mathbf{n})Y^*(\mathbf{n}')[h_l(\omega r)j_l(\omega r) - j_l(\omega r)h_l(\omega r)]$$

$$= \frac{i}{(\omega r)^2}n_\alpha\delta(\mathbf{n}-\mathbf{n}').$$

Taking (7), (14), and (16) into account we obtain ultimately ($r \leqslant r'$):

$$D^0_{\alpha\beta}(\mathbf{r},\mathbf{r}') = 4\pi i\omega\sum_{lm}\frac{1}{l(l+1)}[M^j_{lm,\alpha}(\omega,\mathbf{r})\overline{M}^h_{lm,\beta}(\omega,\mathbf{r}')$$

$$+ N^j_{lm,\alpha}(\omega,\mathbf{r})\overline{N}^h_{lm,\beta}(\omega,\mathbf{r}')] - \frac{4\pi}{\omega^2}n_\alpha n'_\beta\delta(\mathbf{r}-\mathbf{r}'). \tag{18}$$

In a uniform medium with dielectric constant ε the frequency ω should be replaced by $p = \omega\sqrt{\varepsilon}$. The corresponding photon propagator will be designated $D^{p}_{\alpha\beta}(\mathbf{r},\mathbf{r}')$. It satisfies the equation

$$D^p_{\alpha\beta}(\mathbf{r},\mathbf{r}') = D^0_{\alpha\beta}(\mathbf{r},\mathbf{r}') + \alpha\omega^2\int D^0_{\alpha\gamma}(\mathbf{r},\mathbf{r}_1)D^p_{\gamma\beta}(\mathbf{r}_1,\mathbf{r}')d\mathbf{r}_1. \quad (19)$$

We shall now demonstrate a simple and very effective method for instantaneously solving an equation such as (12) for a density distribution $\eta(\mathbf{r}) = \theta(a-r)$. We do everything in symbolic form, without invoking a specific type of Green's function, and adhere only to definite rules according to which a free Green's function acts on functions in terms of which the exact solution is expanded.

Assume that the free propagator can be represented as an expansion $(r<r')$

$$D^0(\mathbf{r},\mathbf{r}') = \sum_l A_l(\omega)f_l(\omega,\mathbf{r})g_l(\omega,\mathbf{r}'),$$

where f_l and g_l are regular and singular at $r=0$ solutions of the free wave equations. These can be $j_l(wr)Y_{lm}(\mathbf{n})$ or $h_l(wr)Y_{lm}(\mathbf{n})$ in the case of a scalar propagator, or $\mathbf{M}^j$, $\mathbf{N}^j$ and $\mathbf{M}^h$, $\mathbf{N}^h$ in the vector case. We must solve Eq. (12), which we rewrite in the form

$$D(\mathbf{r},\mathbf{r}') = D^0(\mathbf{r},\mathbf{r}') + \alpha\omega^2\int D^0(\mathbf{r},\mathbf{r}_1)\eta(\mathbf{r}_1)D(\mathbf{r}_1,\mathbf{r}')d\mathbf{r}_1. \quad (20)$$

Obviously, D must be sought in the form of a signal freely propagating in the medium and a sum of reflected waves whose defining functions must be regular at the origin

$$D(\mathbf{r},\mathbf{r}') = D^p(\mathbf{r},\mathbf{r}') - \sum A_l(p)R_l f_l(p,\mathbf{r})f_l(p,\mathbf{r}'). \quad (21)$$

We have to find the reflection coefficients R_l. Let us formulate the rules according to which a free propagator acts on each term from the right-hand side of Eq. (21)

$$\int D^0(\mathbf{r},\mathbf{r}_1)\eta(\mathbf{r}_1)D^p(\mathbf{r}_1,\mathbf{r}')d\mathbf{r}_1 = \frac{1}{\alpha\omega^2}(D^p - D^0) - \sum A_l(\omega)A_l(p)f_l(\omega,\mathbf{r})f_l(p,\mathbf{r}')W[gg], \quad (22)$$

$$\int D^0(\mathbf{r},\mathbf{r}_1)\eta(\mathbf{r}_1)f_l(p,\mathbf{r}_1)d\mathbf{r}_1 = \frac{1}{\alpha\omega^2}f_l(\omega,\mathbf{r}) - \sum A_l(\omega)g_l(\omega,\mathbf{r})W[gf], \quad (23)$$

where

$$W[gf] = \int\bar{\eta}(\mathbf{r})g(\omega,\mathbf{r})f(p,\mathbf{r})d\mathbf{r} = -\int\eta gf d\mathbf{r} \quad (24)$$

and $\bar{\eta} = 1-\eta$, and agree to let henceforth the function containing ω precede the function containing p. In the derivation of (22) and (23) we used the relation $\eta = 1-\bar{\eta}$ and Eq. (19). Integration over all of space yields the first term on the right-hand sides of (22) and (23), while the second term results from integrating with respect to r with a factor $\bar{\eta}$. Substitution of (21) in (20) yields

$$R_l = W[g_l g_l]/W[g_l f_l]. \quad (25)$$

Equation (25) yields together with (21) the complete solution of the problem.

In the vector case of interest to us nothing changes as a whole. The properties (22) and (23) are obviously valid. Further, the function **M** contains only the harmonic **C**, which is perpendicular to the harmonics **B** and **P** contained in **N**. The Green's function can be divided into two independent parts, the equation for each being solved separately, literally as was done above. The Green's function satisfying Eq. (20) is therefore $(r<r'<a)$:

$$D_{\alpha\beta}(\mathbf{r},\mathbf{r}') = D^p_{\alpha\beta}(\mathbf{r},\mathbf{r}') - 4\pi ip\sum_{lm}\frac{1}{l(l+1)} \times[R^M_l M^j_{lm,\alpha}(p,\mathbf{r})\bar{M}^j_{lm,\beta}(p,\mathbf{r}') + R^N_l N^j_{lm,\alpha}(p,\mathbf{r})\bar{N}^j_{lm,\beta}(p,\mathbf{r}')] = D^p + D^R. \quad (26)$$

An integral type (24) is calculated in Appendix B. The reflection coefficients are:

$$R^M_l = \frac{W[(\mathbf{M}^h_{lm}\bar{\mathbf{M}}^h_{lm})]}{W[(\mathbf{M}^h_{lm}\bar{\mathbf{M}}^j_{lm})]} = \frac{h_l(pa)[p\psi_h(pa) - \omega\psi_h(\omega a)]}{j_l(pa)[p\psi_j(pa) - \omega\psi_h(\omega a)]},$$

$$R^N_l = \frac{W[(\mathbf{N}^h_{lm}\bar{\mathbf{N}}^h_{lm})]}{W[(\mathbf{N}^h_{lm}\bar{\mathbf{N}}^j_{lm})]} = \frac{h_l(pa)[\omega\psi_h(pa) - p\psi_h(\omega a)]}{j_l(pa)[\omega\psi_j(pa) - p\psi_h(\omega a)]},$$

where

$$\psi_z(x) = \frac{z_{l-1}(x)}{z_l(x)} - \frac{l}{x} = \frac{d}{dx}\ln[xz_l(x)].$$

We have obtained the Green's function for the case when both arguments $\mathbf{r}$ and $\mathbf{r}'$ lie inside the sphere. It is easy to extend the results to other cases, for example $r, r' \gg a$. We, however, have no need for this.

To calculate the elastic-scattering cross section it remains to calculate the sum of the two integrals in (11)

$$(\mathbf{e}_i\mathbf{e}_f)\int\theta(a-r)\exp[-i\mathbf{r}(\mathbf{k}_i-\mathbf{k}_f)]d\mathbf{r} + \alpha\omega^2\int\theta(a-r)\theta(a-r')e_{i\alpha}e_{f\beta}D_{\alpha\beta}(\mathbf{r},\mathbf{r}') \times\exp(-i\mathbf{k}_i\mathbf{r} + i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \quad (27)$$

We begin with a transformation of the second integral, in which we substitute D^p and replace θ by $1-\bar{\theta}$ (where $\bar{\theta} = 1-\theta$):

$$\int\theta(a-r)e_{i\alpha}e_{f\beta}D^p_{\alpha\beta}(\mathbf{r},\mathbf{r}')\exp(-i\mathbf{k}_i\mathbf{r})d\mathbf{r} = -\frac{\exp(-i\mathbf{k}_i\mathbf{r})}{\alpha\omega^2}(\mathbf{e}_i\mathbf{e}_f) - \int\theta(r-a)e_{i\alpha}e_{f\beta}D^p_{\alpha\beta}(\mathbf{r},\mathbf{r}')\exp(-i\mathbf{k}_i\mathbf{r})d\mathbf{r}. \quad (28)$$

The first term in the right-hand side of (28) is canceled by the first term of (27). We have therefore for (27)

$$\alpha\omega^2\int[\theta\theta' D^R_{\alpha\beta} - \bar{\theta}\theta' D^p_{\alpha\beta}]e_{i\alpha}e_{f\beta}\exp(-i\mathbf{k}_i\mathbf{r} + i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \quad (29)$$

Owing to the factor $\bar{\theta}\theta'$, the δ-like term in D^p makes no contribution to (29), and the contributions from the M- and N- parts of the propagators can be calculated separately. Since the two calculations are alike, we carry out only one of them—for the part of D containing the functions **M**. Substituting in (29) the part of D that depends on **M**, we obtain

$$-\int\bar{\theta}\theta' e_{i\alpha}e_{f\beta}D^p_{\alpha\beta}(\mathbf{r},\mathbf{r}')\exp(-i\mathbf{k}_i\mathbf{r}+i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

$$=-4\pi ip\sum\frac{1}{l(l+1)}e_{i\alpha}e_{f\beta}\int\theta' M^j_\beta\exp(i\mathbf{k}_f\mathbf{r}')$$

$$\times d\mathbf{r}'\int\bar{\theta}\bar{M}^h_\alpha\exp(-i\mathbf{k}_i\mathbf{r})d\mathbf{r}$$

$$=4\pi ip\sum\frac{(4\pi)^2}{[l(l+1)]^2}W[(\mathbf{M}^j\bar{\mathbf{M}}^j)]W[(\mathbf{M}^j\bar{\mathbf{M}}^h)]$$

$$\times(\mathbf{e}_i\mathbf{C}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{C}^*(\mathbf{n}_f)),\qquad(30)$$

where $\mathbf{n}_i$ and $\mathbf{n}_f$ are unit vectors in the directions of $\mathbf{k}_i$ and $\mathbf{k}_f$, respectively. In the derivation of (30) we used relations (B3) and (B7) of Appendix B. The D^R contribution is calculated similarly:

$$\int\theta\theta' e_{i\alpha}e_{f\beta}D^R_{\alpha\beta}\exp(-i\mathbf{k}_i\mathbf{r}+i\mathbf{k}_f\mathbf{r}')d\mathbf{r}d\mathbf{r}'=-4\pi ip\sum\left[\frac{4\pi}{l(l+1)}\right]^2$$

$$\times W^2[(\mathbf{M}^j\bar{\mathbf{M}}^j)]\frac{W[(\mathbf{M}^h\bar{\mathbf{M}}^h)]}{W[(\mathbf{M}^h\bar{\mathbf{M}}^j)]}(\mathbf{e}_i\mathbf{C}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{C}^*(\mathbf{n}_f)).\quad(31)$$

Combining (30) and (31) we have

$$\frac{4\pi i}{\omega}\left(\frac{4\pi}{p^2-\omega^2}\right)^2\sum\frac{W[(\mathbf{M}^j\bar{\mathbf{M}}^j)]}{W[(\mathbf{M}^h\bar{\mathbf{M}}^j)]}(\mathbf{e}_i\mathbf{C}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{C}^*(\mathbf{n}_f)).\quad(32)$$

In the derivation of this equation we used the relation

$$W[(\mathbf{M}^j\bar{\mathbf{M}}^h)]W[(\mathbf{M}^h\bar{\mathbf{M}}^j)]-W[(\mathbf{M}^h\bar{\mathbf{M}}^h)]W[(\mathbf{M}^j\bar{\mathbf{M}}^j)]$$

$$=\frac{1}{p\omega}\left[\frac{l(l+1)}{p^2-\omega^2}\right]^2,$$

which is a consequence of (B1) and (17). The contribution of the N-part of the photon propagator has a similar structure

$$\frac{4\pi i}{\omega}\left(\frac{4\pi}{p^2-\omega^2}\right)^2\sum\frac{W[(\mathbf{N}^j\bar{\mathbf{N}}^j)]}{W[(\mathbf{N}^h\bar{\mathbf{N}}^j)]}(\mathbf{e}_i\mathbf{B}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{B}^*(\mathbf{n}_f)).\quad(33)$$

Substitution of (32) and (33) in (11) yields

$$\mathcal{T}=2\pi i\frac{4\pi}{\omega^2V}\sum_{lm}\frac{j_l(\omega a)}{h_l(\omega a)}\left\{\frac{p\psi_j(pa)-\omega\psi_j(\omega a)}{p\psi_j(pa)-\omega\psi_h(\omega a)}\right.$$

$$\times(\mathbf{e}_i\mathbf{C}_{lm}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{C}^*_{lm}(\mathbf{n}_f))$$

$$\left.+\frac{\omega\psi_j(pa)-p\psi_j(\omega a)}{\omega\psi_j(pa)-p\psi_h(\omega a)}(\mathbf{e}_i\mathbf{B}_{lm}(\mathbf{n}_i))(\mathbf{e}_f\mathbf{B}^*_{lm}(\mathbf{n}_f)).\right.\quad(34)$$

We are now able to calculate the differential scattering cross section. The transition probability per unit time is

$$dW=2\pi|\mathcal{T}|^2d\rho,$$

where

$$d\rho=\frac{V\omega^2d\mathbf{n}_f}{(2\pi)^3}$$

is the number of final states of the photon per unit energy. The scattering cross section is obtained from dW by dividing it by the flux density $2\pi V^{-1}$. The differential cross section takes ultimately the form

$$\frac{d\sigma}{d\mathbf{n}_f}=\frac{\omega^2V^2}{(2\pi)^3}|\mathcal{T}|^2.$$

This result is fully equivalent to the classical Mie theory of scattering of an electromagnetic wave by a sphere.

3. LIGHT ABSORPTION

We show now how to calculate in our approach the cross section for light absorption by a particle.

The probability of absorbing a light photon of frequency $\omega_i=\omega$ is determined by the golden rule

$$W=2\pi\sum_s|\mathcal{T}_{0s}|^2\delta(\omega-\omega_s),$$

where the connection of the amplitude $\mathcal{T}$ with the S matrix is

$$\langle 0|a_{\mathbf{k}_i}S|s\rangle=2\pi i\delta(\omega-\omega_s)\mathcal{T}_{0s},\qquad(35)$$

the summation is over all the excited states of the electron gas of the particle, and ω_s denotes the corresponding excitation energy. The contribution to W in first-order perturbation theory comes from the second term of the Hamiltonian H_I:

$$W_1=\frac{4\pi^2e^2}{m^2\omega V}e_{k,\alpha}e_{k,\beta}\sum_s|(p_\alpha(\mathbf{k}))_{0s}|^2\delta(\omega-\omega_s),\qquad(36)$$

where

$$(p_\alpha(\mathbf{k}))_{0s}=-i\langle 0|\int\psi^+(\mathbf{r})\nabla_\alpha\psi(\mathbf{r})e^{-i\mathbf{kr}}d\mathbf{r}|s\rangle.$$

Before summing the perturbation-theory series in (35) we change over in (36) from electron-momentum density operator matrix element **p** to the electron-density operator matrix element $\rho(\mathbf{r})=\psi^+(\mathbf{r})\psi(\mathbf{r})$. To this end we consider the commutator matrix element of the Hamiltonian H with the plane wave $\exp(i\mathbf{kr})$, where **k** is the wave vector of the incident photon. Obviously,

$$\langle 0|\int[H,e^{i\mathbf{kr}}]d\mathbf{r}|s\rangle=-\omega_s\langle 0|\int\rho(\mathbf{r})e^{i\mathbf{kr}}d\mathbf{r}|s\rangle.$$

On the other hand, direct calculations yield

$$\langle 0|\int[H,e^{i\mathbf{kr}}]d\mathbf{r}|s\rangle=\frac{k^2}{2m}\langle 0|\int e^{i\mathbf{kr}}\rho(\mathbf{r})d\mathbf{r}|s\rangle$$

$$+\frac{1}{m}\langle 0|\int e^{i\mathbf{kr}}(\mathbf{kp})d\mathbf{r}|s\rangle.$$

Equating the last two expressions and applying the operator $e_{k,\alpha}\nabla_{k,\alpha}$ to both sides of the resultant identity, we have:

$$-\left(\omega_s+\frac{k^2}{2m}\right)e_{k,\alpha}\nabla_{k,\alpha}\langle 0|\int\rho(\mathbf{r})e^{i\mathbf{kr}}d\mathbf{r}|s\rangle$$

$$=\frac{1}{m}\langle 0|\int e^{i\mathbf{kr}}(\mathbf{e}_k\mathbf{p})d\mathbf{r}|s\rangle$$

$$+\frac{i}{m}\langle 0|\int(\mathbf{e}_k\mathbf{r})e^{i\mathbf{kr}}(\mathbf{kp})d\mathbf{r}|s\rangle.\qquad(37)$$

The second term in the right-hand side of (37) is made zero by symmetry. This can be easily verified by considering the identity

$$\int \varphi_0(\mathbf{r})(\mathbf{e}_k\mathbf{r})e^{i\mathbf{kr}}k_\beta\nabla_\beta\varphi_\lambda(\mathbf{r})d\mathbf{r} = -k_\beta e_{k,\gamma}\int(\nabla_\beta\varphi_0(\mathbf{r}))r_\gamma e^{i\mathbf{kr}}\varphi_\lambda(\mathbf{r})d\mathbf{r} - ik^2e_{k,\alpha}\int\varphi_0(\mathbf{r})r_\alpha e^{-i\mathbf{kr}}\varphi_\lambda(\mathbf{r})d\mathbf{r}, \quad (38)$$

where φ_0 and φ_λ are single-electron wave functions of the ground and excited states. Both integrals in the right-hand side of (38) are vector functions whose directions are specified by the only vector $\mathbf{k}$ of the problem. Both terms of (38) are therefore zero, i.e., $(\mathbf{k}\mathbf{e}_k) = 0$.

To sum the perturbation-theory series in (35) we introduced the density–density polarization operator of the system

$$\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega) = i\int_{-\infty}^{\infty}\langle 0|T\rho(\mathbf{r},\tau)\rho^*(\mathbf{r}',0)|0\rangle e^{i\omega\tau}d\tau, \quad (39)$$

where $\rho(\mathbf{r},\tau) = e^{iH\tau}\rho(\mathbf{r})e^{-iH\tau}$ and T is the chronological-ordering operator. It is easy to obtain for the Fourier transform of $\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega)$

$$\Pi_{00}(\mathbf{k},\omega) = \int\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega)\exp[-i\mathbf{k}(\mathbf{r}-\mathbf{r}')]d\mathbf{r}d\mathbf{r}'$$

a spectral representation of the Lehman type

$$\mathrm{Im}\,\Pi_{00}(\mathbf{k},\omega) = \pi\sum_s(\rho_k)_{0s}(\rho_k^+)_{s0}\delta(\omega-\omega_s), \quad (40)$$

where $(\rho_k)_{0s} = \langle 0|\int\rho(\mathbf{r})e^{-i\mathbf{kr}}d\mathbf{r}|s\rangle$. To this end, we consider the correlator

$$\Pi_{00}(\mathbf{k},t,t') = i\langle 0|T\rho(\mathbf{k},t)\rho^+(\mathbf{k},t')|0\rangle,$$

$$\rho(\mathbf{k},t) = \int\psi^+(\mathbf{r},t)\psi(\mathbf{r},t)e^{-i\mathbf{kr}}d\mathbf{r},$$

$$\psi^+(\mathbf{r},t) = e^{iHt}\psi^+(\mathbf{r})e^{-iHt}.$$

We expand Π_{00} in the eigenstates of the electron gas of the particles

$$\Pi_{00}(\mathbf{k},t,t') = \begin{cases} i\sum_s\langle 0|\rho(\mathbf{k},t)|s\rangle\langle s|\rho^+(\mathbf{k},t')|0\rangle, & t>t' \\ i\sum_s\langle 0|\rho^+(\mathbf{k},t')|s\rangle\langle s|\rho(\mathbf{k},t)|0\rangle, & t<t' \end{cases}.$$

A transformation to Schrödinger operators yields

$$\Pi_{00}(\mathbf{k},\tau) = \begin{cases} i\sum_s\exp(-i\omega_s\tau)(\rho_k)_{0s}(\rho_k^+)_{s0}, & \tau>0 \\ i\sum_s\exp(i\omega_s\tau)(\rho_k^+)_{0s}(\rho_k)_{s0}, & \tau<0 \end{cases},$$

where $\tau = t-t'$, $\omega_s = E_s - E_0$ and $H|s\rangle = E_s|s\rangle$. For the Fourier transform of $\Pi_{00}(\mathbf{k},\tau)$ with respect to τ one readily obtains

$$\Pi_{00}(\mathbf{k},\omega) = i\sum_s\int_0^{\infty}\exp[-i(\omega_s-\omega-i\delta)\tau](\rho_k)_{0s}(\rho_k^+)_{s0}d\tau + i\sum_s\int_{-\infty}^{0}\exp[i(\omega_s+\omega-i\delta)\tau](\rho_k^+)_{0s}(\rho_k)_{s0}d\tau$$

$$= \sum_s\frac{1}{\omega_s^2-\omega^2}\{\omega_s[(\rho_k)_{0s}(\rho_k^+)_{s0} + (\rho_k^+)_{0s}(\rho_k)_{s0}] + \omega[(\rho_k)_{0s}(\rho_k^+)_{s0} - (\rho_k^+)_{0s}(\rho_k)_{s0}]\}. \quad (41)$$

Expression (40) is obtained by taking the imaginary parts of both halves of (41), using the identity

$$\mathrm{Im}\frac{1}{\omega_s^2-\omega^2} = \frac{\pi}{2\omega_s}\delta(\omega-\omega_s).$$

Now, using expressions (40) and (37), we can write for the probability of absorption of a photon with allowance for all orders of perturbation theory:

$$W = \frac{2\pi e^2}{\omega V}\left(\omega + \frac{k^2}{2m}\right)^2 e_{k,\alpha}e_{k,\beta}\nabla_{k,\alpha}\nabla_{k,\beta}\mathrm{Im}\,\Pi_{00}(\mathbf{k},\omega). \quad (42)$$

At frequencies $\omega \ll 2mc^2$ it is natural to neglect, as we shall, the second term in the parentheses in the right-hand side of (42).

Changing from the Heisenberg operators in (39) to operators in the interaction representation, we readily obtain for $\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega)$ the expression

$$\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega) = i\int_{-\infty}^{\infty}\langle T\rho^I(\mathbf{r},\tau)\rho^{*I}(\mathbf{r}',0)S\rangle'\exp(i\omega\tau)d\tau,$$

where $\rho^I(\mathbf{r},\tau) = \exp(iH_0\tau)\rho(\mathbf{r})\exp(-iH_0\tau)$ and the primed angle brackets indicates that only connected diagrams need be taken into account in the perturbation-theory expansion of the S matrix. The perturbation-theory series for Π_{00} is shown in Fig. 6. Within the framework of the approximations used in Sec. 2, summation of the series yields

$$\Pi_{00}(\mathbf{r},\mathbf{r}') = \mathcal{P}_{00}(\mathbf{r},\mathbf{r}') + \frac{e^2}{m^2}\int\mathcal{P}_{0\alpha}(\mathbf{r},\mathbf{r}_1)D_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2) \times\mathcal{P}_{\beta 0}(\mathbf{r}_2,\mathbf{r}')d\mathbf{r}_1d\mathbf{r}_2. \quad (43)$$

Using the explicit form of the irreducible polarization operators $\mathcal{P}_{0\alpha}$ and $\mathcal{P}_{\alpha 0}$ obtained in Appendix A, as well as the procedures of the preceding section, the operator $\Pi_{00}(\mathbf{k},\omega)$ can be readily rewritten in the form

$$\Pi_{00}(\mathbf{k},\omega) = \frac{n_0k^2}{m\omega^2}\left[\frac{4}{3}\frac{\pi a^3}{\varepsilon} + \frac{1}{4\pi}\frac{\omega_0^2}{\omega^2}\frac{k_\alpha k_\beta}{k^2} \times\int[\bar\theta\theta' D^P_{\alpha\beta}(\mathbf{r},\mathbf{r}') - \theta\theta' D^R_{\alpha\beta}(\mathbf{r},\mathbf{r}')]\right] \times\exp(-i\mathbf{kr}+i\mathbf{kr}')d\mathbf{r}d\mathbf{r}'. \quad (44)$$

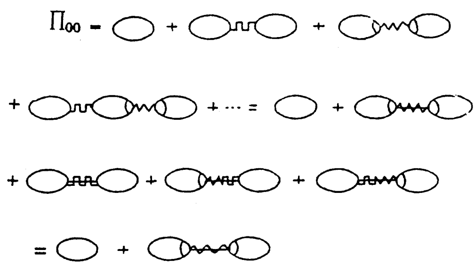

FIG. 6. Perturbation theory series for density–density propagation operator.

The integrals in (44) are again calculated by expanding the propagators in terms of the vector spherical harmonics (13). The M-parts of the propagators make no contribution to $\Pi_{00}(\mathbf{k},\omega)$. The contribution from the B-parts of the N-functions is likewise zero. The final result is quite compact:

$$\sigma_a = \frac{2}{3}\omega a^3 e_{k,\alpha} e_{k,\beta} \nabla_{k,\alpha} \nabla_{k,\beta}$$

$$\times \mathrm{Im}\left\{(\varepsilon - 1)\left[\frac{k^2}{\varepsilon} - \frac{3(\varepsilon - 1)\omega^3}{(pa)^3} \sum_l \frac{l(l+1)(2l+1)\, j_l^2(ka)}{p\psi_h(\omega a) - \omega\psi_j(pa)}\right]\right\}. \tag{45}$$

Equation (45) coincides with the results of the classical-electrodynamics calculation of the cross section for light absorption by a sphere. In the dipole approximation, (45) leads to the known Rayleigh equation:

$$\sigma_a = 4\pi a^2 \frac{\omega a}{c} \mathrm{Im}\frac{\varepsilon - 1}{\varepsilon + 2}.$$

4. SIMPLEST THREE-PHOTON PROCESSES ON THE SURFACE OF A PARTICLE

In this section we use our formalism to calculate electrodynamic processes which cannot be correctly described in the framework of classical electrodynamics. We shall deal with the simplest three-photon processes on surfaces of small metallic particles. Why is classical electrodynamics inadequate here? First, even processes such as mixing of two photons (including second-harmonic generation) can be effected by various methods which are in principle indistinguishable in experiment. We must use then the rules established by quantum mechanics—sum the probability amplitudes corresponding to each channel of the process, and calculate its probability as the squared modulus as the summary amplitude. The so-called cross terms that appear in this approach describe the interference of partial amplitudes and are lost in the classical calculation method. Second, no account is taken in classical electrodynamics of the mutual interaction, via the polarization of the medium, of the photons taking part in the process. Effects of this kind can be completely neglected in a homogeneous medium because the photon–photon interaction constant e^2 is small. These effects are no longer small on the surfaces of small metallic particles near the frequencies of the collective electronic excitations. The photon is said to go off the mass shell—the wave functions of the photons participating in the process cease to be plane electromagnetic waves, and have a pole dependence on the frequency. Therefore the cross sections of many electrodynamic processes near these poles are larger by many orders.

We consider the transformation of two photons into one on the surface of a metallic particle, of two photons into one and the inverse process. It is known that the Furry[4] theorem denies such processes in a uniform medium. This hindrance is lifted here, owing to momentum nonconservation due to the absence of translational symmetry in the system.

The amplitude $\mathcal{J}_{1+2\to3}$ which determines the probability of transformation of the two photons (subscripts 1 and 2) into a third (subscript 3) in accordance the rule

$$W = 2\pi|\mathcal{T}_{1+2\to3}|^2\delta(\omega_1 + \omega_2 - \omega_3),$$

is related to the S-matrix by

$$\langle a_{\mathbf{k}_1,\lambda_1} a_{\mathbf{k}_2,\lambda_2} S a^+_{\mathbf{k}_3,\lambda_3}\rangle = 2\pi i\delta(\omega_1 + \omega_2 - \omega_3)\mathcal{T}_{1+2\to3},$$

where ω_1, ω_2, and ω_3 are respectively the energies of the photons incident on the particles and of the scattered one. To calculate $\mathcal{J}_{1+2\to3}$ we expand the S matrix in a perturbation-theory series. The first nonzero contribution to $\mathcal{J}$ appears in second-order perturbation theory

$$\mathcal{T}_{1+2\to3} = -\frac{e^3}{2m^2}\sqrt{\frac{2\pi}{\omega_1 V}}\sqrt{\frac{2\pi}{\omega_2 V}}\sqrt{\frac{2\pi}{\omega_3 V}}$$

$$\times\{(\mathbf{e}_1\mathbf{e}_2)e_{3,\beta}\int \mathcal{P}_{0\beta}(\mathbf{r},\mathbf{r}_1|\omega_3)\exp(-i\mathbf{k}_1\mathbf{r} - i\mathbf{k}_2\mathbf{r} + i\mathbf{k}_3\mathbf{r})d\mathbf{r}d\mathbf{r}_1$$

$$+ (\mathbf{e}_2\mathbf{e}_3)e_{1,\beta}\int \mathcal{P}_{\beta0}(\mathbf{r},\mathbf{r}_1|\omega_1)\exp(-i\mathbf{k}_2\mathbf{r}_1 + i\mathbf{k}_3\mathbf{r}_1 - i\mathbf{k}_1\mathbf{r})d\mathbf{r}d\mathbf{r}_1$$

$$+ (\mathbf{e}_1\mathbf{e}_3)e_{2,\beta}\int \mathcal{P}_{\beta0}(\mathbf{r},\mathbf{r}_1|\omega_2)\exp(-i\mathbf{k}_1\mathbf{r}_1 + i\mathbf{k}_3\mathbf{r}_1 - i\mathbf{k}_2\mathbf{r})d\mathbf{r}d\mathbf{r}_1\}. \tag{46}$$

The diagrams corresponding to (46) are a), b) and c) of Fig. 7. The diagram d), which appears in the third-order, contains the parameter $(r_0/a)(\omega_0/\omega)$ which is small compared with a), b), and c) and we shall disregard it. The estimates of Sec. 2 allows us to neglect the processes described by diagrams i), j), and k). Finally, the Ward identities, which establish a correspondence between the form of the photon mass operator and the form of the vertex part, allow us to disregard diagrams of type l), which describe the renormalization of the photon vertex. The last fact is important, since it permits renormalization of the wave functions of the real photons involved in the process independently of one another. We shall use the devices of Sec. 2 to sum the perturbation-theory diagrams for the amplitude $\mathcal{J}$. The summation results are shown in Fig. 8 in two perfectly equivalent manners. The renormalized photon wave function Φ is defined in Fig. 9. Figure 10 shows the form of the mixed polarization operator $\Pi_{0\alpha}$.

The physical cause of the renormalization of the wave functions of photons emerging from one and the same vertex (see Fig. 7) is the local interaction of the photons on the particle surface. In linear electrodynamics, where photon–photon interaction is neglected, the outer photon ends are not renormalized.[4]

It remains now to write an analytic expression for the

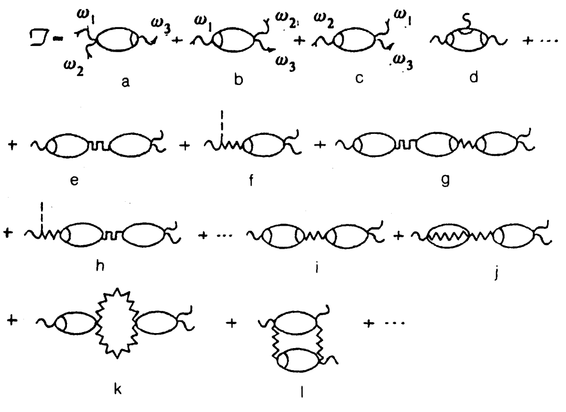

FIG. 7. Perturbation-theory series for the amplitude of transformation of two photons into one.

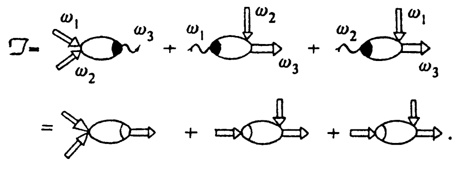

FIG. 8. Two equivalent expressions for the total amplitude of transformation of two photons into one.

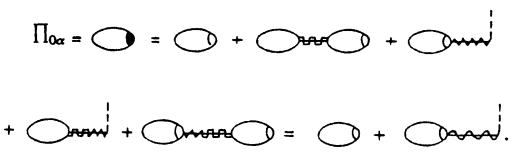

FIG. 10. Definition of mixed polarization density–momentum operator.

amplitude of the process. For example, the contribution of the first diagram of Fig. 8 is

$$\mathcal{T}_1 = -\frac{e^3}{2m^2}\sqrt{\frac{2\pi}{\omega_3 V}}\int \boldsymbol{\Phi}_{\mathbf{k}_1}(\mathbf{r})\boldsymbol{\Phi}_{\mathbf{k}_2}(\mathbf{r}) \times \Pi_{0\alpha}(\mathbf{r},\mathbf{r}_1|\omega_3)e_{k_3,\alpha}\exp(i\mathbf{k}_3\mathbf{r}_1)d\mathbf{r}d\mathbf{r}_1. \quad (47)$$

The renormalized photon wave function $\boldsymbol{\Phi}$ is determined, in accordance with Fig. 9, by the expression

$$\boldsymbol{\Phi}_{\mathbf{k},\alpha}(\mathbf{r}) = \sqrt{\frac{2\pi}{\omega V}}\{e_{k,\alpha}e^{-i\mathbf{k}\mathbf{r}} - \frac{e^2}{m}\int f_{\mathbf{k},\beta}(\mathbf{r}_1)n(\mathbf{r}_1)G^0_{\beta\alpha}(\mathbf{r}_1,\mathbf{r})d\mathbf{r}_1\}, \quad (48)$$

where

$$G^0_{\alpha\gamma}(\mathbf{r},\mathbf{r}') = (2\pi)^{-3}\int \frac{4\pi}{k^2-\omega^2}\left(\delta_{\alpha\gamma} - \frac{k_\alpha k_\gamma}{k^2}\right)e^{-i\mathbf{k}(\mathbf{r}-\mathbf{r}')}d\mathbf{k}$$

is the free-photon polarization in a transverse gauge and

$$f_{\mathbf{k},\gamma}(\mathbf{r}_1) = e_{k,\gamma}e^{-i\mathbf{k}\mathbf{r}_1} - \frac{e^2}{m}\int e_{k,\alpha}e^{-i\mathbf{k}\mathbf{r}'}n(\mathbf{r}')D_{\alpha\gamma}(\mathbf{r}',\mathbf{r}_1)d\mathbf{r}'. \quad (49)$$

The operator $\Pi_{0\alpha}$ is given, according to Fig. 10, by

$$\Pi_{0\alpha}(\mathbf{r},\mathbf{r}') = \mathcal{P}_{0\alpha}(\mathbf{r},\mathbf{r}') + \frac{e^2}{m}\int \mathcal{P}_{0\beta}(\mathbf{r},\mathbf{r}_1) \times D_{\beta\gamma}(\mathbf{r}_1,\mathbf{r}_2)\mathcal{P}_{\gamma\alpha}(\mathbf{r}_2,\mathbf{r}')d\mathbf{r}_1d\mathbf{r}_2.$$

The integrals in (48) and (49) are easy to calculate by using the representation (26) for the propagator D as well as the following expansions for a plane electromagnetic wave and for a free propagator in a transverse gauge $G^0_{\alpha\beta}$:

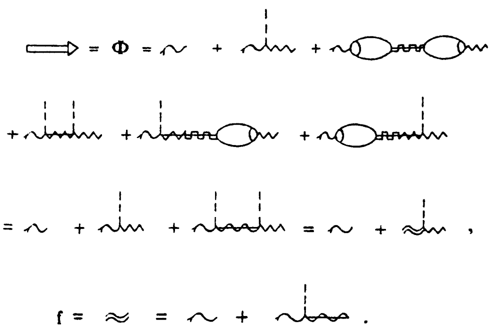

FIG. 9. Construction of renormalized wave function of a photon incident on a particle.

$$e_{k,\alpha}e^{-i\mathbf{k}\mathbf{r}} = 4\pi\sum(-i)^l\frac{1}{\sqrt{l(l+1)}}\{\mathbf{e}_k\mathbf{C}_{lm}(\mathbf{n}_k)M^j_{lm,\alpha}(k,\mathbf{r}) + i\mathbf{e}_k\mathbf{B}_{lm}(\mathbf{n}_k)N^j_{lm,\alpha}(k,\mathbf{r})\},$$

$$G^0_{\alpha\beta}(\mathbf{r},\mathbf{r}') = \theta(r'-r)\{4\pi i\omega\sum\frac{1}{l(l+1)} \times [M^j_{lm,\alpha}(\omega,\mathbf{r})\bar{M}^h_{lm,\beta}(\omega,\mathbf{r}') + N^j_{lm,\alpha}(\omega,\mathbf{r})\bar{N}^h_{lm,\beta}(\omega,\mathbf{r}')] + \frac{4\pi}{\omega^2}\sum_{lm}\frac{\sqrt{l(l+1)}}{2l+1}\frac{r^{l-1}}{(r')^{l+2}}[\sqrt{l}P_{lm,\alpha}(\mathbf{n}) + \sqrt{l+1}B_{lm,\alpha}(\mathbf{n})][\sqrt{l}\bar{B}_{lm,\beta}(\mathbf{n}') - \sqrt{l+1}\bar{P}_{lm,\beta}(\mathbf{n}')] + \theta(r-r')\{4\pi i\omega\sum\frac{1}{l(l+1)} \times [M^h_{lm,\alpha}(\omega,\mathbf{r})\bar{M}^j_{lm,\beta}(\omega,\mathbf{r}') + N^h_{lm,\alpha}(\omega,\mathbf{r})\bar{N}^j_{lm,\beta}(\omega,\mathbf{r}')] + \frac{4\pi}{\omega^2}\sum_{lm}\frac{\sqrt{l(l+1)}}{2l+1}\frac{(r')^{l-1}}{r^{l+2}} \times [\sqrt{l}B_{lm,\alpha}(\mathbf{n}) - \sqrt{l+1}P_{lm,\alpha}(\mathbf{n})] \times [\sqrt{l}\bar{P}_{lm,\beta}(\mathbf{n}') + \sqrt{l+1}\,\bar{B}_{lm,\beta}(\mathbf{n}')],$$

where $\mathbf{n} = \mathbf{r}/r$. As a result we can obtain for $\boldsymbol{\Phi}$ the expression:

$$\Phi_{\mathbf{k},\alpha}(\mathbf{r}) = \sqrt{\frac{2\pi}{\omega V}}\frac{4\pi}{\omega a^2}\sum_{lm}\frac{i^{l-1}}{h_l(\omega a)}\left\{\frac{j_l^{-1}(pa)}{\sqrt{l(l+1)}} \times \left[\frac{\mathbf{e}_k\mathbf{C}_{lm}(\mathbf{n}_k)}{\omega\psi_h(\omega a) - p\psi_j(pa)}\bar{M}^j_{lm,\alpha}(p,\mathbf{r}) + i\frac{\mathbf{e}_k\mathbf{B}_{lm}(\mathbf{n}_k)}{p\psi_h(\omega a) - \omega\psi_j(pa)}N^j_{lm,\alpha}(p,\mathbf{r})\right] - i\frac{\omega_0^2}{\omega^2}\frac{l\sqrt{l+1}}{2l+1}\left(\frac{r}{a}\right)^l\frac{1}{pr} \times [\sqrt{l}\bar{P}_{lm,\alpha}(\mathbf{n}) + \sqrt{l+1}\bar{B}_{lm,\alpha}(\mathbf{n})]\frac{\mathbf{e}_k\mathbf{B}_{lm}(\mathbf{n}_k)}{p\psi_h(\omega a) - \omega\psi_j(pa)}\right\}. \quad (50)$$

In the limiting case of low frequencies we have

$$
\mathbf{\Phi}_{\mathrm{k}}(\mathbf{r}) = \sqrt{\frac{2\pi}{\omega V}} \left\{ \frac{\omega^2 + \bar{\omega}^2}{\omega^2 - \bar{\omega}^2(1 - i\bar{g})} \mathbf{e}_k - i \frac{\omega^2}{\omega^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} (\mathbf{k}\mathbf{r})\mathbf{e}_k - \frac{2}{5} i \frac{\omega_0^2}{\omega^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} (\mathbf{e}_k\mathbf{r})\mathbf{k} \right\}, \tag{51}
$$

where $\bar{\omega} = (\omega_0/\sqrt{3})(1 - \frac{2}{5}\bar{\gamma}^2)$ is the frequency of a dipole surface plasmon in a spherical particle and $\bar{g} = \bar{\gamma}^3/3$, where $\bar{\gamma} = \omega_0 a/\sqrt{3}$ is the width of the dipole plasma resonance and is due to transfer of the plasmon energy into the transverse electromagnetic field (called the radiation width). Next $\bar{\bar{\omega}} = \sqrt{\frac{2}{5}}\omega_0(1 - \frac{1}{14}\bar{\bar{\gamma}})$, $\bar{\bar{g}} = \frac{1}{30}\bar{\bar{\gamma}}^5$ and $\bar{\bar{\gamma}} = \sqrt{\frac{2}{5}}\omega_0 a$ are the corresponding values indicative of the quadrupole surface plasmon. It is instructive to compare expression (51) with the expansion of a plane electromagnetic wave, to verify the strength of the photon wave-function renormalization used by us, especially near plasma-resonance frequencies in the particle.

We shall not write down the unwieldy expressions for the amplitude for the general case, and confine ourselves to the results in the long-wave limit. Obviously, $\mathcal{J}$ has three poles due to the possibility of excitation of a surface plasmon by each of the photons participating in the process

$$
\begin{aligned}
\mathcal{T}_{1+2\to3} = {} & \frac{a^3\omega_0^2 e}{6m} \sqrt{\frac{2\pi}{\omega_1 V}} \sqrt{\frac{2\pi}{\omega_2 V}} \sqrt{\frac{2\pi}{\omega_3 V}} \left\{ \frac{\omega_3^2 + \bar{\omega}^2}{\omega_3^2 - \bar{\omega}^2(1 + i\bar{g})} \right. \\
& \times \left[\frac{\omega_1^2 + \bar{\omega}^2}{\omega_1^2 - \bar{\omega}^2(1 - i\bar{g})} \frac{\omega_2}{\omega_3} \frac{\omega_2^2(\mathbf{e}_2\mathbf{e}_3)(\mathbf{e}_1\mathbf{n}_2) + \bar{\bar{\omega}}^2(\mathbf{e}_1\mathbf{e}_2)(\mathbf{e}_3\mathbf{n}_2)}{\omega_2^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} \right. \\
& \left. + \frac{\omega_2^2 + \bar{\omega}^2}{\omega_2^2 - \bar{\omega}^2(1 - i\bar{g})} \frac{\omega_1}{\omega_3} \frac{\omega_1^2(\mathbf{e}_1\mathbf{e}_3)(\mathbf{e}_2\mathbf{n}_1) + \bar{\bar{\omega}}^2(\mathbf{e}_1\mathbf{e}_2)(\mathbf{e}_3\mathbf{n}_1)}{\omega_1^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} \right] \\
& - \frac{\omega_1^2 + \bar{\omega}^2}{\omega_1^2 - \bar{\omega}^2(1 - i\bar{g})} \left[\frac{\omega_2^2 + \bar{\omega}^2}{\omega_2^2 - \bar{\omega}^2(1 - i\bar{g})} \frac{\omega_3}{\omega_1} \right. \\
& \times \frac{\omega_3^2(\mathbf{e}_2\mathbf{n}_3)(\mathbf{e}_1\mathbf{e}_3) + \bar{\bar{\omega}}^2(\mathbf{e}_2\mathbf{e}_3)(\mathbf{e}_1\mathbf{n}_3)}{\omega_3^2 - \bar{\bar{\omega}}^2(1 + i\bar{\bar{g}})} \\
& \left. - \frac{\omega_3^2 + \bar{\omega}^2}{\omega_3^2 - \bar{\omega}^2(1 + i\bar{g})} \frac{\omega_2}{\omega_1} \frac{\omega_2^2(\mathbf{e}_3\mathbf{n}_2)(\mathbf{e}_1\mathbf{e}_2) + \bar{\bar{\omega}}^2(\mathbf{e}_3\mathbf{e}_2)(\mathbf{e}_1\mathbf{n}_2)}{\omega_2^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} \right] \\
& - \frac{\omega_2^2 + \bar{\omega}^2}{\omega_2^2 - \bar{\omega}^2(1 - i\bar{g})} \\
& \times \left[\frac{\omega_1^2 + \bar{\omega}^2}{\omega_1^2 - \bar{\omega}^2(1 - i\bar{g})} \frac{\omega_3}{\omega_2} \frac{\omega_3^2(\mathbf{e}_1\mathbf{n}_3)(\mathbf{e}_2\mathbf{e}_3) + \bar{\bar{\omega}}^2(\mathbf{e}_1\mathbf{e}_3)(\mathbf{e}_2\mathbf{n}_3)}{\omega_3^2 - \bar{\bar{\omega}}^2(1 + i\bar{\bar{g}})} \right. \\
& \left. \left. - \frac{\omega_3^2 + \bar{\omega}^2}{\omega_3^2 - \bar{\omega}^2(1 + i\bar{g})} \frac{\omega_1}{\omega_2} \frac{\omega_1^2(\mathbf{e}_3\mathbf{n}_1)(\mathbf{e}_1\mathbf{e}_2) + \bar{\bar{\omega}}^2(\mathbf{e}_3\mathbf{e}_1)(\mathbf{e}_2\mathbf{n}_1)}{\omega_1^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} \right] \right\}.
\end{aligned}
$$

Here $\mathbf{n} = \mathbf{k}/|k|$. The three poles cannot be realized simultaneously. The maximum signal is observed if two plasmons are excited at once. Analysis of the expression for $\mathcal{J}$ shows that this occurs in the following cases: 1) The incident photons excite dipole and quadrupole plasmons, while the emitted one excites no plasmon whatever; 2) one of the incident photons excites a dipole plasmon and the emitted a quadrupole one, or vice versa. In the first case ($\omega_1 \approx \bar{\omega}$, $\omega_2 \approx \bar{\bar{\omega}}$), for example, the power emitted by the particle in the direction of the unit vector $\mathbf{n}_{k_3}$ as a result of an elementary $1 + 2 \to 3$ act as determined by the expression

$$
\begin{aligned}
\frac{dP}{d\mathbf{n}_{k_3}} = {} & \frac{\pi}{2} \left(\frac{Q_1 Q_2 a^6}{mc^2} \right) \left(\frac{l_0 \bar{\omega}}{c} \right) \bar{\omega} \left(\frac{\bar{\omega} + \bar{\bar{\omega}}}{2\bar{\omega} + \bar{\bar{\omega}}} \right)^2 \\
& \times \frac{\bar{\omega}^2 \bar{\bar{\omega}}^2}{(\omega_1^2 - \bar{\omega}^2)^2 + \bar{\omega}^4 \bar{g}^2} \frac{\bar{\bar{\omega}}^4}{(\omega_2^2 - \bar{\bar{\omega}}^2)^2 + \bar{\bar{\omega}}^4 \bar{\bar{g}}^2} \\
& \times [(\mathbf{e}_{k_3}\mathbf{e}_{k_2})(\mathbf{e}_{k_1}\mathbf{n}_{k_2}) + (\mathbf{e}_{k_1}\mathbf{e}_{k_2})(\mathbf{e}_{k_3}\mathbf{n}_{k_2})]^2,
\end{aligned}
$$

where l_0 is the electron classical radius, while Q_1 and Q_2 are the energy densities in light beams with frequencies ω_1 and ω_2, respectively.

It is easy to perform similar calculations for the inverse of the above process—transformation of one photon of frequency ω_1 into two emitted photons with frequencies ω_2 and ω_3 ($\omega_1 = \omega_2 + \omega_3$). The maximum signal is observed if: 1) $\omega_2 \approx \bar{\omega}$, $\omega_3 \approx \bar{\bar{\omega}}$, 2) $\omega_2 \approx \bar{\bar{\omega}}$, $\omega_3 \approx \bar{\omega}$, 3) $\omega_1 \approx \bar{\bar{\omega}}$, $\omega_2 \approx \bar{\omega}$, 4) $\omega_1 \approx \bar{\bar{\omega}}$, $\omega_3 \approx \bar{\omega}$. The calculation shows, for example, that at $\omega_2 \approx \bar{\omega}$ and $\omega_3 \approx \bar{\bar{\omega}}$ we have

$$
\begin{aligned}
\mathcal{T}_{1\to2+3} = {} & \frac{\omega_0^2 e}{6m} \sqrt{\frac{2\pi}{(\bar{\omega} + \bar{\bar{\omega}})V}} \sqrt{\frac{2\pi}{\bar{\omega} V}} \sqrt{\frac{2\pi}{\bar{\bar{\omega}} V}} \\
& \times \frac{a^3 \bar{\omega}}{2\bar{\omega} + \bar{\bar{\omega}}} \frac{\bar{\omega}^2}{\omega_2^2 - \bar{\omega}^2(1 - i\bar{g})} \\
& \times \frac{\bar{\bar{\omega}}^2}{\omega_3^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})} [(\mathbf{e}_{k_1}\mathbf{e}_{k_3})(\mathbf{e}_{k_2}\mathbf{n}_{k_3}) + (\mathbf{e}_{k_2}\mathbf{e}_{k_3})(\mathbf{e}_{k_1}\mathbf{n}_{k_3})].
\end{aligned}
$$

Integration over the states of one of the emitted photons (of frequency ω_3) yields the following expression for the differential cross section that determines the probability of observing one of the photons of interest to us, incident in a direction specified by a unit vector $\mathbf{n}k_2$ in an energy interval dE_2 near $\omega_2 \approx \bar{\omega}$

$$
\begin{aligned}
\frac{d^2\sigma}{d\mathbf{n}_{k_2} dE_2} = {} & \frac{1}{12\pi} \frac{1}{mc^2} (l_0 a) \left(\frac{\bar{\omega} a}{c} \right)^5 \frac{1}{\bar{\bar{g}}^2} \frac{\bar{\omega}^3}{(\bar{\omega} + \bar{\bar{\omega}})(2\bar{\omega} + \bar{\bar{\omega}})^2} \\
& \times \frac{\bar{\omega}^4}{(\omega_2^2 - \bar{\omega}^2)^2 + \bar{\omega}^4 \bar{g}^2} \\
& \times \frac{1}{2} \sum_{\lambda_3} [(\mathbf{e}_{k_1}\mathbf{e}_{k_3,\lambda_3})^2 + (\mathbf{e}_{k_2}\mathbf{e}_{k_3,\lambda_3})^3 \\
& + 2(\mathbf{e}_{k_1}\mathbf{e}_{k_3,\lambda_3})(\mathbf{e}_{k_2}\mathbf{e}_{k_3,\lambda_3})(\mathbf{e}_{k_1}\mathbf{e}_{k_2})],
\end{aligned}
$$

where λ is the photon polarization index.

The cross section of the process near $\omega_2 \approx \bar{\bar{\omega}}$ and $\omega_3 \approx \bar{\omega}$ is determined by a similar equation

$$\frac{d^2\sigma}{d\mathbf{n}_{k_2}dE_2}=\frac{9}{\pi}\frac{1}{mc^2}(l_0a)\left(\frac{\bar{\bar{\omega}}a}{c}\right)^5\frac{1}{g^2}\frac{\bar{\omega}^3}{(\bar{\omega}+\bar{\bar{\omega}})(2\bar{\omega}+\bar{\bar{\omega}})^2}$$

$$\times\frac{\bar{\bar{\omega}}^4}{(\omega_2^2-\bar{\bar{\omega}}^2)^2+\bar{\bar{\omega}}^4\bar{\bar{g}}^2}$$

$$\times\frac{1}{2}\sum_{\lambda_3}[(\mathbf{e}_{k_2}\mathbf{e}_{k_3,\lambda_3})(\mathbf{e}_{k_1}\mathbf{n}_{k_2})+(\mathbf{e}_{k_1}\mathbf{e}_{k_2})(\mathbf{e}_{k_3,\lambda_3}\mathbf{n}_{k_2})]^2.$$

Numerical estimates show that for Ag or Au particles with $a=200$ Å the cross section of the process $1+2\rightarrow3$ near the plasma resonances is 10^{-4} of the cross section of elastic scattering of light by the particle, while the power of the signal connected with the transformation $1\rightarrow2+3$, drawn from one particle, is 10^{-8} W if pulsed lasers are used. This permits complete observation of both effects in experiment. A curious feature of the considered processes is the total absence of scattering in the "forward" and "backward" scattering of the light polarized in the scattering plane.

To conclude this section, we call attention once more to the existence of two three-photon mechanisms of processes on the surfaces of small metallic particles. The first was considered above. The second is connected with diagram d) of Fig. 7. In the former case the probability of the considered essentially nonlinear process, as seen above, is determined completely by the characteristics of the linear electromagnetic response of the particle. In the second there appears inevitably in the process a particle polarizability that depends on the external-field intensity, or a quadratic susceptibility. The mechanism realized depends on the value of the parameter $(r_0/a)(\omega_0/\omega)$. For particles with $a\approx10^2$–10^3 Å in the optical range, the dominant mechanism is the one considered by us. An alternate approach to the description of three-photon processes in small metallic particles, based on a combination of Maxwell's equations and the hydrodynamics of an electron gas of a particle, was developed in Refs. 5 and 6.

5. GIANT INELASTIC SCATTERING OF LIGHT BY A PARTICLE

The renormalization of the wave functions of photons in an inhomogeneous metallic sample, a phenomenon considered in Sec. 4, influences substantially the inelastic scattering of light by a metallic particle. It is known that the expression for the cross section of this process has a pole if the energy transferred to the particle coincides with energy of the surface plasmon in the particle.[7,8] It is said then that a surface plasmon can be excited in the particle in the dumped-energy channel. Recognizing that the wave functions of the two photons participating in the process cease to be plane waves [see (50) or (51)], we see that plasmon excitation and the appearance of additional poles in the cross section of the process can occur also in the channels of both photons. In the situation of greatest interest two poles are realized simultaneously; for example, a quadrupole surface plasmon of frequency $\bar{\bar{\omega}}\approx\sqrt{\frac{2}{5}}\omega_0$ is excited in the incident-photon channel, while in the discarded-energy channel or in the emitted-photon channel the plasmon is dipole with frequency $\bar{\omega}\approx\omega_0/\sqrt{3}<\bar{\bar{\omega}}$ in these cases the probability of elastic scattering of light by a particle is higher by several orders than customarily expected.

In the present section we calculate the differential cross section for inelastic scattering of light by a small metallic particle with account taken of the renormalization of the photon wave functions.

Let ω_i be the energy of the photon incident on the particle, ω_f that of the emitted, and $\omega\equiv\omega_{if}=\omega_i-\omega_f$ the energy transferred to the electron gas of the particle. The probability of the process is determined by the golden rule

$$W=2\pi\sum_s|\mathcal{T}_{0s}|^2\delta(\omega_{if}-\omega_s),$$

where the summation is over all the excited states f the electrons and ω_s is the excitation energy. The amplitude $\mathcal{T}_{0S}$ is connected with the S matrix by the relation

$$\langle0|a_{\mathbf{k}_i}Sa^+_{\mathbf{k}_f}|s\rangle=\delta_{if}-2\pi i\mathcal{T}_{0s}\delta(\omega_{if}-\omega_s).\tag{52}$$

All the necessary preparations for the summation of the perturbation theory series for $\mathcal{T}_{0S}$ in (52) were in fact already made in the preceding sections. Obviously,

$$W=2\frac{e^4}{m^2}\,\mathrm{Im}\,\Pi_{00}(\mathbf{k}_i,\mathbf{k}_f|\omega_{if}),$$

where

$$\Pi_{00}(\mathbf{k},\mathbf{k}_f|\omega_{if})=\int\mathbf{\Phi}_{\mathbf{k}_i}(\mathbf{r})\mathbf{\Phi}^*_{\mathbf{k}_f}(\mathbf{r})\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega_{if})\mathbf{\Phi}_{\mathbf{k}_f}(\mathbf{r}')\mathbf{\Phi}^*_{\mathbf{k}_i}(\mathbf{r}')d\mathbf{r}d\mathbf{r}',$$

$\Pi_{00}(\mathbf{r},\mathbf{r}'|\omega)$ is the density–density polarization operator of the system, with which we deal in Sec. 3, and $\mathbf{\Phi}$ is the renormalized wave function of a photon in a particle and has been investigated in Sec. 4.

We confine ourselves next to consideration of a small particle, to shorten the calculations. Owing to the angular-momentum conservation law, the multipolarity of the wave functions of the surface plasmons excited either by photons or in the channel of energy transfer to the particles cannot be the same. The maximum elastic-scattering probability is realized if: 1) The incident and outgoing photons excite respectively a quadrupole ($\omega_i\approx\bar{\bar{\omega}}$) or a dipole ($\omega_f\approx\bar{\omega}$) plasmon, and no plasmon is excited at all in the ejected-energy channel ($\omega=\omega_i-\omega_f\approx\bar{\bar{\omega}}-\bar{\omega}$); 2) either the incident photon excites a quadrupole plasmon, the emitted photon excites nothing, and a dipole plasmon is excited in the momentum-transfer channel ($\omega\approx\bar{\omega}$). The probability of the second process is easier to calculate, for it suffices here to deal only with the pole part of the dipole photon propagator in the particle [cf. the general expression (26) for a propagator]:

$$D_{\alpha\beta}(\mathbf{r},\mathbf{r}')\approx\frac{2}{(\omega^2-\omega_0^2)a^3}\frac{\bar{\omega}^2}{\omega^2-\bar{\omega}^2(1-i\bar{g})}\delta_{\alpha\beta}.$$

The explicit form of the function $\mathbf{\Phi}$ is given by (51). After simple calculations the differential cross section of the inelastic scattering in the second case can be written in the form

$$\frac{d^2\sigma}{d(\omega/\omega)d\mathbf{n}_{k_f}}=\frac{4}{9}\frac{a^2}{(2\pi)^2}\frac{\lambda_0(\bar{\bar{\omega}}-\bar{\omega})}{c}\frac{l_0(\bar{\bar{\omega}}-\bar{\omega})}{c}$$

$$\times\frac{a\bar{\bar{\omega}}}{c}\frac{\bar{\bar{\omega}}^2}{\bar{\omega}^2-\omega_0^2}\frac{\omega_0^3}{\bar{\omega}^2\bar{\bar{\omega}}}$$

$$\times\left[\frac{(\bar{\bar{\omega}}-\bar{\omega})^2+\bar{\omega}^2}{(\bar{\bar{\omega}}-\bar{\omega})^2-\bar{\omega}^2}\right]^2\frac{\bar{\omega}^4\bar{g}}{(\omega^2-\bar{\omega}^2)^2-\bar{\omega}^4\bar{g}^2}$$

$$\times\frac{\bar{\bar{\omega}}^4}{(\omega_i^2-\bar{\bar{\omega}})^2-\bar{\bar{\omega}}^4\bar{\bar{g}}^2}[(\mathbf{e}_i\mathbf{e}_f)^2+(\mathbf{n}_{k_i}\mathbf{e}_f)^2],\tag{53}$$

where $\mathbf{n}_{k_i}$ and $\mathbf{n}_{k_f}$ are unit vectors in the directions of the incident and scattered photons, and λ_0 is the Compton wavelength. The connection of the frequencies and the widths of the dipole and quadrupole surface plasmons with the parameters of the particle is established by the relations of Sec. 4.

The influence of renormalization of the photon wave functions on the cross section of the process is quite strong. Expression (53) contains, besides the well-known pole in the energy-transfer channel, a pole due to excitation of a dipole plasmon in the particle, also an additional quadrupole plasma resonance connected with the incident photon. In the case when both poles are realized simultaneously, the inelastic-scattering signal is $\bar{\bar{g}}^{-2}$ times stronger than the signal connected with the familiar pole in the energy-transfer channel. Since $\bar{\bar{g}} = \frac{1}{30}(\bar{\bar{\omega}}a/c)^5 \ll 1$ ($g \approx 10^{-5}$ for particles with $a \approx 10^2$ Å), the inelastic-scattering signal can become of the same order as the elastic light-scattering signal.

In this connection, we wish to add the following. Tremendous interest had attracted in its time the surface-enhanced Raman scattering of light by molecules adsorbed either by rough surfaces of a number of noble metals, or on surfaces of small metallic particles.[9] The anomalous Raman-scattering signal was attributed in a number of models[10,11] to amplification of the electromagnetic field near the particle or to a separate roughness of the surface on account of excitation of a surface plasmon in near the frequency of the dipole surface plasmon. In practice this band is wider, ranging from the infrared to the ultraviolet. The results of the present section allow us to examine the problem from a different point of view—to relate the enhancement of the field near the particle not to excitation of a plasmon in the elastic scattering channel, but with an anomalously high intensity of inelastic scattering of light by the particle. In this case, as we have seen (see cases 1 and 2), the enhancement of the field should be expected in a wide spectral band: a) near the plasma frequency, corresponding to a small spill of the incident particle energy to the plasma and to excitation of plasmons by both photons; b) far from the plasma frequencies, corresponding to excitation of plasmons in the channel of the spilled energy and the incident photon.

6. PHOTOEFFECT

Interest in the photoeffect in ultradispersed systems was initiated in Ref. 12, where experiment revealed an anomalous increase (compared with a planar surface) of the photoelectron yield from metallic aerosol particles. The characteristic of the photo-yield turned out to be very sensitive to the size of the particles and to the state of their surface, which provides a fair chance of using this effect for diagnostics of atmospheric aerosol. We shall show in the present section how this phenomenon can be described in the framework of our approach.

Consider the absorption of a photon frequency ω_1 accompanied by excitation of a hole of energy ω_2 in the particle and emission of an electron of energy $\omega_3 = \omega_1 - \omega_2$.

The probability of the process is determined by the golden rule

$$W = 2\pi|\mathcal{T}|^2\delta(\omega_1 - \omega_2 - \omega_3),$$

where the amplitude $\mathcal{T}$ is connected with the S-matrix by the relation

$$\langle a_{\mathbf{k}_1} S b^+_{\mathbf{k}_1-\mathbf{k}_2} b_{\mathbf{k}_2}\rangle = -2\pi i\delta(\omega_1 - \omega_2 - \omega_3)\mathcal{T}.$$

In first-order perturbation theory, using (1) and (2), we have

$$\mathcal{T} = -\frac{e}{mc}\sqrt{\frac{2\pi c}{\omega_1 V}}\, e_{k_1,\alpha}\int \exp(-i\mathbf{k}_1\mathbf{r})\varphi_{k_3}(\mathbf{r})\nabla_\alpha\varphi^*_{k_2}(\mathbf{r})d\mathbf{r}, \quad (54)$$

where φ_{k_3} and φ_{k_2} are the wave functions of the photoelectron and hole. We use relation (37) to eliminate, as before, the gradients of the wave functions under the integral sign in (54). Then, however, the second term in the right-hand side of (37) is no longer zero. The reason is that in this case, beside the vector $\mathbf{k}$, there are other preferred directions specified, for example, by the wave vector of the incident photoelectrons. The direction of the vector integrals in the right-hand side of (38) is not the same as the direction $\mathbf{k}$, and the relation

$$\omega_{\lambda\lambda'}e_{k,\alpha}\nabla_{k,\alpha}\int\varphi_\lambda(\mathbf{r})e^{i\mathbf{kr}}\varphi^*_{\lambda'}(\mathbf{r})d\mathbf{r} = \frac{i}{m}\int\varphi_\lambda(\mathbf{r})e^{i\mathbf{kr}}e_{k,\alpha}\frac{\partial}{\partial r_\alpha}\varphi^*_{\lambda'}(\mathbf{r})d\mathbf{r}, \quad (55)$$

which we have used in Sec. 3, does not hold in this case. It is easily seen, however, that the second term in the right-hand side of (37) contains a small parameter ka compared with the remaining ones. If we confine ourselves to small metallic particles, relation (55) can be used with accuracy up to terms of order ka. We shall deal hereafter just with such particles.

Using (55), we have in first-order perturbation theory:

$$\mathcal{T} = \frac{e\omega_1}{c}\sqrt{\frac{2\pi c}{\omega_1 V}}\, e_{k_1,\alpha}\int\varphi_{k_3}(\mathbf{r})r_\alpha\exp(-i\mathbf{k}_1\mathbf{r})\varphi^*_{k_2}(\mathbf{r})d\mathbf{r}. \quad (56)$$

The manner of taking the higher perturbation-theory orders into account is shown in Fig. 11. It is seen from this figure that the summation prescription is the following: the plane electromagnetic wave $\mathbf{e}_k\exp(i\mathbf{kr})$ in (56) must be replaced by the function $\mathbf{f}_\mathbf{k}(\mathbf{r})$ defined by Eq. (49) of Sec. 4.

With allowance for all orders of perturbation theory, the amplitude takes the form

$$\mathcal{T} = \frac{e\omega_1}{c}\int\varphi_{k_3}(\mathbf{r})r_\alpha f_{\mathbf{k}_1,\alpha}(\mathbf{r})\varphi^*_{k_2}(\mathbf{r})d\mathbf{r}, \quad (57)$$

where we have in the dipole approximation

$$f_{\mathbf{k},\alpha}(\mathbf{r}) = \sqrt{\frac{2\pi c}{\omega V}}\left\{\frac{\omega^2}{\omega^2 - \bar{\omega}^2(1 - i\bar{g})}e_{k,\alpha} - \frac{5\omega^2 - \omega_0^2}{5[\omega^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})]}i(\mathbf{kr})e_{k,\alpha} - \frac{\omega_0^2}{5[\omega^2 - \bar{\bar{\omega}}^2(1 - i\bar{\bar{g}})]}i(\mathbf{e}_k\mathbf{r})k_\alpha\right\}. \quad (58)$$

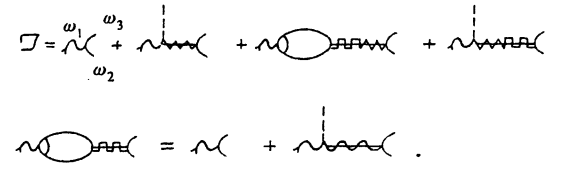

FIG. 11. Perturbation-theory series for photoeffect amplitude.

Thus, with (57) and (58) taken into account, W is determined by the square of the matrix element $\mathbf{r}$:

$$W = 2\pi\delta(\omega_1 - \omega_2 - \omega_3)\frac{2\pi c}{\omega_1 V}\left(\frac{e\omega_1}{c}\right)^2 |(\mathbf{er})_{2,3}|^2. \quad (59)$$

The idea of calculating $|\mathbf{r}_{2,3}|^2$ dates back to Ref. 13. We represent the square of the matrix element r in the form

$$(r_\alpha)_{2,3}(r_\beta)_{2,3} = \frac{\delta_{\alpha\beta}}{3\pi\nu_2}\int dr dr_0(\mathbf{r}\mathbf{r}_0)\int_0^\infty W_{\mathbf{r}_0}(\mathbf{r}, t)dt,$$

where ν_2 is the density of the hole states in the particle, and $W_{\mathbf{r}_0}(\mathbf{r},t)$ is the probability of observing a hole at a point with coordinate $\mathbf{r}$ at an instant of time t if the hole position at $t = 0$ is characterized by the vector $\mathbf{r}_0$. $W_{\mathbf{r}_0}(\mathbf{r},t)$ satisfies the diffusion equation

$$\frac{\partial}{\partial t}W_{\mathbf{r}_0}(\mathbf{r}, t) = D\Delta W_{\mathbf{r}_0}(\mathbf{r}, t) \quad (60)$$

with the boundary condition

$$W_{\mathbf{r}_0}(\mathbf{r}, t = 0) = \delta(\mathbf{r} - \mathbf{r}_0)\frac{\delta(a - r)}{4\pi a^2},$$

where D is the diffusion coefficient of the hole in the metal. We expand $W_{\mathbf{r}_0}(\mathbf{r},t)$ in a series of Legendre polynomials

$$W_{\mathbf{r}_0}(\mathbf{r}, t) = \sum_l W_l(r, t)P_l(\cos\vartheta),$$

where ϑ is the angle between $\mathbf{r}$ and $\mathbf{r}_0$, and integrate the equation over t

$$W_{\mathbf{r}_0}(\mathbf{r}, t = \infty) - \delta(\mathbf{r} - \mathbf{r}_0)\frac{\delta(a - r)}{4\pi a^2}$$
$$= D\sum_l\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{l(l + 1)}{r^2}\right]u_l P_l(\cos\vartheta), \quad (61)$$

where $u_l = \int_0^\infty W_l(r,t)dt$. Introducing the function

$$\psi_l = \int dr_0(\mathbf{r}\mathbf{r}_0)u_l(r)P_l(\cos\vartheta),$$

and integrating (61) over $\mathbf{r}_0$ with a weight $(\mathbf{r}_0\mathbf{r})/r$ we readily obtain for ψ_l the equation

$$\sum_l [r^2\psi_l'' - l(l + 1)\psi_l] = -\frac{r^4\delta(a - r)}{4\pi a^2 D}. \quad (62)$$

The solution of (62) for $r < a$ takes the form

$$\psi_l^<(r) = A_l r^{l+1}. \quad (63)$$

For $r > a$ we have

$$\psi_l^>(r) = B_l r^{-l}. \quad (64)$$

The boundary conditions for (62) are obtained by integrating (62) over a vanishingly narrow spherical layer near the particle surface, and take the form

$$\psi_l^<(r = a) = \psi_l^>(r = a),$$

$$\sum_l [(\psi_l^>(r = a))' - (\psi_l^<(r = a))'] = -\frac{1}{4\pi D}. \quad (65)$$

Using (63)–(65), we rewrite (62) in the form

$$\sum_l a^l(2l + 1)A_l = \frac{1}{4\pi D}.$$

We stipulate that

$$3aA_1 = 1/4\pi D,$$

whereas

$$\sum_{l=2}^\infty (2l + 1)a^l A_l = 0. \quad (66)$$

This makes it possible to confine ourselves in the expression

$$|\mathbf{r}_{2,3}|^2 = \sum_l \int \psi_l(r)dr$$

to the dipole terms, since the sum of the terms discarded in this case is small in accordance with condition (66). Ultimately,

$$|\mathbf{r}_{2,3}|^2 = \frac{a^4}{45\pi\nu_2 D}.$$

Multiplying W by the density of states of the emitted electron and hole and integrating over their energies, we have for the differential flux density of the photoelectrons in the direction of the unit vector $\mathbf{n}_3$

$$\frac{d^2 j_3}{d\mathbf{n}_3 d(E_3/\hbar\omega_1)} = \frac{2}{45\pi}Q_1\frac{e^2}{\hbar c}\frac{a^4}{D}mE_3\frac{\omega_1^4}{(\omega_1^2 - \bar\omega^2)^2 + \bar\omega^4\bar g^2},$$

where Q_l is the energy density of the incident light and E_3 is the photoelectron energy. The cross section of the process is resonant if the frequency of the incident photon is close to the frequency $\bar\omega$ of the dipole surface plasmon in the particle.

An anomalously high photoyield of electrons from small metal particles is observed experimentally also at incident-light frequencies lower than the frequency of the dipole surface plasmon.[14] The photoelectron spectrum has a maximum at frequencies $\simeq 0.08\omega_0$ even on a flat metallic surface.[15] The cause of these anomalies is the abrupt change over distances $l \simeq \lambda_F$) of the electron density and of the electromagnetic field near a particle boundary or a half-plane edge.[14–16] The wave vector $\mathbf{k}$ of the incident photon inside the metal increases resonantly, owing to the renormalization near the electromagnetic eigenmodes of the transition layer, and can become comparable with l^{-1}. In this case the electromagnetic response of the electron gas of the sample is described by two nonlocal dielectric constants—longitudinal $\varepsilon_l(k,\omega)$ and transverse $\varepsilon_t(k,\omega)$ $(\varepsilon_l - \varepsilon_t \sim k\lambda_F \simeq \lambda_F/l)$ (Ref. 17). The anomalies of the electron photoyield are attributed to excitation, in the sample, of additional longitudinal modes characterized by the condition $\varepsilon_l(k,\omega) = 0$ (Ref. 16). In our approach, the effects of nonlocality of the electromagnetic response of the sample are not manifested, since they involve allowance for the next terms of the expansion in the parameter $(r_0/a)(\omega_0/\omega)$ when the irreducible polarization operators $\mathscr{P}_{00}$, $\mathscr{P}_{0\alpha}$, $\mathscr{P}_{\alpha 0}$ are calculated, and also with allowance for diagrams containing momentum–momentum correlators [e.g., diagram b) of Fig. 1].

7. CONCLUSION

Certain rules established by classical electrodynamics are violated when it comes to describing multiphoton processes near surfaces of metallic particles. The photon–photon interaction, which is of low importance in a homogeneous medium, is enhanced by several orders of magnitude near particle-gas collective-excitation frequencies. For particles with radius 200 Å, the gain is 10^8. As a result, the

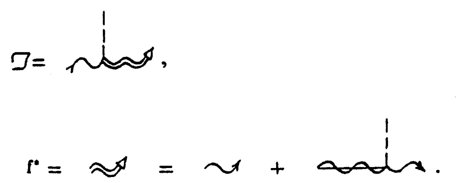

FIG. 12. Equivalent representation of the amplitude of elastic scattering of light by a particle as a transformation of a photon into a plasmon-polariton.

photon goes off the mass shell near the particle surface in the region of the plasma resonances, or else its wave function is renormalized and ceases to be plane. Effects of this kind were not considered in the classical theory, yet we have seen that they are quite substantial. In addition to multiphoton processes, they are manifested also in inelastic scattering of light by metallic particles and enhance considerably the role of the inelastic channel in the dissipation of the incident-radiation energy. Incidentally, the photon wavefunction renormalization (connected with the H_I term quadratic in **A**) we have considered is not the only one encountered in the considered problems. Even elastic scattering of light (Sec. 2) can be described by another (perfectly different) method as a transformation of a photon into a plasmon–polariton—a photon renormalized by a particle. The amplitude of this process is shown in Fig. 12. The double wavy line shown there is the function **f*** known from Sec. 4 or a plasmon–polariton wave function. The description to use is a matter of taste. Another feature of multiphoton processes, which does not fit the classical description, is interference of the probability amplitudes corresponding to different methods of realizing these processes. Examples of this kind increase in number when the electrodynamics of multiparticle systems is considered. All this had prompted us to develop, as an alternative to classical electrodynamics, the quantum approach, whose main features were demonstrated above, to a description of electromagnetic processes in an inhomogeneous medium.

In our approach it is possible to set the limits of validity of classical-electrodynamics equations, such as the Mie equations for elastic scattering and absorption of light by a sphere. We have used for irreducible polarization operators a representation based on expansion in the parameter $\varepsilon_F/N^{1/3}\omega \approx (r_0/a)(\omega_0/\omega)$ (ε_F is the Fermi energy, N the total number of conduction electrons in a particle, r_0 the Thomas–Fermi screening radius, and ω_0 the classical plasma frequency). If this parameter becomes comparable with unity, the classical equations will no longer hold. It is easy to obtain an estimate of the limiting frequency ω. For particles with $a \approx 10^3$ Å we have $N^{1/3} \approx 10^2$ and $\varepsilon_F N^{-1/3} \approx 10^{-2}$ eV, corresponding to frequencies $\omega \approx 10^{13}$ Hz or to wavelengths $\lambda \approx 10^{-4}$ m. Violations of the Mie theory should therefore expected in the far infrared and in the microwave band.

APPENDIX A

We give here the explicit forms of the irreducible polarization operators, shown in Fig. 2, of an electron gas of particles

$$\mathcal{P}_{00}(\mathbf{r}, \mathbf{r}'|\omega) = i\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}, \tau)\rho^{*I}(\mathbf{r}', 0)\rangle e^{i\omega\tau} d\tau,$$

$$\mathcal{P}_{\alpha 0}(\mathbf{r}, \mathbf{r}'|\omega) = i\int_{-\infty}^{\infty} \langle Tp^I_\alpha(\mathbf{r}, \tau)\rho^{*I}(\mathbf{r}', 0)\rangle e^{i\omega\tau} d\tau,$$

$$\mathcal{P}_{0\alpha}(\mathbf{r}, \mathbf{r}'|\omega) = i\int_{-\infty}^{\infty} \langle T\rho^I(\mathbf{r}, \tau)p^{*I}_\alpha(\mathbf{r}', 0)\rangle e^{i\omega\tau} d\tau,$$

where $\rho^I(\mathbf{r},\tau)$ and $p^I_\alpha(\mathbf{r},\tau)$ are operators of the electron density and the electron-momentum density in the interaction representation, and the averaging is over the ground state of the electron gas.

In the random-phase approximation, the operator $\mathcal{P}_{\alpha 0}$ takes the form

$$\mathcal{P}_{\alpha 0}(\mathbf{r}, \mathbf{r}'|\omega) = -i\sum_{\lambda\lambda'} \varphi_\lambda(\mathbf{r})\nabla_\alpha\varphi^*_{\lambda'}(\mathbf{r}) \frac{n_\lambda - n_{\lambda'}}{\varepsilon_\lambda - \varepsilon_{\lambda'} + \omega} \varphi^*_\lambda(\mathbf{r}')\varphi_{\lambda'}(\mathbf{r}'), \tag{A1}$$

where φ_λ, η_λ, and ε_λ are the single-electron wave functions, occupation numbers, and energies, respectively. In all the calculations we need not the polarization operators themselves, but integrals which are the products of $\mathcal{P}$ with certain functions $V(\mathbf{r})$ of the coordinates. Such integrals are defined by matrix elements $V(\mathbf{r})$ over the single-electron wave functions. Simple quasiclassical reasoning shows the matrix elements $V_{\lambda\lambda'}$ are proportional to the Fourier component $V[\mathbf{r}(t)]$

$$V_{\lambda\lambda'} \propto \int dt \exp[i(\varepsilon_\lambda - \varepsilon_{\lambda'})t]\, V(\mathbf{r}(t)),$$

where $\mathbf{r}(t)$ is determined by the classical equation of motion of the electrons. For sufficiently small particles ($a \lesssim l_0$, l_0 is the mean free path of the electron in the metal) the characteristic time of variation of $\mathbf{r}(t)$ is estimated at $t \approx a/v_F$, where v_F is the Fermi velocity, $V_{\lambda\lambda'}$ has a resonance at characteristic energies $\varepsilon_\lambda - \varepsilon'_\lambda \approx v_F/a \approx (\varepsilon_F/N^{1/3})$, where ε_F is the Fermi energy and N is the total number of conduction electrons in the particle. At frequencies $\omega \gg \varepsilon_F/N^{1/3}$ the energy denominator in (A1) can be expanded in powers of $(\varepsilon_\lambda - \varepsilon_{\lambda'})/\omega$. Retaining the first terms of this expansion, $\mathcal{P}_{\alpha 0}$ can be represented in the form

$$\mathcal{P}_{\alpha 0}(\mathbf{r}, \mathbf{r}'|\omega) = -\frac{i}{\omega}\sum_{\lambda,\lambda'} \varphi_\lambda(\mathbf{r}_1)\nabla_{1\alpha}\varphi_{\lambda'}(\mathbf{r}_1)(n_\lambda - n_{\lambda'})\varphi_\lambda(\mathbf{r}')\varphi_{\lambda'}(\mathbf{r}')\delta(\mathbf{r}_1 - \mathbf{r})d\mathbf{r}_1. \tag{A2}$$

Integration by parts and the completeness condition of the single-electron functions

$$\sum_\lambda \varphi_\lambda(\mathbf{r})\varphi^*_\lambda(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$$

make it possible to express (A2) in the form

$$\frac{i}{\omega}\sum_\lambda \nabla'_\alpha\varphi_\lambda(\mathbf{r}')n_\lambda\delta(\mathbf{r} - \mathbf{r}')\varphi^*_\lambda(\mathbf{r}') + \frac{i}{\omega}\sum_\lambda \varphi_\lambda(\mathbf{r}')\varphi^*_\lambda(\mathbf{r}')n_\lambda\nabla'_\alpha\delta(\mathbf{r} - \mathbf{r}') + \frac{i}{\omega}\sum_\lambda \varphi_\lambda(\mathbf{r}')\nabla'_\alpha\varphi^*_\lambda(\mathbf{r}')n_\lambda\delta(\mathbf{r} - \mathbf{r}').$$

Using the relation

$$\sum_\lambda n_\lambda \varphi_\lambda(\mathbf{r})\varphi^*_\lambda(\mathbf{r}) = n(\mathbf{r}),$$

we have finally:

$$\mathcal{P}_{\alpha 0}(\mathbf{r}, \mathbf{r}'|\omega) = \frac{i}{\omega}\nabla'_\alpha[n(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}')].$$

The operator $\mathcal{P}_{0\alpha}$ is obtained similarly

$$\mathcal{P}_{0\alpha}(\mathbf{r}, \mathbf{r}'|\omega) = \frac{i}{\omega}\nabla_\alpha[n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')].$$

It is easiest to obtain the operator $\mathcal{P}_{00}$ by using Eq. (10):

$$\mathcal{P}_{00}(\mathbf{r}, \mathbf{r}'|\omega) = \frac{1}{m\omega^2}\nabla_\alpha[n(\mathbf{r})\nabla_\alpha\delta(\mathbf{r}-\mathbf{r}')].$$

APPENDIX B

We calculate here some integrals extensively used in the main text.

The integral $W[\mathbf{M}\bar{\mathbf{M}}]$ is calculated as follows:

$$W[(\mathbf{M}^z\bar{\mathbf{M}}^Y)] = \int d\mathbf{r}\bar{\theta}(a-r)\mathbf{M}^z_{lm}(\omega,\mathbf{r})\bar{\mathbf{M}}^Y_{lm}(p,\mathbf{r})$$

$$= l(l+1)\int_0^\infty z_l(\omega r)y_l(pr)r^2dr$$

$$= \frac{a^2 l(l+1)}{p^2-\omega^2}[pz_l(\omega a)y_{l-1}(pa) - \omega z_{l-1}(\omega a)y_l(pa)]$$

$$= \frac{l(l+1)a^2 z_l(\omega a)y_l(pa)}{p^2-\omega^2}[p\psi_y(pa) - \omega\psi_z(\omega a)], \quad \text{(B1)}$$

where y and z are arbitrary spherical Bessel functions and

$$\psi_z(x) = \frac{d}{dx}\ln[xz_l(x)] = \frac{z_{l-1}(x)}{z_l(x)} - \frac{l}{x}.$$

The last equality is a consequence of the recurrence relations for spherical Bessel functions. The integrals in (B.1) have been tabulated.[18] The calculation of $W[(\mathbf{N}^z\bar{\mathbf{N}}^Y)]$ is somewhat more complicated:

$$W[(\mathbf{N}^z\bar{\mathbf{N}}^Y)] = \int d\mathbf{r}\bar{\theta}(a-r)\mathbf{N}^z_{lm}(\omega,\mathbf{r})\bar{\mathbf{N}}^Y_{lm}(p,\mathbf{r})$$

$$= \frac{l(l+1)}{p\omega}\{\int_a^\infty l(l+1)z_l(\omega r)y_l(pr)dr$$

$$+ \int_a^\infty \frac{d}{dr}[rz_l(\omega r)]\frac{d}{dr}[ry_l(pr)]dr\}.$$

Integrating by parts the second term on the right and using the identity $r(d^2/dr^2)(ry_l) = (d/dr)[r^2(d/dr)y_l]$, we can transform the expression in the braces into

$$\int_a^\infty dr[l(l+1)z_ly_l - z_l\frac{d}{dr}(r^2\frac{d}{dr}y_l)] + rz_l\frac{d}{dr}(ry_l)\Big|_{r=a}. \quad \text{(B2)}$$

Using the equation for y_l

$$l(l+1)y_l - \frac{d}{dr}r^2\frac{d}{dr}y_l = p^2r^2y_l,$$

we rewrite (B2) in the form

$$rz_l\frac{d}{dr}ry_l\Big|_{r=a} + p^2\int_a^\infty r^2z_ly_l\,dr.$$

The integral is taken here in the same manner as in (B1). Calculating it and using the identity

$$\frac{d}{dr}ry_l(pr) = pry_{l-1}(pr) - ly_l(pr),$$

we obtain ultimately

$$W[(\mathbf{N}^z\bar{\mathbf{N}}^Y)] = \frac{l(l+1)}{p\omega}$$

$$\times\left\{\frac{a^2p\omega}{p^2-\omega^2}[\omega z_l(\omega a)y_{l-1}(pa)\right.$$

$$\left. - pz_{l-1}(\omega a)y_l(pa)] + alz_l(\omega a)y_l(pa)\right\}$$

$$= \frac{l(l+1)a^2}{p^2-\omega^2}z_l(\omega a)y_l(pa)[\omega\psi_y(pa) - p\psi_z(\omega a)].$$

We now calculate two integrals used in the determination of the cross section of elastic scattering of light [see Eq. (30)]. To this end we need the following integral representations[3]

$$4\pi i^{l-1}\mathbf{L}^j_{lm}(r,\mathbf{k}) = \int e^{i\mathbf{kr}}\mathbf{P}_{lm}(\mathbf{n})dn,$$

$$\frac{4\pi i^l}{\sqrt{l(l+1)}}\mathbf{M}^j_{lm}(r,\mathbf{k}) = \int e^{i\mathbf{kr}}\mathbf{C}_{lm}(\mathbf{n})dn,$$

$$\frac{4\pi i^{l-1}}{\sqrt{l(l+1)}}\mathbf{N}^j_{lm}(r,\mathbf{k}) = \int e^{i\mathbf{kr}}\mathbf{B}_{lm}(\mathbf{n})dn.$$

We calculate the first integral

$$\int e^{i\mathbf{kr}}\bar{\mathbf{M}}^j_{lm}(p,\mathbf{r})\theta(a-r)d\mathbf{r} = \sqrt{l(l+1)}\int_0^a r^2drj_l$$

$$\times(pr)\int dn\mathbf{C}_{lm}(\mathbf{n})e^{i\mathbf{kr}}$$

$$= 4\pi i^l\sqrt{l(l+1)}\int_0^a r^2drj_l(pr)j_l(kr)\mathbf{C}_{lm}(\mathbf{n}_k)$$

$$= -\frac{4\pi i^l}{\sqrt{l(l+1)}}W[(\mathbf{M}^j_{lm}\bar{\mathbf{M}}^j_{lm})]\mathbf{C}_{lm}(\mathbf{n}_k). \quad \text{(B3)}$$

The calculation of the second integral is more complicated

$$\int e^{i\mathbf{kr}}\mathbf{N}^j_{lm}(p,\mathbf{r})\theta(a-r)d\mathbf{r} = \int_0^a r^2dr[l(l+1)$$

$$\times\frac{j_l(pr)}{pr}\int\mathbf{P}_{lm}(\mathbf{n})e^{i\mathbf{kr}}dn$$

$$+ \sqrt{l(l+1)}\frac{1}{pr}\frac{d}{dr}(rj_l(pr))\int\mathbf{B}_{lm}(\mathbf{n})e^{i\mathbf{kr}}dn]$$

$$= 4\pi i^{l-1}\int_0^a r^2dr[l(l+1)\frac{j_l(pr)}{pr}\mathbf{L}_{lm}(r,\mathbf{k})$$

$$+ \frac{1}{pr}\frac{d}{dr}(rj_l(pr))\mathbf{N}_{lm}(r,\mathbf{k})]. \quad \text{(B4)}$$

Expressing **L** and **M** in terms of **P** and **B**, we obtain the coefficient of **P**:

$$\frac{4\pi i^{l-1} l(l+1)}{pk} \int_0^a dr \left[r \frac{d}{dr} j_l(pr) j_l(kr) + j_l(pr) j_l(kr) \right]$$

$$= \frac{4\pi i^{l-1} l(l+1)}{pk} j_l(pa) j_l(ka) a. \qquad \text{(B5)}$$

The coefficient of **B** is

$$\frac{4\pi i^{l-1}\sqrt{l(l+1)}}{pk} \int_0^a r^2 dr \{ l(l+1) \frac{j_l(kr) j_l(pr)}{r^2}$$

$$+ \frac{1}{r^2} \frac{d}{dr} [r j_l(kr)] \frac{d}{dr} [r j_l(pr)] = - \frac{4\pi i^{l-1}}{\sqrt{l(l+1)}} W[(\mathbf{N}^j_{lm} \bar{\mathbf{N}}^j_{lm})]. \qquad \text{(B6)}$$

Combining expressions (B4)–(B6) we obtain ultimately

$$\int e^{i\mathbf{kr}} \mathbf{N}^j_{lm}(p, \mathbf{r}) \theta(a-r) d\mathbf{r} = \frac{4\pi i^{l-1} l(l+1) a}{pk} \times j_l(ka) j_l(pa) \mathbf{P}_{lm}(\mathbf{n}_k)$$

$$- \frac{4\pi i^{l-1}}{\sqrt{l(l+1)}} W[(\mathbf{N}^j_{lm} \bar{\mathbf{N}}^j_{lm})] \mathbf{B}_{lm}(\mathbf{n}_k). \qquad \text{(B7)}$$

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