

LIGHT SCATTERING BY A GAS IN THE PRESENCE OF AN INHOMOGENEOUS ELECTRIC FIELD

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Synopsis

An equation is derived for the intensity of the light scattered by a gas immersed in an inhomogeneous electric field, and formulas for the depolarisation ratio D and Rayleigh's ratio S are obtained therefrom. Investigation of the effect of the field gradient upon D is shown to provide a direct method of determining the quadrupole moment of axially-symmetric molecules. For a gas of spherical molecules, similar investigation of D and S allows to determine directly their hyperpolarizability B as induced by the field gradient.

§ 1. *Introduction.* Light scattering in the presence of a strong *homogeneous* electric field by a gas whose molecules are small as compared to the light wavelength has been the object of papers by Rocard¹), Andrews and Buckingham²), and this author³)⁴). Generally, anisotropic molecules on undergoing orientation in the electric field produce a change in the intensity and polarization of the light scattered. If scattering is investigated in the conditions of fig. 1*a*, the depolarization ratio for a gas consisting of axially symmetric non-dipolar molecules is given by the formula⁴)

$$D(E_z) = 1 - \frac{a_{\parallel} - a_{\perp}}{7kT} E_z^2, \quad (1)$$

with a_{\parallel} and a_{\perp} denoting, respectively, the electric polarizabilities parallel and perpendicular to the symmetry axis of the molecule. From eq. (1), investigation of the effect of a strong *homogeneous* electric field on the depolarization ratio makes possible the *direct* determination of the molecule's electrical anisotropy.

Obviously, if a gas consisting of quadrupolar molecules is immersed in an *inhomogeneous* electric field, orientation of the quadrupoles will occur leading to a change in the intensity and polarization of the scattered light. If we provide for the experimental conditions of fig. 1*b*, the following formula is obtained for the depolarization ratio, as will be proved further on:

$$D(E_{zz}) = 1 - \frac{2\Theta}{7kT} E_{zz}; \quad (2)$$

here, Θ is the electrical quadrupole moment of an axially symmetric molecule and E_{zz} is the z -component of the electric field gradient. Hence, investigation of the depolarization ratio of light scattered in the presence of a strong inhomogeneous electric field constitutes a new and *direct* method of measuring the value and sign of the molecule's quadrupole moment. Another method of direct determination of the quadrupole moment was outlined by Debye⁵⁾ and elaborated with much insight by Buckingham⁶⁾ to yield quantitative results. It consists in measuring the amount of birefringence induced in a gas by the gradient of the electric field produced by the condenser of fig. 1*b*.

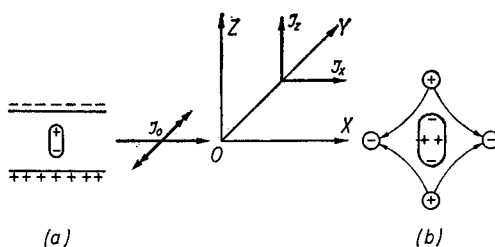


Fig. 1. The left-hand side shows schematically an anisotropic gas molecule oriented along the lines of force of a homogeneous electric field, E_z . To the right is the four-wire condenser yielding the electric field gradient $E_{zz} = -E_{xx}$ at its centre and orienting the quadrupolar molecules of a gas^{5) 6)}. The primary light beam, of intensity I_0 , is plane polarized with its electric vector oscillating parallel to the Y -axis and propagates in the direction of the X -axis. Light scattering observation is along the Y -axis. The quantities I_x and I_z are the scattered light components oscillating in the directions of the X - and Z -axes, respectively.

As compared with the Debye-Buckingham method, that proposed in the present paper has the advantage of yielding the value of the quadrupole moment directly, in accordance with eq. (2), whereas the birefringence of a gas is moreover dependent on the optical anisotropy of its molecules. Our method, however, presents the drawback that the effect consisting in variations of the depolarization ratio as due to the field gradient is extremely small, so that its detection and experimental investigation will be no easy matter.

An external electric field, homogeneous or inhomogeneous, is able to produce a change in the light scattered, even if the scattering molecules are spherical. In the latter case, however, one has to use natural light in order to obtain this effect, and observation of the light scattered should take place at an angle ϑ with the direction of incidence. The degree of depolarization in the presence of a strong uniform electric field is given by the following formula³⁾:

$$D(E_z) = \left(1 - \frac{2}{3} \frac{\gamma}{\alpha} E_z^2 \right) \cos^2 \vartheta, \quad (3)$$

wherein α is the mean polarizability of a spherical molecule, and γ its hyperpolarizability due to the square of the uniform electric field strength.

In the present paper it will be proved that, for spherical scattering molecules immersed in an inhomogeneous electric field, eq. (3) has to be replaced by

$$D(E_{zz}) = \left(1 - \frac{B}{\alpha} E_{zz}\right) \cos^2 \theta, \quad (4)$$

with B denoting the hyperpolarizability produced in the spherical molecule by the gradient of the electric field strength.

The hyperpolarizability γ appears in the theory of the optical birefringence induced by a uniform electric field⁷⁾, whereas the hyperpolarizability B occurs in that of the optical birefringence produced in a gas by an electric field gradient⁶⁾.

The hyperpolarizabilities γ and B , moreover, occur in the following formulas accounting for Rayleigh's ratio:

$$S(E_z) = S_0^{is} \left(1 + \frac{\gamma}{\alpha} E_z^2\right), \quad (5)$$

$$S(E_{zz}) = S_0^{is} \left(1 + \frac{B}{\alpha} E_{zz}\right), \quad (6)$$

where S_0^{is} defines Rayleigh's ratio for isotropically polarizable molecules able to scatter light in the absence of an external electric field.

In the present paper, after some general considerations on light scattering by a gas immersed in an inhomogeneous electric field, we shall proceed to calculate the depolarization ratio and Rayleigh's ratio for the simplest possible cases.

§ 2. *Fundamentals of the theory.* Consider an assembly of N identical, non-interacting molecules possessing a permanent electric quadrupole moment defined by the tensor⁶⁾

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_n e_n (3r_{n\alpha}r_{n\beta} - r_n^2 \delta_{\alpha\beta}), \quad (7)$$

wherein e_n is the n -th electric charge of the molecule, and \mathbf{r}_n its radius vector.

Now, let this assembly of molecules be immersed in the inhomogeneous electric field produced by the four-wire condenser shown in fig. 1*b*. We denote the direction of the oscillations of the electric vector \mathbf{E} in the incident light beam by the unit vector \mathbf{e} and in the scattered light by the unit vector \mathbf{n} ; we at first assume \mathbf{e} and \mathbf{n} to be oriented quite arbitrarily with respect to the laboratory coordinate system XYZ. The intensity of the light scattered, as observed at a point distant by $R_0 \gg \lambda$ from the origin of XYZ,

is now given by⁸⁾

$$I(E_{zz}) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{NI_0}{R_0^2} \left\langle \frac{\partial m_\alpha}{\partial E_\gamma} \frac{\partial m_\beta}{\partial E_\delta} n_\alpha n_\beta e_\gamma e_\delta \right\rangle_{E_{zz}}. \quad (8)$$

Herein, m_α is the α -component of the dipole moment induced in the molecule by the oscillating electric field E associated with the incident light wave of intensity I_0 . The statistical average in (8) is defined as

$$\langle \Phi \rangle_{E_{zz}} = \frac{\int \Phi(\tau, E_{zz}) e^{-\frac{u(\tau, E_{zz})}{kT}} d\tau}{\int e^{-\frac{u(\tau, E_{zz})}{kT}} d\tau}, \quad (9)$$

where $\Phi(\tau, E_{zz})$ is an arbitrary function of state and $u(\tau, E_{zz})$ is the potential energy of the molecule when its configuration is τ , in the presence of the electric field gradient $E_{zz} = -E_{xx}$.

For molecules with quadrupole moment defined by (7) we have, on restricting ourselves to the term linear in the field gradient only,

$$u(\tau, E_{zz}) = u(\tau, 0) - \frac{1}{3}\Theta_{\alpha\beta}E_{\alpha\beta} = u(\tau, 0) - \frac{1}{3}\Theta_{\alpha\beta}(k_\alpha k_\beta - i_\alpha i_\beta) E_{zz}, \quad (10)$$

where \mathbf{i} and \mathbf{k} are unit vectors in the directions of the X and Z axes of the laboratory system, respectively.

Analogously, in the same approximation, the differential polarizability of the molecule is

$$\frac{\partial m_\alpha}{\partial E_\beta} = \alpha_{\alpha\beta} + \frac{1}{3}B_{\alpha\beta;\gamma\delta}E_{\gamma\delta} = \alpha_{\alpha\beta} + \frac{1}{3}B_{\alpha\beta;\gamma\delta}(k_\gamma k_\delta - i_\gamma i_\delta) E_{zz}, \quad (11)$$

with $\alpha_{\alpha\beta}$ standing for the polarizability tensor of the isolated molecule, and $B_{\alpha\beta;\gamma\delta}$ for its hyperpolarizability tensor. The tensor $B_{\alpha\beta;\gamma\delta}$, which describes the change in polarizability caused by the electric field gradient, was introduced and discussed for spherical and axially symmetric molecules by Buckingham⁶⁾.

By (10) and (11), eq. (8) yields to within E_{zz} on averaging over all possible orientations of the molecule with respect to the axes of the laboratory system (see Appendix),

$$\begin{aligned} I(E_{zz}) = & \left(\frac{2\pi}{\lambda}\right)^4 \frac{NI_0}{90R_0^2} \left\{ 90f_1\alpha^2 + f_2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) + \right. \\ & + 12g_1\alpha \left(B_{\alpha\beta;\alpha\beta} + \frac{1}{3\alpha} B_{\alpha\alpha;\beta\gamma}\alpha_{\beta\gamma} + \frac{1}{kT} \alpha_{\alpha\beta}\Theta_{\alpha\beta} \right) E_{zz} + \\ & + \frac{2}{7}(3g_2 - 2g_1) \left[2(3\alpha_{\alpha\beta}B_{\alpha\gamma;\beta\gamma} - \alpha_{\alpha\alpha}B_{\beta\gamma;\beta\gamma} - B_{\alpha\alpha;\beta\gamma}\alpha_{\beta\gamma}) + \right. \\ & \left. \left. + \frac{1}{kT} (3\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\Theta_{\beta\gamma} - 2\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\Theta_{\beta\gamma}) \right] E_{zz} \right\}, \quad (12) \end{aligned}$$

wherein $\alpha = \frac{1}{3}\alpha_{\alpha\alpha}$ is the mean polarizability of the molecule, and

$$\begin{aligned} f_1 &= (\mathbf{n} \cdot \mathbf{e})^2, \quad g_1 = (\mathbf{n} \cdot \mathbf{e})[(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k}) - (\mathbf{n} \cdot \mathbf{i})(\mathbf{e} \cdot \mathbf{i})], \\ f_2 &= 3 + (\mathbf{n} \cdot \mathbf{e})^2, \quad g_2 = (\mathbf{n} \cdot \mathbf{k})^2 + (\mathbf{e} \cdot \mathbf{k})^2 - (\mathbf{n} \cdot \mathbf{i})^2 - (\mathbf{e} \cdot \mathbf{i})^2. \end{aligned} \quad (13)$$

Eq. (12) holds for a gas the molecules of which possess arbitrary symmetry and for arbitrary conditions of observation of the light scattered.

If, in particular, the molecules present the spherical symmetry,

$$\begin{aligned} \alpha_{\alpha\beta} &= \alpha\delta_{\alpha\beta}, \quad \Theta_{\alpha\beta} = 0, \\ B_{\alpha\beta:\gamma\delta} &= \frac{1}{4}B(-2\delta_{\alpha\beta}\delta_{\gamma\delta} + 3\delta_{\alpha\gamma}\delta_{\beta\delta} + 3\delta_{\alpha\delta}\delta_{\beta\gamma}), \end{aligned} \quad (14)$$

and eq. (12) reduces to

$$I(E_{zz}) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{R_0^2} \left\{ f_1 + g_1 \frac{B}{\alpha} E_{zz} \right\}, \quad (15)$$

$B = \frac{2}{15}B_{\alpha\beta:\alpha\beta}$ being the mean hyperpolarizability of the molecule. At zero field gradient ($E_{zz} = 0$), eq. (15) reduces to the well-known Rayleigh formula⁹⁾.

In the case of strongly anisotropic molecules, we are justified in omitting the numerically small terms relating to the tensor $B_{\alpha\beta:\gamma\delta}$ in eq. (12); on assuming moreover the axial symmetry, we obtain

$$I(E_{zz}) = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{5R_0^2} \left\{ 5f_1 + f_2\kappa^2 + \frac{\kappa\Theta}{7kT} [14g_1 + (3g_2 - 2g_1)\kappa] E_{zz} \right\}, \quad (16)$$

since

$$\begin{aligned} \alpha_{\alpha\beta} &= \alpha\{\delta_{\alpha\beta} + \kappa(3s_\alpha s_\beta - \delta_{\alpha\beta})\}, \\ \Theta_{\alpha\beta} &= \frac{1}{2}\Theta(3s_\alpha s_\beta - \delta_{\alpha\beta}). \end{aligned} \quad (17)$$

Herein, $\kappa = (\alpha_{\parallel} - \alpha_{\perp})/3\alpha$ is the anisotropy of polarizability of the axially symmetric molecule, $\Theta = \Theta_{33} = -2\Theta_{11} = -2\Theta_{22}$ is its quadrupole moment, and \mathbf{s} is the unit vector along the axis of symmetry.

§ 3. *Depolarization ratio.* Our problem now consists in calculating the appropriate measurable quantity and in choosing, to our best advantage, the conditions of observation of the scattered light. Thus, let us assume for simplicity that the incident light beam is polarized and propagates in the X-axis direction with its electric vector oscillating at the angle φ to the Z-axis, $\mathbf{e} = \mathbf{j} \sin \varphi + \mathbf{k} \cos \varphi$. If scattered light observation is carried out along the Y-axis, the depolarization ratio is defined as the ratio of the scattered intensity component oscillating in the direction of the X-axis ($\mathbf{n} = \mathbf{i}$) and the component oscillating along the Z-axis ($\mathbf{n} = \mathbf{k}$). By eq. (16), these components are of the form:

$$I_x = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{5R_0^2} \left\{ 3\kappa^2 + \frac{3\kappa^2 \Theta}{7kT} (\cos^2 \varphi - 1) E_{zz} \right\}, \quad (18)$$

$$I_z = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{5R_0^2} \left\{ 3\kappa^2 + (5 + \kappa^2) \cos^2 \varphi + \frac{\kappa \Theta}{7kT} [3\kappa + (14 + \kappa) \cos^2 \varphi] E_{zz} \right\}. \quad (19)$$

Since

$$D(E_{zz}) = \frac{I_x}{I_z} = D_0 + \left\{ \frac{1}{I_z} \left(\frac{dI_x}{dE_{zz}} - \frac{I_x}{I_z} \frac{dI_z}{dE_{zz}} \right) \right\}_{E_{zz}=0} E_{zz}, \quad (20)$$

we have by eqs. (18) and (19) for the case of a gas of axially symmetric molecules

$$D(E_{zz}) = D_0 \left\{ 1 - \frac{\Theta}{21kT} [3(1 - \cos^2 \varphi + D_0) + (1 + 14\kappa^{-1}) D_0 \cos^2 \varphi] E_{zz} \right\}, \quad (21)$$

with

$$D_0 = \left\{ \frac{I_x}{I_z} \right\}_{E_{zz}=0} = \frac{3\kappa^2}{3\kappa^2 + (5 + \kappa^2) \cos^2 \varphi} \quad (22)$$

denoting the depolarization ratio of the light scattered in the absence of an external electric field ($E_{zz} = 0$).

If, in particular, the electric vector of the incident light beam oscillates in a plane parallel to the Z-axis ($\varphi = 0$), eqs. (21) and (22) become

$$D(E_{zz}) = D_0 \left\{ 1 - \frac{2\Theta}{21kT} (2 + 7\kappa^{-1}) D_0 E_{zz} \right\}, \quad (23)$$

$$D_0 = \frac{3\kappa^2}{5 + 4\kappa^2}. \quad (24)$$

Eqs. (21) and (22) undergo extreme simplification with the plane of oscillation of the incident beam parallel to the Y-axis ($\varphi = 90^\circ$), i.e. when conditions are as shown in fig. 1*b*. Indeed, we now have $D_0 = 1$ and

$$D(E_{zz}) = 1 - \frac{2\Theta}{7kT} E_{zz}. \quad (25)$$

Here, the change in depolarization ratio due to the electric field gradient is seen to depend directly on the ratio of the quadrupole moment and kT . Thus, eq. (25) provides a simple, direct method of measuring the value of the quadrupole moment of the molecule and of determining its sign.

If the incident light is non-polarized, $\cos^2 \varphi$ has to be replaced by $\frac{1}{2}$ in eqs. (21) and (22), yielding

$$D(E_{zz}) = D_0 \left\{ 1 - \frac{\Theta}{42kT} [3 + 7(1 + 2\kappa^{-1}) D_0] E_{zz} \right\}, \quad (26)$$

$$D_0 = \frac{6\kappa^2}{5 + 7\kappa^2}. \quad (27)$$

Eqs. (24) and (27) are the well-known Gans-Cabannes formulas⁹⁾.

Let us now consider light scattering by a gas consisting of spherical molecules, and assume observation to be carried out at an angle ϑ with the direction of the incident beam. Eq. (15) now yields

$$I_x = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{R_0^2} \sin^2 \varphi \cos^2 \vartheta, \quad (28)$$

$$I_z = \left(\frac{2\pi}{\lambda}\right)^4 \frac{\alpha^2 N I_0}{R_0^2} \left\{ 1 + \frac{B}{\alpha} E_{zz} \right\} \cos^2 \varphi, \quad (29)$$

and, by (20), we have

$$D(E_{zz}) = \left(1 - \frac{B}{\alpha} E_{zz}\right) \cos^{-2} \varphi \sin^2 \varphi \cos^2 \vartheta. \quad (30)$$

If the incident light is non-polarized, this yields the formula

$$D(E_{zz}) = \left(1 - \frac{B}{\alpha} E_{zz}\right) \cos^2 \vartheta \quad (31)$$

admitting of direct determination of the hyperpolarizability B induced in the spherical molecule by an electric field gradient.

§ 4. *Rayleigh's ratio.* Rayleigh's ratio or the scattering ratio is defined as

$$S = \frac{(I_x + I_z) R_0^2 \rho}{N I_0}; \quad (32)$$

herein, $\rho = N/V$ is the number density of the scattering gas. On substitution of (28) and (29) herein, we obtain, for molecules having the spherical symmetry,

$$S(E_{zz}) = \left(\frac{2\pi}{\lambda}\right)^4 \alpha^2 \rho \left\{ \sin^2 \varphi \cos^2 \vartheta + \left(1 + \frac{B}{\alpha} E_{zz}\right) \cos^2 \varphi \right\}. \quad (33)$$

For non-polarized incident light and perpendicular observation ($\vartheta = 90^\circ$), eq. (33) reduces to

$$S(E_{zz}) = S_0^{is} \left(1 + \frac{B}{\alpha} E_{zz}\right), \quad (34)$$

with

$$S_0^{is} = \frac{1}{2} \left(\frac{2\pi}{\lambda}\right)^4 \alpha^2 \rho \quad (35)$$

denoting Rayleigh's ratio for isotropically polarizable molecules scattering at zero external electric field. On rewriting eq. (34) in the form

$$\frac{S_0^{is}(E_{zz}) - S_0^{is}}{S_0^{is}} = \frac{B}{\alpha} E_{zz}, \quad (36)$$

we see that measurement of the relative change in Rayleigh's ratio produced by an electric field gradient yields directly the value of the hyperpolarizability B of a spherical molecule, since its mean polarizability α is generally known from molecular refraction.

By (18), (19) and the definition of eq. (32), we have for the quadrupolar gas

$$S(E_{zz}) = \frac{1}{5} \left(\frac{2\pi}{\lambda} \right)^4 \alpha^2 \rho \left\{ 6\kappa^2 + (5 + \kappa^2) \cos^2\varphi + \frac{2\kappa\Theta}{7kT} (7 + 2\kappa) \cos^2\varphi E_{zz} \right\}. \quad (37)$$

For natural light $\cos^2\varphi = \frac{1}{2}$, and

$$S(E_{zz}) = S_0^{is} \left\{ 1 + \frac{13}{5} \kappa^2 + \frac{2\kappa\Theta}{35kT} (7 + 2\kappa) E_{zz} \right\}, \quad (38)$$

whereas, for polarized light of which the oscillations are parallel to the Z-axis,

$$S(E_{zz}) = 2S_0^{is} \left\{ 1 + \frac{7}{5} \kappa^2 + \frac{2\kappa\Theta}{35kT} (7 + 2\kappa) E_{zz} \right\}. \quad (39)$$

For incident light oscillating in the plane of observation ($\varphi = 90^\circ$), eq. (37) yields

$$S = \frac{12}{5} S_0^{is} \kappa^2. \quad (40)$$

In this particular case the Rayleigh ratio is seen to remain unaffected by the field gradient. This is so because, by eqs. (18) and (19) at $\varphi = 90^\circ$, the contributions to the components I_x and I_z from the latter are equal but of opposite sign, thus cancelling out.

Eqs. (23), (26), (38) and (39) are seen not to depend on the molecule's quadrupole moment Θ alone, but to contain moreover the anisotropy of polarizability κ which, obviously, can always be determined from Kerr's constant or from eq. (24) or (27).

One may consider eqs. (12), (15) and (16) for cases described by various other conditions, possibly even better adapted to experimental investigation. E.g., the incident beam might propagate along the Y-axis, parallel to the axis of the condenser $l(b)$, with observation taking place in the XY-plane or in a plane forming some angle with the latter.

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APPENDIX

Expanding the right hand side of eq. (8) in powers of E_{zz} and on taking into account (10) and (11) we have, to within terms linear in E_{zz} ,

$$\begin{aligned}
 I(E_{zz}) = & \left(\frac{2\pi}{\lambda}\right)^4 \frac{NI_0}{R_0^2} \left\{ \alpha_{\alpha\gamma}\alpha_{\beta\delta} \langle n_\alpha n_\beta e_\gamma e_\delta \rangle + \right. \\
 & + \frac{1}{3}(\alpha_{\alpha\gamma}B_{\beta\delta:\epsilon\eta} + \alpha_{\beta\delta}B_{\alpha\gamma:\epsilon\eta}) \langle n_\alpha n_\beta e_\gamma e_\delta (k_\epsilon k_\eta - i_\epsilon i_\eta) \rangle E_{zz} + \\
 & + \frac{1}{3kT} \alpha_{\alpha\gamma}\alpha_{\beta\delta}\Theta_{\epsilon\eta} [\langle n_\alpha n_\beta e_\gamma e_\delta (k_\epsilon k_\eta - i_\epsilon i_\eta) \rangle - \\
 & \left. - \langle n_\alpha n_\beta e_\gamma e_\delta \rangle \langle k_\epsilon k_\eta - i_\epsilon i_\eta \rangle] E_{zz} + \dots \right\}. \tag{A.1}
 \end{aligned}$$

In the expansion, the respective products of the components n_α , e_α , i_α and k_α have still to be averaged over all possible directions of the unit vectors \mathbf{n} , \mathbf{e} , \mathbf{i} and \mathbf{k} ; this yields

$$\begin{aligned}
 \langle i_\alpha i_\beta \rangle = & \langle k_\alpha k_\beta \rangle = \frac{1}{3}\delta_{\alpha\beta}, \\
 \langle n_\alpha n_\beta e_\gamma e_\delta \rangle = & \frac{1}{30}\{2[2 - (\mathbf{n} \cdot \mathbf{e})^2] \delta_{\alpha\beta}\delta_{\gamma\delta} + [3(\mathbf{n} \cdot \mathbf{e})^2 - 1](\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})\}, \\
 \langle n_\alpha n_\beta e_\gamma e_\delta k_\epsilon k_\eta \rangle = & \frac{1}{210}\{2[8 - 5(\mathbf{n} \cdot \mathbf{e})^2 - 5(\mathbf{n} \cdot \mathbf{k})^2 - 5(\mathbf{e} \cdot \mathbf{k})^2 + \\
 & + 8(\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k})] \delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\eta} + [-5 + 4(\mathbf{n} \cdot \mathbf{e})^2 + 4(\mathbf{n} \cdot \mathbf{k})^2 + 11(\mathbf{e} \cdot \mathbf{k})^2 - \\
 & - 12(\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k})] \delta_{\alpha\beta}(\delta_{\gamma\epsilon}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\delta\epsilon}) + \\
 & + [-5 + 4(\mathbf{n} \cdot \mathbf{e})^2 + 4(\mathbf{e} \cdot \mathbf{k})^2 + 11(\mathbf{n} \cdot \mathbf{k})^2 - 12(\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k})] \delta_{\gamma\delta}(\delta_{\alpha\epsilon}\delta_{\beta\eta} + \\
 & + \delta_{\alpha\eta}\delta_{\beta\epsilon}) + [-5 + 4(\mathbf{e} \cdot \mathbf{k})^2 + 4(\mathbf{n} \cdot \mathbf{k})^2 + 11(\mathbf{n} \cdot \mathbf{e})^2 - 12(\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k})] \times \\
 & \times \delta_{\epsilon\eta}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + [2 - 3(\mathbf{n} \cdot \mathbf{e})^2 - 3(\mathbf{n} \cdot \mathbf{k})^2 - 3(\mathbf{e} \cdot \mathbf{k})^2 + \\
 & + 9(\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \cdot \mathbf{k})(\mathbf{e} \cdot \mathbf{k})][\delta_{\alpha\gamma}(\delta_{\beta\epsilon}\delta_{\delta\eta} + \delta_{\beta\eta}\delta_{\delta\epsilon}) + \\
 & + \delta_{\alpha\delta}(\delta_{\beta\epsilon}\delta_{\gamma\eta} + \delta_{\beta\eta}\delta_{\gamma\epsilon}) + \delta_{\alpha\epsilon}(\delta_{\beta\gamma}\delta_{\delta\eta} + \delta_{\gamma\eta}\delta_{\beta\delta}) + \\
 & + \delta_{\alpha\eta}(\delta_{\beta\gamma}\delta_{\delta\epsilon} + \delta_{\gamma\epsilon}\delta_{\beta\delta})\}], \tag{A.2}
 \end{aligned}$$

where $\delta_{\alpha\beta}$ is a unit tensor whose components are unity for $\alpha = \beta$ and zero for $\alpha \neq \beta$. Since the tensors $\alpha_{\alpha\beta}$ and $\Theta_{\alpha\beta}$ are entirely symmetrical, while $B_{\alpha\beta:\gamma\delta}$ is symmetrical in the pairs of indices α, β and γ, δ , and since $\delta_{\alpha\beta}\Theta_{\alpha\beta} = \delta_{\gamma\delta}B_{\alpha\beta:\gamma\delta} = 0$, we have, by (A.2),

$$\begin{aligned}
 \alpha_{\alpha\gamma}\alpha_{\beta\delta} \langle n_\alpha n_\beta e_\gamma e_\delta \rangle = & \frac{1}{90}\{90f_1\alpha^2 + f_2(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta})\}, \\
 \alpha_{\alpha\gamma}B_{\beta\delta:\epsilon\eta} \langle n_\alpha n_\beta e_\gamma e_\delta (k_\epsilon k_\eta - i_\epsilon i_\eta) \rangle = & \frac{1}{105}\{7g_1(\alpha_{\alpha\alpha}B_{\beta\gamma:\beta\gamma} + \\
 & + B_{\alpha\alpha:\beta\gamma}\alpha_{\beta\gamma}) + (3g_2 - 2g_1)(3\alpha_{\alpha\beta}B_{\alpha\gamma:\beta\gamma} - \alpha_{\alpha\alpha}B_{\beta\gamma:\beta\gamma} - B_{\alpha\alpha:\beta\gamma}\alpha_{\beta\gamma})\}, \\
 \alpha_{\alpha\gamma}\alpha_{\beta\delta}\Theta_{\epsilon\eta} \langle n_\alpha n_\beta e_\gamma e_\delta (k_\epsilon k_\eta - i_\epsilon i_\eta) \rangle = & \frac{1}{105}\{42g_1\alpha_{\alpha\beta}\Theta_{\alpha\beta} + \\
 & + (3g_2 - 2g_1)(3\alpha_{\alpha\beta}\alpha_{\alpha\gamma}\Theta_{\beta\gamma} - 2\alpha_{\alpha\alpha}\alpha_{\beta\gamma}\Theta_{\beta\gamma})\}, \tag{A.3}
 \end{aligned}$$

wherein the functions f_1 , f_2 , g_1 and g_2 are given by (13). Substitution of (A.3) in the expansion (A.1) immediately yields eq. (12).

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