Notes on Optical Constants. By Mr C. G. DARWIN, F.R.S., Tait Professor of Natural Philosophy in the University of Edinburgh.

II. *The Lateral Scattering from a Gas.*

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1. The tensor calculus introduced in a recent paper* proves a powerful method of investigating the light scattered laterally as exemplified in the blue of the sky. The late Lord Rayleigh† worked out the effect on the polarisation of having non-spherical molecules, and the present note is practically a repetition of his work but with a somewhat greater generality. The method has the advantage that it does not become unmanageable for molecules of a more complicated type of asymmetry, whereas a perusal of his work suggests that it would be a very complicated matter to give the lateral scattering from a set of arbitrary orientated "optically active" molecules. As this case has at present no practical interest, I have merely indicated the procedure so that it could easily be applied when required.

The calculations depend on the fact that laterally the waves from the molecules are all out of phase, and therefore the intensity is simply the sum of the intensities from each of them. The total intensity can be measured, but the most accurate observation is to study the degree of polarisation observed at right angles to the incident beam. This has been done by the present Lord Rayleigh‡, and we shall here give a short discussion of his results, following in general the lines laid down by his father before these experiments had been made.

2. We define the wave scattered by a molecule by the equation

$$\Pi_\beta = \rho_{\alpha\beta} E_\alpha^0 e^{ik(ct-r)}/r.$$

Here E_α^0 is the periodic electric force at the molecule, Π_β is the Hertzian vector of the scattered wave and $\rho_{\alpha\beta}$ is the molecular scattering tensor. If the atoms were not arbitrarily orientated it would be connected with the scattering index of matter in bulk by the relation $\sigma_{\alpha\beta} = 4\pi N \rho_{\alpha\beta}$, where N is the number of molecules in unit volume. We are assuming that the scattering indices form a tensor of the second rank only and are thus excluding natural gyration, but an inherent magnetic gyration is admissible.

* "The Optical Constants of Matter," *Camb. Phil. Soc. Trans.* vol. XXIII, p. 137 (1924). I use the notation of that work without explanation, marking references with a *.

† Rayleigh, *Phil. Mag.* vol. XXXV, p. 373 (1918).

‡ Rayleigh, *Proc. Roy. Soc.* A, 97, p. 435 (1920).

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Take a set of permanent axes x, and a second set x' which are fixed to the molecule and so are arbitrarily orientated with regard to x. Let the connecting direction cosines be given by

$$x_\alpha = l_{\alpha\phi} x_\phi' \qquad \text{.....(2·1).}$$

The constants ρ refer to the x' axes. For these axes the incident force has components $E_\phi' = l_{\alpha\phi} E_\alpha^0$ and the scattered wave is thus

$$\Pi_\chi' = \rho_{\phi\chi} l_{\alpha\phi} E_\alpha^0 e^{ik(ct-r)}/r.$$

Transforming back we have

$$\Pi_\beta = \rho_{\phi\chi} l_{\alpha\phi} l_{\beta\chi} E_\alpha^0 e^{ik(ct-r)}/r \qquad \text{.....(2·2).}$$

We first find the refractive index. To do this we must average over all orientations and we find as the scattering indices

$$\sigma_{\alpha\beta} = 4\pi N \rho_{\phi\chi} \overline{l_{\alpha\phi} l_{\beta\chi}},$$

$\overline{l_{\alpha\phi} l_{\beta\chi}}$ vanishes unless $\alpha = \beta$ and $\phi = \chi$ and in that case it is $\frac{1}{3}$. We thus put

$$\overline{l_{\alpha\phi} l_{\beta\chi}} = \tfrac{1}{3} (\alpha\beta)(\phi\chi) \qquad \text{.....(2·3),}$$

and have

$$\sigma_{\alpha\beta} = \frac{4\pi}{3} N \rho_{\phi\phi} (\alpha\beta).$$

Thus the refractive index is

$$\frac{3(n^2-1)}{n^2+2} = \frac{4\pi}{3} N (\rho_{11} + \rho_{22} + \rho_{33}) \qquad \text{.....(2·4).}$$

3. We next examine the wave emitted by a single atom so as to obtain the intensities of its polarised components. We do this for a point at a great distance from the molecule in a direction of which the cosines are m_α. Then in carrying out the differentiations it suffices to write

$$\frac{\partial}{\partial x_\alpha} \frac{e^{ik(ct-r)}}{r} \text{ as } -ikm_\alpha \frac{e^{ik(ct-r)}}{r}$$

We have

$$E_\kappa = k^2 \Pi_\kappa - \frac{\partial^2 \Pi_\beta}{\partial x_\kappa \partial x_\beta} = k^2 \rho_{\phi\chi} l_{\alpha\phi} l_{\beta\chi} E_\alpha^0 \{(\beta\kappa) - m_\beta m_\kappa\} \frac{e^{ik(ct-r)}}{r} \qquad (3·1).$$

The intensity of the wave is proportional to the product of this by its conjugate. We denote the conjugate of $\rho_{\phi\chi}$ as $\tilde{\rho}_{\phi\chi}$ etc. and have

$$I_\kappa = \frac{k^4}{r^2} \rho_{\phi\chi} \tilde{\rho}_{\psi\omega} l_{\alpha\phi} l_{\beta\chi} l_{\gamma\psi} l_{\delta\omega} E_\alpha^0 \tilde{E}_\gamma^0 \{(\beta\kappa) - m_\beta m_\kappa\} \{(\delta\kappa) - m_\delta m_\kappa\} \quad (3·2),$$

where the expression is *not summed for* κ. This expression is to be averaged for all orientations, and this averaging constituted the troublesome part of the problem. It was carried out by Rayleigh

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by using the Eulerian angles, but the tensor calculus will simplify the procedure a great deal.

4. We require the average value of $l_{\alpha\phi} l_{\beta\chi} l_{\gamma\psi} l_{\delta\omega}$, say $T^{\alpha\beta\gamma\delta}_{\phi\chi\psi\omega}$. This is evidently a tensor of the eighth rank. The only quantities on which it can depend are "spherical tensors" $(\alpha\beta)$, etc. T must therefore be a sum of terms each involving four factors and containing all the eight letters. The x and x' axes are quite independent so that we shall not get factors like $(\alpha\phi)$ at all. A high degree of symmetry will exist, for α is quite indifferent to χ, ψ, ω though it has a special relationship with ϕ. There are two tensors only satisfying these conditions, viz.:

$$T_1 = (\alpha\beta)(\gamma\delta)(\phi\chi)(\psi\omega) + (\alpha\gamma)(\beta\delta)(\phi\psi)(\chi\omega) + (\alpha\delta)(\beta\gamma)(\phi\omega)(\chi\psi) \quad \ldots\ldots(4{\cdot}1),$$

$$T_2 = (\alpha\beta\gamma\delta)(\phi\chi\psi\omega) \quad \ldots\ldots(4{\cdot}2),$$

where $(\alpha\beta\gamma\delta)$ is short for

$$(\alpha\beta)(\gamma\delta) + (\alpha\gamma)(\beta\delta) + (\alpha\delta)(\beta\gamma) \quad \ldots\ldots(4{\cdot}3).$$

It follows that $T^{\alpha\beta\gamma\delta}_{\phi\chi\psi\omega} = AT_1 + BT_2$, where A, B are two numerical constants. To determine them we have to evaluate two special cases. This can be done by the use of the Eulerian angles; but this is unnecessary, for we need only start by evaluating $\overline{l_{11}{}^2} = \frac{1}{3}$, $\overline{l_{11}{}^4} = \frac{1}{5}$. Then $\overline{l_{11}{}^2(l_{11}{}^2 + l_{12}{}^2 + l_{13}{}^2)} = \frac{1}{3}$ and so $\overline{l_{11}{}^2 l_{12}{}^2} = \frac{1}{15}$. Next $\overline{l_{11}{}^2(l_{12}{}^2 + l_{22}{}^2 + l_{32}{}^2)} = \frac{1}{3}$, so that $\overline{l_{11}{}^2 l_{22}{}^2} = \frac{2}{15}$. If we take this last and $\overline{l_{11}{}^4} = \frac{1}{5}$ (the intermediate relation does not give a separate equation) and substitute in the tensor formula we find

$$T^{\alpha\beta\gamma\delta}_{\phi\chi\psi\omega} = \tfrac{1}{6} T_1 - \tfrac{1}{30} T_2 \quad \ldots\ldots(4{\cdot}4).$$

Of course with only four factors it is quite possible to treat the matter in detail—there is only one other type of non-vanishing average $\overline{l_{11}\, l_{12}\, l_{21}\, l_{22}} = -\frac{1}{30}$. But if we required an average of six factors there are a great many types that do not vanish and it is troublesome to be sure that none have been overlooked. We require to work out three special cases here, and the resulting formula is

$$l_{\alpha\phi} l_{\beta\chi} l_{\gamma\psi} l_{\delta\omega} l_{\zeta\tau} l_{\eta\upsilon} = T^{\alpha\beta\gamma\delta\zeta\eta}_{\phi\chi\psi\omega\tau\upsilon} = \tfrac{1}{6} T_1 - \tfrac{1}{30} T_2 + \tfrac{1}{105} T_3 \quad \ldots(4{\cdot}5),$$

where

$$T_1 = (\alpha\beta)(\gamma\delta)(\zeta\eta)(\phi\chi)(\psi\omega)(\tau\upsilon) + \ldots,$$

$$T_2 = (\alpha\beta)(\phi\chi)(\gamma\delta\zeta\eta)(\psi\omega\tau\upsilon) + \ldots,$$

$$T_3 = (\alpha\beta\gamma\delta\zeta\eta)(\phi\chi\psi\omega\tau\upsilon).$$

In this $(\alpha\beta\gamma\delta\zeta\eta)$ means the sum of the fifteen expressions of the type $(\alpha\beta)(\gamma\delta)(\zeta\eta)$. It will readily be believed that without some process of the present kind the matter would become impossible. These tensors come in if it is required to evaluate the scattering

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from an optically active molecule, and I have in fact worked out the solution quite easily, but the result is not of sufficient interest to give here.

We may also note that similar formulae can be found when there is an odd number of factors, but these involve the curl tensor. For example,

$$\overline{l_{a\phi} l_{\beta\chi} l_{\gamma\psi}} = \tfrac{1}{6} [\alpha\beta\gamma] [\phi\chi\psi] \qquad \text{.....(4·6),}$$

a result which we shall use later.

5. We shall now apply our result to (3·2) and have (not summing for κ)

$$I_\kappa = \frac{Nk^4}{30r^2} \rho_{\phi\chi} \tilde{\rho}_{\psi\omega} E_a{}^0 \tilde{E}_\gamma{}^0 \{(\beta\kappa) - m_\beta m_\kappa\} \{(\delta\kappa) - m_\delta m_\kappa\} (5T_1 - T_2)$$

.....(5·1).

Take the force of the incident wave along x_1. Then we can put $\alpha = 1$, $\gamma = 1$ and $E_a{}^0 \tilde{E}_\gamma{}^0 = I_0$ the incident intensity. First observe from the direction x_2, so that $m_1 = m_3 = 0$, $m_2 = 1$. Take the strong component, which is that polarised along x_1. Then $\kappa = 1$ and the terms in m_κ drop out. It follows that $\beta = \delta = 1$. We now have T_1 as $(\phi\chi)\,(\psi\omega) + (\phi\psi)\,(\chi\omega) + (\phi\omega)\,(\chi\psi) = (\phi\chi\psi\omega)$ since all the other factors in the terms are unity. In T_2 we have $(\alpha\beta\gamma\delta) = 3$. Thus

$$\frac{I_1}{I_0} = \frac{Nk^4}{30r^2} \rho_{\phi\chi} \tilde{\rho}_{\psi\omega} \cdot 2(\phi\chi\psi\omega) = \frac{1}{15} \frac{Nk^4}{r^2} \{\rho_{\phi\phi} \tilde{\rho}_{\psi\psi} + \rho_{\phi\chi} \tilde{\rho}_{\phi\chi} + \rho_{\phi\chi} \tilde{\rho}_{\chi\phi}\}$$

.....(5·2).

Next take the weak component, for which $\kappa = 3$. Again the terms in m_κ drop out, but now we have to put $\beta = \delta = 3$. In this case the only factors that do not vanish are $(\alpha\gamma)$, $(\beta\delta)$, and so we have

$$T_1 = (\phi\psi)\,(\chi\omega), \qquad T_2 = (\phi\chi\psi\omega),$$

and therefore

$$\frac{I_3}{I_0} = \frac{1}{30} \frac{Nk^4}{r^2} \rho_{\phi\chi} \tilde{\rho}_{\psi\omega} \{5\,(\phi\psi)\,(\chi\omega) - [(\phi\chi)\,(\psi\omega) + (\phi\psi)\,(\chi\omega) + (\phi\omega)\,(\chi\psi)]\}$$

$$= \frac{1}{30} \frac{Nk^4}{r^2} \{4\rho_{\phi\chi} \tilde{\rho}_{\phi\chi} - \rho_{\phi\phi} \tilde{\rho}_{\psi\psi} - \rho_{\phi\chi} \tilde{\rho}_{\chi\phi}\} \qquad \text{.....(5·3).}$$

Lastly, take the observation along the direction x_1 and consider the component along x_3. Then $m_1 = 1$, $m_2 = m_3 = 0$, and again the terms in m_κ drop out. We have to take $\beta = \delta = 3$ and it is obvious that we shall get the same value as (5·3).

If now our gas is illuminated by unpolarised light going along x_3 and observed along x_2 we shall have as the two components $I_1 + I_3$ along x_1 and $2I_3$ along x_3. Thus the ratio of the intensity of the two components will be

$$P = \frac{2I_3}{I_1 + I_3} = 2 \cdot \frac{4\rho_{\phi\chi} \tilde{\rho}_{\phi\chi} - \rho_{\phi\phi} \tilde{\rho}_{\chi\chi} - \rho_{\phi\chi} \tilde{\rho}_{\chi\phi}}{6\rho_{\phi\chi} \tilde{\rho}_{\phi\chi} + \rho_{\phi\phi} \tilde{\rho}_{\chi\chi} + \rho_{\phi\chi} \tilde{\rho}_{\chi\phi}} \qquad \text{...(5·4).}$$

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For a substance composed of transparent non-magnetic molecules we have $\rho_{\phi\chi} = \rho_{\chi\phi}$ and the ρ's are all real. We choose principal axes and write $\rho_{11} = A$, $\rho_{22} = B$, $\rho_{33} = C$. Then

$$P = 2 . \frac{[3(A^2+B^2+C^2) - (A+B+C)^2]}{7(A^2+B^2+C^2) + (A+B+C)^2}$$

$$= 2 . \frac{A^2+B^2+C^2-BC-CA-AB}{4(A^2+B^2+C^2)+BC+CA+AB} \quad \ldots(5{\cdot}5),$$

which is the formula given by Rayleigh. Since $A+B+C$, or $\rho_{\phi\phi}$, can be calculated from the refractive index, an observation of the polarisation enables us to find

$$(B-C)^2 + (C-A)^2 + (A-B)^2.$$

6. We shall now apply these results to the experiments of Lord Rayleigh on the common gases. Among his results are the following:

	H_2	N_2	O_2	CO_2
$100P$	3·83	4·06	9·4	11·7

The most remarkable feature is the great value for oxygen compared with nitrogen. In their ordinary physical properties, boiling point, viscosity, dielectric constant and refractive index (including the position of ultraviolet absorption bands), they are not very dissimilar, and yet we find that the scattering of nitrogen is much more like that of hydrogen, though there many of these properties are widely different. This suggested that the scattering might be associated with the one property in which oxygen differs from the others, its magnetism; we shall show that this cannot be so in the next section, but it will be convenient first to make a more definite calculation of the asymmetry of the various molecules.

In order to do this we suppose the molecule to be like a dielectric spheroid, which we naturally assume to be prolate for a diatomic substance. In a uniform electric field E_1, E_2, E_3 the potential of an ellipsoid at a distant external point is

$$V = E_1 \frac{abc}{3} \frac{1}{L + 1/(K_0-1)} \frac{x_1}{r^3} + E_2 \frac{abc}{3} \frac{1}{M + 1/(K_0-1)} \frac{x_2}{r^3}$$

$$+ E_3 \frac{abc}{3} \frac{1}{N + 1/(K_0-1)} \frac{x_3}{r^3},$$

where L, M, N are the "demagnetising coefficients" given by

$$L = \frac{abc}{2} \int_0^\infty \frac{d\lambda}{(a^2+\lambda)\sqrt{(a^2+\lambda)(b^2+\lambda)(c^2+\lambda)}}, \text{ etc.}$$

and K_0 is the dielectric constant. In our present case we take

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$a > b = c$. From V we can at once set down the Hertzian vector, which leads to

$$A = \frac{ab^2}{3} \frac{1}{L + 1/(K_0 - 1)},$$

$$B = C = \frac{ab^2}{3} \frac{1}{M + 1/(K_0 - 1)}.$$

Since $L + 2M = 1$ we can calculate the ratio $b : a$, if we are given $B : A$ and if we know the value of K_0.

I have worked out two cases. The least possible asymmetry of shape will be that when the molecule is supposed a perfect conductor, and this we obtain by taking $K_0 = \infty$. But a more natural assumption is to take the molecules as having such a dielectric constant as will give rise to the proper value for the gas in bulk, or more accurately, as will give the proper refractive index for the light concerned. There must be a good deal of doubt as to what is the proper volume to assign to the molecule, but in default of better information we take $\frac{1}{4}b$, where b is Van der Waals' constant, as the actual volume of the molecules in a cubic centimetre. If n is the refractive index at normal density we then have, regarding the molecules as spheres for this part of the calculation,

$$\frac{3(K_0 - 1)}{K_0 + 2} = \frac{n^2 - 1}{b/4}.$$

If they are spheroids the relation is more troublesome, but in view of the doubt attaching to Van der Waals' constant, it is not worth while treating the more complicated case. The table shows the results.

	H_2	N_2	O_2	CO_2
$100P$	3·83	4·06	9·40	11·70
B/A	0·60	0·59	0·44	0·40
b/a Cond.	0·65	0·65	0·52	0·48
K_0	3·40	3·90	4·20	6·10
b/a (K_0)	0·31	0·35	0·15	0·23

Of course no great importance attaches to the exact values of the numbers, but still there can be no doubt that the experiments show a very curious difference in the shapes of the nitrogen and oxygen molecules.

7. In ordinary substances a magnetic field produces its optical effects by directly changing the scattering indices of the molecules. But a paramagnetic molecule has a magnetic field of its own and it seemed possible that this might exert an intrinsic gyratory effect —of course of quite a different kind from that corresponding to natural "optical activity." When there is no field the intrinsic gyration will not show itself at all in the propagation of the direct wave, but it would be expected to show itself in the lateral scattering. In a magnetic field the orientation of the molecules should

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lead to an extra term in the gyration. There is independent support for such a suggestion in that though the gyration of oxygen is of the same general magnitude as that of the other gases, yet the dispersion of gyration is quite abnormal and unexplained. We shall show that an intrinsic gyration sufficient to account for the excess of the lateral scattering would lead to a gyration in a magnetic field many hundred times too large.

Let us suppose that the scattering tensor for the oxygen atom is as follows: $\rho_{11} = A$, $\rho_{22} = \rho_{33} = B$, $\rho_{23} = -\rho_{32} = iG$, $\rho_{12} = \ldots = 0$. For a transparent medium G must be real and we can at once apply (5·4) and have

$$P = 2 \cdot \frac{4(A^2+2B^2+2G^2) - (A+2B)^2 - (A^2+2B^2-2G^2)}{6(A^2+2B^2+2G^2) + (A+2B)^2 + (A^2+2B^2-2G^2)}$$
$$= 6 \cdot \frac{(A-B)^2+5G^2}{5(A+2B)^2+7(A-B)^2+15G^2}.$$

We assume that $B : A$ has the same value as for nitrogen, and so can deduce $G/(A+2B)$; and then G can be determined from the refractive index by (2·4).

Let us suppose that each molecule has a magnetic moment μ along the axis x_1', and that a field of strength H acts along x_3. The classical theory then implies a distribution law $e^{l_{31}\mu H/kT}$. It is probable* that we ought to use some quantum law and so shall take for a weak field a distribution $1 + ql_{31}\mu H/kT$, where $q = 1$ on the classical theory. The magnetic moment per unit volume, which measures κ the susceptibility, is

$$\kappa H = N\overline{l_{31}\mu\,(1 + ql_{31}\mu H/kT)} = \tfrac{1}{3}qHN\mu^2/kT,$$

and with μ taken as 2 Bohr magnetons this is roughly correct.

The optical constants are given by

$$\sigma_{\alpha\beta} = 4\pi N\rho_{\phi\chi}\overline{l_{\alpha\phi}l_{\beta\chi}\,(1 + ql_{31}\mu H/kT)}$$

from which we derive by (2·3), (4·6)

$$\sigma_{11} = \sigma_{22} = \sigma_{33} = \sigma = 4\pi N\,(A+2B)/3,$$

and
$$\sigma_{12} = -\sigma_{21} = i\tau_1 = 4\pi Nq\,(\mu H/kT)\,[\tfrac{1}{6}\rho_{23} - \tfrac{1}{6}\rho_{32}]$$
$$= 4\pi N\frac{\kappa H}{N\mu}iG\dagger$$
$$= i\frac{\kappa H}{N\mu}\sigma \cdot \frac{3G}{A+2B},$$

and to this we may add a quantity $i\tau_2$ to represent the direct change in the optical constants produced by the field.

* See Sommerfeld, *Atomic Structure* (Eng. transl.), p. 251.

† If q is a function of the l's, this may not be accurate, but its order of magnitude must be right.

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Siertsema* has measured the gyration of oxygen and, reduced to standard conditions, his result for blue light is

$$\tau = 3{\cdot}37 \times 10^{-14} \times H.$$

The scattering from nitrogen gives $(A - B)/(A + 2B) = 0{\cdot}188$, and using this we find

$$3G/(A + 2B) = 0{\cdot}297.$$

We also have $\sigma = 2\,(n - 1) = 5{\cdot}46 \times 10^{-4}$,

$$\kappa = 1{\cdot}23 \times 10^{-7}.$$

The magnetic moment of a gramme molecule of Bohr magnetons is 5600 E.M.U., and so if we take $\mu = 2$ B.M. we have $N\mu = 0{\cdot}50$.

Hence $\tau_1 = 3{\cdot}99 \times 10^{-11} \times H.$

This is altogether too great, and we conclude that the abnormal scattering from oxygen cannot be explained in this way.

* L. H. Siertsema, *Arch. Neerl.* vol. II, p. 291 (1899).

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