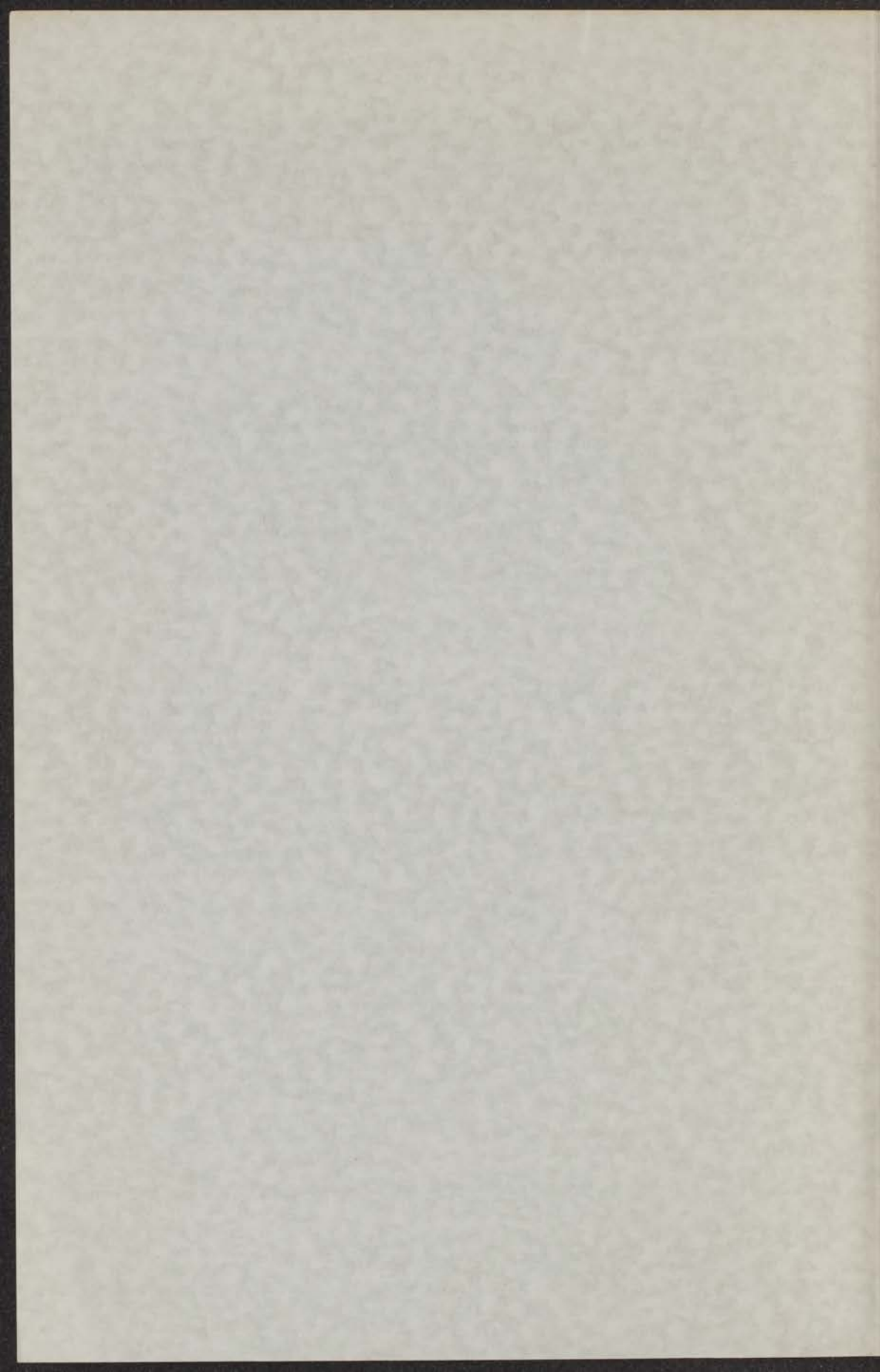# ON THE THEORY
OF OPTICAL ACTIVITY

R. H. TERWIEL

STELLINGEN

I

Het is mogelijk de door Hoek gepostuleerde ontwikkeling van de Hertz-
vector die het secundaire stralingsveld van een molecuul beschrijft streng
te rechtvaardigen.

> H. Hoek, Physica **8** (1941) 209.
> Hoofdstuk I van dit proefschrift.

II

De bewering van Condon dat bij beschouwingen over optische activiteit
alle grootheden waarin het electrische quadrupoolmoment optreedt ver-
waarloosd mogen worden, is onjuist.

> E. U. Condon, Rev. mod. Physics **9** (1937) 432.
> Hoofdstuk I van dit proefschrift.

III

Born's methode van het relatieve electrische dipoolmoment is niet
a priori equivalent met de methode waarbij naast het gewone electrische
moment het magnetische dipoolmoment in aanmerking wordt genomen.
Eerstgenoemde methode kan hooguit *a posteriori* als werkmethode gerecht-
vaardigd worden.

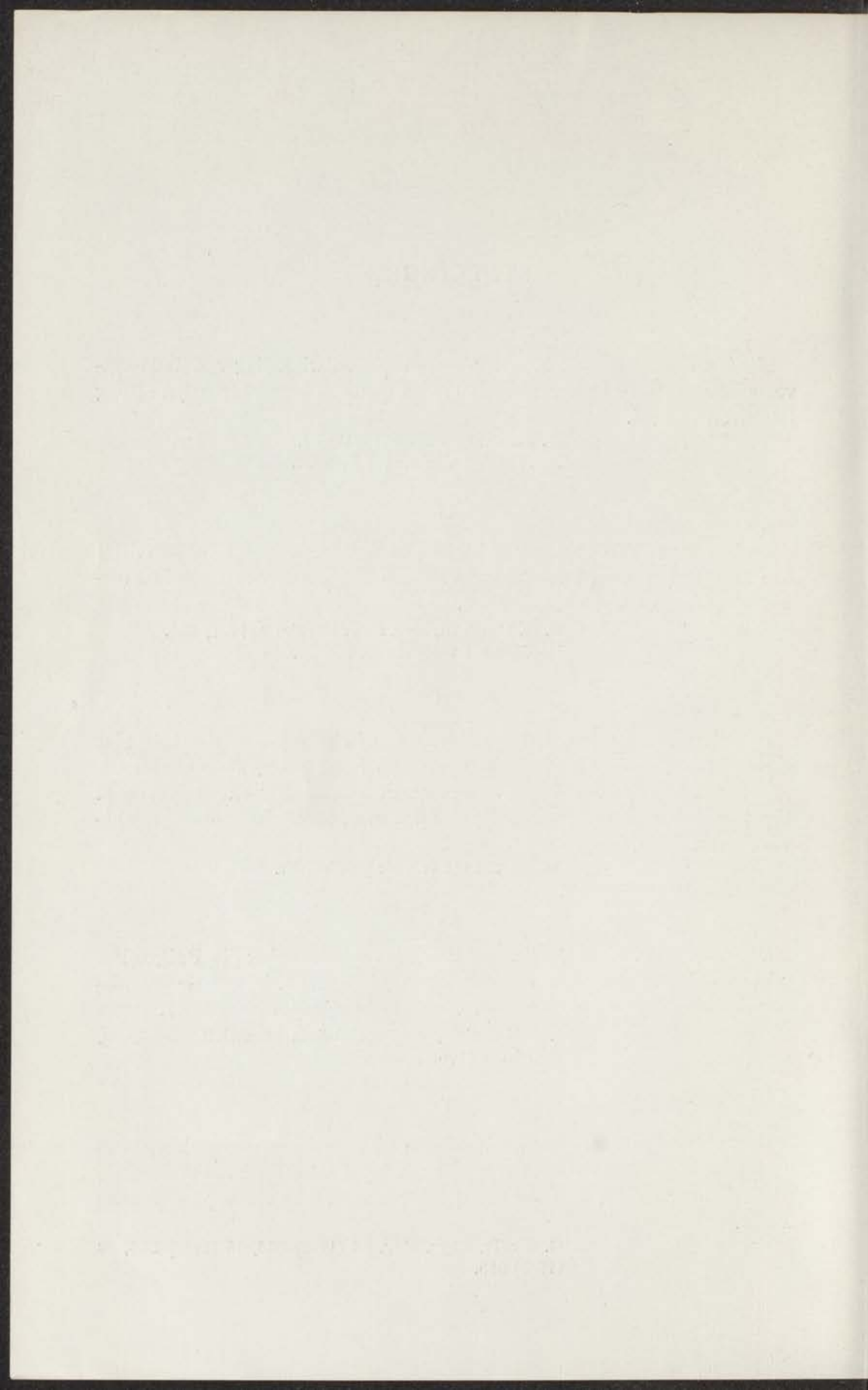> Hoofdstuk III van dit proefschrift.

IV

Voor een anharmonische lineaire keten is de benadering die Prigogine
gebruikt bij het aantonen van een irreversibele evolutie van de energie-
distributiefunctie in het algemeen voor zijn bewijs niet toereikend.

> I. Prigogine, Non-equilibrium statistical mechanics,
> New York (1963).

V

De operator van Breit correspondeert niet met de wisselwerkingsterm
in Darwin's Hamiltoniaan maar met een benadering daarvan waarbij de
wisselwerking tussen de twee deeltjes als een zwakke storing beschouwd
wordt.

> G. Breit, Phys. Rev. **34** (1929) 553, **36** (1930) 383, **39**
> (1932) 616.

VI

De quantum mechanische autocorrelatiefunctie ontleent zijn naam slechts aan de *formele* analogie met de klassieke autocorrelatiefunctie en niet aan de fysische betekenis van het klassieke begrip „autocorrelatiefunctie".

VII

M.b.v. de methode die van Kampen ontwikkeld heeft voor het afleiden van de Mayer-clusterontwikkeling voor een klassiek gas, kan men ook op eenvoudige wijze voor een quantum-gas de viriaalcoëfficiënten, uitgedrukt in clusterintegralen, afleiden.

N. G. van Kampen, Physica **27** (1961) 783.

VIII

Bij het bestuderen van laminaire en turbulente stroming van He II in wijde capillairen volgens de methode van Staas, Taconis en van Alphen, verdient het aanbeveling in de apparatuur een extra thermometer op te nemen.

F. A. Staas, K. W. Taconis en W. M. van Alphen, Physica **27** (1961) 893.

IX

Ten onrechte beweert Vineyard dat de kans dat een random walker op een rooster bij de $(n + 1)^e$ stap op een roosterpunt belandt waar hij nog niet eerder geweest is, gelijk is aan de kans dat hij gedurende de eerste n stappen niet in de oorsprong terugkeert. Hij beroept zich hierbij op een uitspraak van Dvoretzky en Erdös, maar ziet over het hoofd dat bij deze auteurs een "random walk" anders gedefiniëerd is.

A. Dvoretzky en P. Erdös, Second Berkeley Symposium on Mathematical Statistics and Probability, Berkeley (1951), pg. 353.
G. H. Vineyard, J. Math. Physics **4** (1963) 1191.

X

De door Vineyard als toepassing van zijn algemene formalisme ontwikkelde methode voor het berekenen van de asymptotische waarde van het aantal verschillende roosterpunten waar een random walker op een rooster door komt, is niet, zoals hij beweert, onafhankelijk van de op het berekenen van de ontsnappingskans gebaseerde methode, doch slechts een omslachtige variant daarvan.

G. H. Vineyard, J. Math. Physics **4** (1963) 1191.

ON THE THEORY OF OPTICAL ACTIVITY

ON THE THEORY
OF OPTICAL ACTIVITY

DOOR

ROBERT HARKO TERWIEL

GEBOREN TE DEN HAAG IN 1939

Aan mijn ouders
Aan mijn vrouw

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgen hier enkele gegevens over mijn studie.

In 1956 legde ik het eindexamen gymnasium-β af aan het Gymnasium Haganum te Den Haag, waarna ik gedurende een jaar een High School bezocht in de Verenigde Staten, daartoe in staat gesteld door een beurs van de American Field Service. In 1957 begon ik mijn studie aan de Universiteit te Leiden en legde in juni 1959 het candidaatsexamen natuur- en wiskunde (A') af. Vervolgens was ik gedurende twee maanden werkzaam bij de Universiteit van Californië, La Jolla, waar ik deel uitmaakte van een researchgroep die onder leiding van Prof. Dr. J. A. Arnold onderzoek verrichtte over kosmische straling. In oktober 1959 hervatte ik mijn studie te Leiden en legde in januari 1962 het doctoraalexamen af met hoofdvak theoretische natuurkunde en bijvakken wiskunde en mechanica.

Vanaf maart 1961 was ik werkzaam op het Instituut-Lorentz voor theoretische natuurkunde, waar ik onder leiding van Prof. Dr. P. Mazur onderzoek verrichtte op het gebied van de statistische mechanica, o.m. over de statistische mechanica van materie in een electromagnetisch veld.

CONTENTS

CONTENTS

INTRODUCTION

A monochromatic plane light-wave impinging on matter in vacuo will induce oscillating electric and magnetic moments in each molecule. As a result the molecules become radiation-sources themselves. The exact microscopic radiation field corresponding to a certain configuration of the molecules is a superposition of the external field of the light-wave and the secondary radiation fields from all molecules. Whereas these microscopic fields are propagated with the velocity of light in vacuo, c, the observable macroscopic field is propagated in the medium with a velocity different from c.

In this thesis the propagation of light in isotropic, optically active media will be investigated. The structure of optically active molecules gives rise to circular double refraction, *i.e.* right and left circularly polarized plane waves are propagated in the medium with different velocities, which causes a rotation of the direction of polarization of linearly polarized light passing through the medium. The theory of optical activity may be considered to be an extension of the theory of ordinary dispersion: whereas in the latter the ratio of the linear dimensions of a molecule to the wavelength of the light is considered to be negligibly small, the essential feature of a theoretical treatment of optical activity consists in taking into account, to first order, the finiteness of this ratio.

In chapter I we shall give a general theory of optical activity in an isotropic medium consisting of identical molecules. Without specifying the molecular model we shall investigate the influence of a monochromatic plane light-wave impinging on a molecule. With the time dependent quantum mechanical perturbation theory expressions will be derived for the induced molecular moments. Then the secondary radiation field of a molecule will be calculated. With these results we shall derive the equations describing "dynamical equilibrium" in a medium consisting of N molecules, *i.e.* describing the state in which every molecule undergoes the influence of the external field and the secondary radiation fields from all other molecules. Next we derive from these relations integral equations for the macroscopic field quantities. Whereas in earlier treatments of optical activity the macroscopic field quantities were obtained by means of a spatial

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averaging procedure, we shall in this thesis employ the averaging procedure of statistical mechanics. More specifically, the macroscopic quantities will be defined as ensemble averages over a canonical ensemble. Thus we shall be able to investigate the influence of statistical correlation and fluctuation effects, which have always been neglected in previous treatments. With the integral equations for the average field quantities the propagation of the light-wave in the medium will be examined. It will be shown that the external field is compensated by a part of the average field (extinction theorem). Furthermore the difference of the velocities of propagation of right and left circularly polarized plane waves will be calculated.

In chapter II the general theory will be extended to the case of a two-component system.

Finally, in chapter III, the molecular quantities occurring in the general theory will be calculated for a specific molecular model, namely Born's coupled oscillators model. Then, using the general theory developed in chapters I and II, a discussion will be given of the method employed by Born in his treatment of optical activity, the socalled method of the relative electric moment.

Parts of the contents of this thesis have been published in Physica (Physica **30** (1964) 625). The rest will appear shortly.

OPTICAL ROTATORY POWER OF AN ISOTROPIC
ONE-COMPONENT SYSTEM

Synopsis

A molecular theory of optical activity in an isotropic medium consisting of identical particles is presented, based on work by Rosenfeld and Hoek. Taking Rosenfeld's quantum mechanical treatment of the one particle problem as basis, a detailed investigation of the mechanism of propagation of light through the medium is made, extending Mazur and Mandel's treatment of light propagation in non-polar media. A generalized expression for the optical rotatory power is derived, taking into account statistical correlation and fluctuation effects.

§ 1. *Introduction.* Optical activity is the phenomenon that a medium rotates the plane of polarization of linearly polarized light that is transmitted through it. Fresnel showed that the basic feature of the propagation of light in an optically active medium is circular double refraction: the velocity of propagation for right and left circularly polarized waves is different. The rotation to the right of the plane of polarization of the linearly polarized light (for an observer viewing the lightbeam in the direction opposite to the direction of propagation) per cm of the medium is

$$\varphi = \frac{\pi}{\lambda}(n_l - n_r), \qquad (1)$$

where φ is expressed in radians, λ is the vacuum wavelength and $n_l(n_r)$ is the refractive index for left (right) circularly polarized light; φ is called the optical rotatory power.

The first molecular theories of optical activity were given independently by Born [1]) and Oseen [2]). Their work was a natural extension of the ordinary theory of dispersion, taking into account, to first order, the variation of the phase of the light-wave over distances of the order of the diameter of a molecule. As molecular model they used a spatial distribution of coupled oscillators. In 1928 Rosenfeld [3]) formulated a quantum mechanical theory of optical activity. Hoek [4]) made a detailed investigation into the mechanism which is responsible for the propagation of the light-wave through the me-

dium, proceeding along lines initiated by Lorentz, Ewald and Oseen. His approach may be summarized as follows:

Under the influence of the incident light-wave every molecule begins to radiate itself. A state of dynamical equilibrium is established in which every molecule undergoes the influence of the external field and the secondary radiation fields from all other molecules. From the exact molecular equations describing the equilibrium state one derives by means of an averaging procedure integral equations for certain macroscopic averages of the field strengths. One then shows that these equations allow for a right and left circulary polarized plane wave to propagate through the medium with different velocities. This leads to a general expression for the optical rotatory power.

We shall follow Hoek's method. Our approach will however deviate from his in two respects. Firstly, whereas Hoek's work is based on the old coupled oscillators model, we shall take as a starting point Rosenfeld's quantum mechanical theory, which is to be preferred to the classical approach. In doing so we are able to blend the until now rather disconnected work of Rosenfeld and Hoek together into a general, unified theory. Secondly, whereas Hoek obtains the macroscopic quantities by a method of averaging over physically infinitesimal volume elements, we shall use the statistical method developped by Mazur and Mandel [5]), based on work of Kirkwood [6]), Yvon [7]), and de Boer, van der Maesen and ten Seldam [8]). An attempt to investigate the influence of statistical correlation and fluctuation effects has previously been made by Goossens [9]) using the Onsager-Böttcher field [10]).

In § 2 we give a presentation of Rosenfeld's theory, closely following Condon [11]). The influence of a light-wave impinging on a molecule is investigated, and expressions for the induced electric dipole and quadrupole moment and the magnetic dipole moment are obtained. In § 3 the multipole expansion for the secondary radiation field of a molecule is given. Then in § 4 we set up the equations describing the dynamical equilibrium in a medium consisting of N identical molecules. In § 5 we derive the integral equations for the statistical averages of the exciting field strength and its derivatives. From these integral equations we derive in § 6 a general expression for the optical rotatory power. Finally in § 7 we show the connection between microscopic and macroscopic theory.

§ 2. *The reaction of a molecule under a monochromatic plane light-wave.* A molecule is acted upon by a monochromatic light-wave of circular frequency ω. For the electric field vector we write

$$E = \mathrm{Re}\, \boldsymbol{E}^- \mathrm{e}^{-i\omega t}, \tag{2a}$$

$$= \tfrac{1}{2}(\boldsymbol{E}^- \mathrm{e}^{-i\omega t} + \boldsymbol{E}^+ \mathrm{e}^{i\omega t}). \tag{2b}$$

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This field may be derived from the divergence-free vector potential

$$A = -\frac{c}{\omega} \operatorname{Re} i\, E^- e^{-i\omega t} \qquad (3)$$

according to

$$E = -\frac{1}{c}\frac{\partial A}{\partial t}. \qquad (4)$$

The magnetic field vector B is given by

$$B = \operatorname{rot} A \qquad (5a)$$

$$= -\frac{c}{\omega}\operatorname{Re} \operatorname{rot} E^- e^{-i\omega t}. \qquad (5b)$$

Let the molecule consist of point particles with charges $e_k(k = 1, 2, ...)$. We assume the molecule as a whole to be electrically neutral ($\sum_k e_k = 0$) and to possess no permanent electric or magnetic moments.

Assuming the field strengths to be such that we are in the region of linearity, *i.e.* that the responses depend linearly on the exciting field strengths, we may drop all perturbation terms in the Hamiltonian H that are non-linear in A and write

$$H = H_0 + H_1(t), \qquad (6)$$

where H_0 is the Hamiltonian of the unperturbed system and where *)

$$H_1(t) = -\sum_k \frac{e_k}{c}\, \dot{r}_k \cdot A(r_k). \qquad (7)$$

We note that H_1 is hermitian, since A is divergence-free, and that the operators $\dot{r}_k$ in (7) refer to the unperturbed system:

$$\dot{r}_k = -\frac{i}{\hbar}[r_k, H_0]. \qquad (8)$$

Let $|a\rangle$, where a stands for a set of quantum numbers specifying the state of the system, be a complete set of energy-eigenstates of the unperturbed

---

*) Note that in (7) we have neglected the spins of the constituent particles. When the spins are taken into account, (7) is modified to

$$H_1(t) = -\sum_k \frac{e_k}{m_k c} \{p_k \cdot A(r_k) + \tfrac{1}{2}g_k s_k \cdot \operatorname{rot} A(r_k)\}, \qquad (7')$$

where $g_k(e_k/2m_k c)$ is the gyromagnetic ratio of particle k.
The formulae we shall derive from (7) can immediately be changed into the corresponding formulae resulting from (7') by replacing the expression for the magnetic moment (cf. (22)) by

$$m = \sum_k \frac{e_k}{2m_k c}(r_k \times p_k + g_k s_k).$$

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system:

$$H_0 |a\rangle = E_a |a\rangle. \tag{9}$$

The unitary operator $U(t, t_0)$ describing the time evolution in the interval (t_0, t) of the state vector in the Schrödinger representation can be expanded in powers of the perturbation operator [12]:

$$U(t, t_0) = U^{(0)}(t, t_0) + \sum_{n=1}^{\infty} U^{(n)}(t, t_0), \tag{10a}$$

where

$$U^{(0)}(t, t_0) = e^{-(i/\hbar)H_0(t-t_0)},$$

$$U^{(n)}(t, t_0) = \frac{1}{(i\hbar)^n} \int\limits_{t > t_n > \dots > t_1 > t_0} dt_1 \dots dt_n\, e^{-(i/\hbar)H_0(t-t_n)} \tag{10b}$$

$$H_1(t_n)\, e^{-(i/\hbar)H_0(t_n-t_{n-1})}\, H_1(t_{n-1}) \dots H_1(t_1)\, e^{-(i/\hbar)H_0(t_1-t_0)}. \tag{10c}$$

Denoting the state of the system at the initial time t_0 by $|\psi(t_0)\rangle$, the expectation value of a dynamical quantity F at time t is given by

$$\langle\psi(t)|\, F\, |\psi(t)\rangle = \langle\psi(t_0)|\, U^\dagger(t, t_0)\, F\, U(t, t_0)\, |\psi(t_0)\rangle. \tag{11}$$

From (10) it then follows that the first order correction of this expectation value is

$$\langle\psi(t_0)|\, U^{(0)\dagger}(t, t_0)\, F\, U^{(1)}(t, t_0)\, |\psi(t_0)\rangle +$$

$$+ \langle\psi(t_0)|\, U^{(1)\dagger}(t, t_0)\, F\, U^{(0)}(t, t_0)\, |\psi(t_0)\rangle =$$

$$= 2\, \mathrm{Re}\, \langle\psi(t_0)|\, U^{(0)\dagger}(t, t_0)\, F\, U^{(1)}(t, t_0)\, |\psi(t_0)\rangle. \tag{12}$$

For the perturbation H_1 we write

$$H_1(t) = \tfrac{1}{2}(H^- e^{-i\omega t} + H^+ e^{i\omega t}), \tag{13a}$$

where according to (3) and (7),

$$H_1^\mp = \pm\, i \sum_k \frac{e_k}{\omega}\, \dot{\boldsymbol{r}}_k \cdot \boldsymbol{E}^\mp(\boldsymbol{r}_k). \tag{13b}$$

Now let $|\psi(t_0)\rangle$ be the stationary state

$$|\psi(t_0)\rangle = e^{-(i/\hbar)E_a t_0} |a\rangle \tag{14}$$

and let the perturbation be switched on adiabatically at $t_0 = -\infty$. Then (12) reduces to

$$- \mathrm{Re}\left\{ \sum_b \langle a|\, F\, |b\rangle\, \langle b|\, H_1^-\, |a\rangle\, \frac{e^{-i\omega t}}{W_{ba} - E} \right.$$

$$\left. + \sum_b \langle a|\, F\, |b\rangle\, \langle b|\, H_1^+\, |a\rangle\, \frac{e^{i\omega t}}{W_{ba} + E} \right\}, \tag{15}$$

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with the abbreviations

$$W_{ba} \equiv E_b - E_a; \quad E \equiv \hbar\omega. \tag{16}$$

Let the disturbing field be a plane wave, *i.e.*

$$\boldsymbol{E}^{\mp}(\boldsymbol{r}) = \boldsymbol{E}^{\mp}(\boldsymbol{r}')\, e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}, \tag{17}$$

where $\boldsymbol{k}$ is a vector in the direction of propagation, of magnitude $k = 2\pi/\lambda = \omega/c$, λ being the wavelength. Let $\boldsymbol{r}'$ be the "centre" of the molecule, *i.e.* a fixed reference point inside the molecule. Expanding the $\boldsymbol{E}^{\mp}(\boldsymbol{r}_k)$ in $H_1^{\mp}$ (cf. (13)) around their value at $\boldsymbol{r}'$, we obtain for the matrix elements of $H_1^{\mp}$ expansions in which successive terms correspond to ascending orders in d/λ, where d is of the order of the extension of the molecular wave function. Thus we obtain, assuming $d/\lambda \ll 1$,

$$\langle b|\, H_1^{\mp} \,|a\rangle =$$

$$= \pm \frac{i}{\omega} \langle b| \sum_k e_k \dot{x}_{k\alpha}\{E_\alpha^{\mp}(\boldsymbol{r}') + (x_{k\beta}-x_\beta')\, E_{\alpha\beta}^{\mp}(\boldsymbol{r}') + \ldots\} |a\rangle \tag{17a}$$

$$= \pm \frac{i}{\omega} \langle b| \sum_k e_k\, \dot{x}_{k\alpha}\, E_\alpha^{\mp}(\boldsymbol{r}') \,|a\rangle \left\{1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots\right\}, \tag{17b}$$

where the components of a vector $\boldsymbol{r}$ are denoted by $x_\alpha(\alpha = 1, 2, 3)$ and where we used the notation

$$\frac{\partial^{(n)}}{\partial x_\beta'\, \partial x_\gamma' \, \ldots}\, E_\alpha^{\mp}(\boldsymbol{r}') \equiv E_{\alpha\beta\gamma\ldots}^{\mp}(\boldsymbol{r}'), \tag{18}$$

with the convention, to be used from now on, that the occurrence of identical *greek* indices implies a summation over these indices.

According to (15) and (17b) the first order correction of the expectation value of F may be written as

$$F^{(0)} + F^{(1)} + \ldots = F^{(0)} \left\{1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots\right\}. \tag{19}$$

Taking for F the electric dipole moment operator

$$\boldsymbol{p} = \sum_k e_k(\boldsymbol{r}_k - \boldsymbol{r}') = \sum_k e_k\, \boldsymbol{r}_k, \tag{20}$$

(where the last equality follows from the fact that the total charge of the molecule vanishes), the electric quadrupole moment operator

$$\mathsf{q} = \tfrac{1}{2} \sum_k e_k(\boldsymbol{r}_k - \boldsymbol{r}')\, (\boldsymbol{r}_k - \boldsymbol{r}') \tag{21}$$

and the magnetic dipole moment operator

$$\boldsymbol{m} = \frac{1}{2c} \sum_k e_k(\boldsymbol{r}_k - \boldsymbol{r}') \times \dot{\boldsymbol{r}}_k, \tag{22}$$

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all three defined with respect to the centre of the molecule, we thus obtain the induced moments p^{ind}, q^{ind} and m^{ind} in the following form:

$$p^{\text{ind}} = p^{(0)} + p^{(1)} + \ldots = p^{(0)} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\}$$

$$q^{\text{ind}} = q^{(0)} + q^{(1)} + \ldots = q^{(0)} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\} \quad (23)$$

$$m^{\text{ind}} = m^{(0)} + m^{(1)} + \ldots = m^{(0)} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\}$$

Introducing complex amplitudes p^-, q^- and m^- according to

$$\left. \begin{aligned} p^{\text{ind}} &= \operatorname{Re} \; p^- \, e^{-i\omega t} \\ q^{\text{ind}} &= \operatorname{Re} \; q^- \, e^{-i\omega t} \\ m^{\text{ind}} &= \operatorname{Re} \; m^- \, e^{-i\omega t} \end{aligned} \right\}, \quad (24)$$

(23) corresponds to the following expansions of p^-, q^- and m^-

$$p^- = p^{(0)-} + p^{(1)-} + \ldots = p^{(0)-} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\}$$

$$q^- = q^{(0)-} + q^{(1)-} + \ldots = q^{(0)-} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\} \quad (23a)$$

$$m^- = \mathrm{m}^{(0)-} + \mathrm{m}^{(1)-} + \ldots = m^{(0)-} \left\{ 1 + \mathcal{O}\left(\frac{d}{\lambda}\right) + \ldots \right\} \Bigg\}$$

Furthermore, the order of magnitude of the components of q^- and m^- relative to the components of p^- is

$$\frac{q_{\alpha\beta}^-}{p_\gamma^-} = \mathcal{O}(d); \quad \frac{\frac{c}{\omega} m_\alpha^-}{p_\beta^-} = \mathcal{O}(d). \quad (25a)$$

Similarly

$$\frac{q_{\alpha\beta}^{(n)-}}{p_\gamma^{(n)-}} = \mathcal{O}(d); \quad \frac{\frac{c}{\omega} m_\alpha^{(n)-}}{p_\beta^{(n)-}} = \mathcal{O}(d). \quad (n = 1, 2, \ldots) \quad (25b)$$

Now in § 3 the Hertzvector $Z(r, t)$ describing the secondary radiation field of a molecule with oscillating moments will be shown to be (cf. (77d) and (89))

$$Z(r, t) = \operatorname{Re} Z^-(r) \, e^{-i\omega t}, \quad (26a)$$

with

$$Z_\alpha^-(r) = \frac{e^{ik|r-r'|}}{|r - r'|} p_\alpha^- + \left\{ \frac{\partial}{\partial x_\mu} \frac{e^{ik|r-r'|}}{|r - r'|} \right\} \left\{ -q_{\alpha\mu}^- + \frac{1}{ik} \delta_{\gamma\mu\alpha} m_\gamma^- \right\} + \ldots \quad (26b)$$

where $\delta_{\alpha\beta\gamma}$ is the Levi-Civita tensor,

$$\delta_{\alpha\beta\gamma} = \begin{cases} 1 \text{ if } \alpha, \beta, \gamma = 1, 2, 3 \text{ cycl.} \\ -1 \text{ if } \alpha, \beta, \gamma = 2, 1, 3 \text{ cycl.} \\ 0 \text{ otherwise} \end{cases} \tag{27}$$

According to (25a) the second term in the right hand side of (26b) is of order d/λ relative to the first. In fact, since $d/\lambda \ll 1$, all contributions to $\mathbf{Z}^-$ of higher order in d/λ have been neglected in deriving (26b). If we now introduce into (26b) the expansions (23a) the Hertzvector is seen to consist of a leading term

$$Z_\alpha^{(0)-}(\mathbf{r}) = \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} p_\alpha^{(0)-}, \tag{28}$$

all other terms being of relative order $(d/\lambda)^n$, $(n = 1, 2, ...)$. Of these terms we shall retain only those of relative order d/λ, i.e. according to (25b):

$$Z_\alpha^{(1)-}(\mathbf{r}) = \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} p_\alpha^{(1)-} + \left\{ \frac{\partial}{\partial x_\mu} \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \right\} \left\{ -q_{\alpha\mu}^{(0)-} + \frac{1}{ik} \delta_{\gamma\mu\alpha} m_\gamma^{(0)-} \right\}. \tag{29}$$

From these considerations it follows that we should determine $\mathbf{p}^{\text{ind}}$ to first order in d/λ, $\mathbf{q}^{\text{ind}}$ and $\mathbf{m}^{\text{ind}}$ to zeroth order only.

We now proceed to calculate $\mathbf{p}^{(0)}$, $\mathbf{p}^{(1)}$, $\mathbf{q}^{(0)}$ and $\mathbf{m}^{(0)}$ starting from (15) and (17a). Using (20) and (8), the first term in the right hand side of (17a) may be written

$$\mp \frac{W_{ba}}{\hbar\omega} \langle b| p_\alpha |a\rangle E_\alpha^\mp (\mathbf{r}'). \tag{30}$$

The second term in the right hand side of (17a) may be split into a symmetric and an antisymmetric part and then, using (8), (21) and (22), be rewritten as

$$\mp \frac{W_{ba}}{\hbar\omega} \langle b| q_{\alpha\beta} |a\rangle E_{\alpha\beta}^\mp(\mathbf{r}') \mp i \frac{c}{\omega} \delta_{\alpha\beta\gamma} \langle b| m_\gamma |a\rangle E_{\alpha\beta}^\mp(\mathbf{r}'). \tag{31}$$

We then obtain from (15) and (30)

$$p_\alpha^{(0)} = 2 \sum_b \text{Re} \left\{ \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| p_\beta |a\rangle E_\beta + \right.$$

$$\left. + i\hbar \frac{W_{ba}^2}{E^2(W_{ba}^2 - E^2)} \langle a| p_\alpha |b\rangle \langle b| p_\beta |a\rangle \dot{E}_\beta \right\}. \tag{32}$$

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Using (15) and (31) we find

$$
p_\alpha^{(1)} = 2 \sum_b \mathrm{Re} \left\{ \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, q_{\beta\gamma} \, |a\rangle \, E_{\beta\gamma} \, + \right.
$$

$$
+ \, i\hbar \, \frac{W_{ba}^2}{E^2(W_{ba}^2 - E^2)} \, \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, q_{\beta\gamma} \, |a\rangle \, \dot{E}_{\beta\gamma} \, +
$$

$$
+ \, \frac{c}{\omega^2} \, \frac{W_{ba}}{W_{ba}^2 - E^2} \, \delta_{\beta\gamma\delta} \, \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, m_\beta \, |a\rangle \, \dot{E}_{\delta\gamma} \, -
$$

$$
\left. - \, ic \, \frac{\hbar}{W_{ba}^2 - E^2} \, \delta_{\beta\gamma\delta} \, \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, m_\beta \, |a\rangle \, E_{\delta\gamma} \right\}. \tag{33}
$$

Thus, calculating the induced dipole moment to first order in d/λ, one has to take into account the electric field and its derivatives at the centre of the molecule, *i.e.* the variation of the electric field within the molecule; this implies that one has taken into account the magnetic field at the centre of the molecule, since

$$
\mathrm{rot} \, \boldsymbol{E} = - \, \frac{1}{c} \, \frac{\partial \boldsymbol{B}}{\partial t}. \tag{34}
$$

Similarly one obtains for $q^{(0)}$ and $\boldsymbol{m}^{(0)}$, using (15) and (30),

$$
q_{\alpha\beta}^{(0)} = 2 \sum_b \mathrm{Re} \left\{ \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| \, q_{\alpha\beta} \, |b\rangle \, \langle b| \, p_\gamma \, |a\rangle \, E_\gamma \, + \right.
$$

$$
\left. + \, i\hbar \, \frac{W_{ba}^2}{E^2(W_{ba}^2 - E^2)} \, \langle a| \, q_{\alpha\beta} \, |b\rangle \, \langle b| \, p_\gamma \, |a\rangle \, \dot{E}_\gamma \right\}, \tag{35}
$$

$$
m_\alpha^{(0)} = 2 \sum_b \mathrm{Re} \left\{ \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| \, m_\alpha \, |b\rangle \, \langle b| \, p_\beta \, |a\rangle \, E_\beta \, + \right.
$$

$$
\left. + \, i \, \frac{W_{ba}^2}{E^2(W_{ba}^2 - E^2)} \, \langle a| \, m_\alpha \, |b\rangle \, \langle b| \, p_\beta \, |a\rangle \, \dot{E}_\beta \right\}. \tag{36}
$$

The terms in (32), (33), (35) and (36) containing a factor $W_{ba}^2/[E^2(W_{ba}^2 - E^2)]$ can be simplified by using the identity

$$
\frac{W_{ba}^2}{E^2(W_{ba}^2 - E^2)} = \frac{1}{E^2} + \frac{1}{W_{ba}^2 - E^2} \tag{37}
$$

and the fact that the quantity

$$
\sum_b \langle a| \, O_1 \, |b\rangle \, \langle b| \, O_2 \, |a\rangle = \langle a| \, O_1 O_2 \, |a\rangle,
$$

O_1 and O_2 being hermitian operators, is real if O_1 and O_2 commute. We then

find for $\boldsymbol{p}^{(0)-}$, $\boldsymbol{p}^{(1)-}$, $q^{(0)-}$ and $\boldsymbol{m}^{(0)-}$

$$p_\alpha^{(0)-} = \left\{2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| p_\beta |a\rangle\right\} E_\beta^- +$$

$$+ i\left\{2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| p_\beta |a\rangle\right\} E_\beta^-, \qquad (38)$$

$$p_\alpha^{(1)-} = \left\{2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| q_{\beta\gamma} |a\rangle\right\} E_{\beta\gamma}^- +$$

$$+ i\left\{2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| q_{\beta\gamma} |a\rangle\right\} E_{\beta\gamma}^- -$$

$$- i\,\frac{c}{\omega}\left\{2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| m_\delta |a\rangle\right\} \delta_{\delta\gamma\beta}\, E_{\beta\gamma}^- +$$

$$+ \frac{c}{\omega}\left\{2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| m_\delta |a\rangle\right\} \delta_{\delta\gamma\beta}\, E_{\beta\gamma}^-, \qquad (39)$$

$$q_{\alpha\beta}^{(0)-} = \left\{2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| q_{\alpha\beta} |b\rangle \langle b| p_\gamma |a\rangle\right\} E_\gamma^- +$$

$$+ i\left\{2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| q_{\alpha\beta} |b\rangle \langle b| p_\gamma |a\rangle\right\} E_\gamma^-, \qquad (40)$$

$$m_\alpha^{(0)-} = \left\{2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| m_\alpha |b\rangle \langle b| p_\beta |a\rangle\right\} E_\beta^- +$$

$$+ i\left\{2 \operatorname{Im} \sum_b \frac{1}{E} \langle a| m_\alpha |b\rangle \langle b| p_\beta |a\rangle\right\} E_\beta^- +$$

$$+ i\left\{2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| m_\alpha |b\rangle \langle b| p_\beta |a\rangle\right\} E_\beta^-. \qquad (41)$$

We introduce the following abbreviations:

$$\rho_{\alpha\beta\ldots\gamma\delta\ldots}^{AB} \equiv 2 \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| A_{\alpha\beta\ldots} |b\rangle \langle b| B_{\gamma\delta\ldots} |a\rangle, \qquad (42a)$$

$$\sigma_{\alpha\beta\ldots\gamma\delta\ldots}^{AB} \equiv 2 \operatorname{Im} \sum_b \frac{E}{W_{ba}^2 - E^2} \langle a| A_{\alpha\beta\ldots} |b\rangle \langle b| B_{\gamma\delta\ldots} |a\rangle, \qquad (42b)$$

$$\tau_{\alpha\beta\ldots\gamma\delta\ldots}^{AB} \equiv 2 \operatorname{Im} \sum_b \frac{1}{E} \langle a| A_{\alpha\beta\ldots} |b\rangle \langle b| B_{\gamma\delta\ldots} |a\rangle, \qquad (42c)$$

where $A_{\alpha\beta\ldots}$, $B_{\gamma\delta\ldots}$ are components of the tensor-operators $\boldsymbol{A}$ and $\boldsymbol{B}$. Further-

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more let

$$\alpha_{\alpha\beta} \equiv \rho^{pp}_{\alpha\beta} + i\,\sigma^{pp}_{\alpha\beta}, \tag{43a}$$

$$\alpha_{\alpha\beta\gamma} \equiv \rho^{pq}_{\alpha\beta\gamma} + i\sigma^{pq}_{\alpha\beta\gamma} - i\frac{c}{\omega}\,\rho^{pm}_{\alpha\delta}\,\delta_{\delta\gamma\beta} + \frac{c}{\omega}\,\sigma^{pm}_{\alpha\delta}\,\delta_{\delta\gamma\beta}, \tag{43b}$$

$$\alpha'_{\alpha\beta\gamma} \equiv \rho^{qp}_{\alpha\beta\gamma} + i\,\sigma^{qp}_{\alpha\beta\gamma}, \tag{43c}$$

$$\alpha'_{\alpha\beta} \equiv \rho^{mp}_{\alpha\beta} + i\,\tau^{mp}_{\alpha\beta} + i\,\sigma^{mp}_{\alpha\beta}. \tag{43d}$$

Then (38)–(41) can be written in the more compact form

$$p^{(0)-}_{\alpha} = \alpha_{\alpha\beta}\,E^{-}_{\beta}, \tag{44}$$

$$p^{(1)-}_{\alpha} = \alpha_{\alpha\beta\gamma}\,E^{-}_{\beta\gamma}, \tag{45}$$

$$q^{(0)-}_{\alpha\beta} = \alpha'_{\alpha\beta\gamma}\,E^{-}_{\gamma}, \tag{46}$$

$$m^{(0)}_{\alpha} = \alpha'_{\alpha\beta}\,E^{-}_{\beta}. \tag{47}$$

For later use we shall determine the averages of the tensors (43) over all orientations of the molecule, all orientations having equal weight 1. Let $l_{\alpha\alpha'}(\omega)$ be the direction cosines of the axes $x_{\alpha'}$ of the molecular frame of reference of a molecule with orientation ω with respect to the axes x_{α} of the frame of reference fixed in space, where ω stands for the orientational coordinates, e.g. Eulerian angles, normalized in such a way that

$$\int \mathrm{d}\omega = 1, \tag{48}$$

the integration extending over all orientations. Then, using the relations [13]

$$\int l_{\alpha\alpha'}(\omega)\,l_{\beta\beta'}(\omega)\,\mathrm{d}\omega = \tfrac{1}{3}\,\delta_{\alpha\beta}\,\delta_{\alpha'\beta'}, \tag{49}$$

$$\int l_{\alpha\alpha'}(\omega)\,l_{\beta\beta'}(\omega)\,l_{\gamma\gamma'}(\omega)\,\mathrm{d}\omega = \tfrac{1}{6}\,\delta_{\alpha\beta\gamma}\,\delta_{\alpha'\beta'\gamma'}, \tag{50}$$

we have, denoting the orientational average of a quantity A by $\overline{A}^{\,-\omega}$:

$$\overline{\rho^{pp}_{\alpha\beta}}^{\,\omega} = (\tfrac{1}{3}\delta_{\alpha'\beta'}\,\rho^{pp}_{\alpha'\beta'})\,\delta_{\alpha\beta}, \tag{51}$$

$$\overline{\rho^{pq}_{\alpha\beta\gamma}}^{\,\omega} = (\tfrac{1}{6}\,\delta_{\alpha'\beta'\gamma'}\,\rho^{pq}_{\alpha'\beta'\gamma'})\,\delta_{\alpha\beta\gamma}, \tag{52}$$

and similar relations for the other tensors in (43). Using the definitions (42), (51) and (52) we find

$$\overline{\rho^{pp}_{\alpha\beta}}^{\,\omega} = \left(\tfrac{2}{3}\,\mathrm{Re}\,\sum_b \frac{W_{ba}}{W^2_{ba} - E^2}\,\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{p}\,|a\rangle\right)\delta_{\alpha\beta}, \tag{53}$$

$$\overline{\sigma^{pp}_{\alpha\beta}}^{\,\omega} = 0, \tag{54}$$

$$\overline{\rho^{pq}_{\alpha\beta\gamma}}^{\,\omega} = \overline{\sigma^{pq}_{\alpha\beta\gamma}}^{\,\omega} = \overline{\rho^{qp}_{\alpha\beta\gamma}}^{\,\omega} = \overline{\sigma^{qp}_{\alpha\beta\gamma}}^{\,\omega} = 0, \tag{55}$$

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$$\overline{\rho_{\alpha\delta}^{pm}}^{\omega} = \overline{\rho_{\alpha\delta}^{mp}}^{\omega} = \left(\tfrac{2}{3}\operatorname{Re}\sum_b \frac{W_{ba}}{W_{ba}^2 - E^2}\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{m}\,|a\rangle\right)\delta_{\alpha\delta}, \qquad (56)$$

$$\overline{\sigma_{\alpha\delta}^{pm}}^{\omega} = -\overline{\sigma_{\alpha\delta}^{mp}}^{\omega} = \left(\tfrac{2}{3}\operatorname{Im}\sum_b \frac{E}{W_{ba}^2 - E^2}\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{m}\,|a\rangle\right)\delta_{\alpha\delta}, \qquad (57)$$

$$\overline{\tau_{\alpha\beta}^{mp}}^{\omega} = 0. \qquad (58)$$

Defining g_0, h_1 and h_2 by

$$g_0 \equiv \tfrac{2}{3}\operatorname{Re}\sum_b \frac{W_{ba}}{W_{ba}^2 - E^2}\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{p}\,|a\rangle, \qquad (59)$$

$$h_1 \equiv \tfrac{2}{3}\operatorname{Im}\sum_b \frac{\hbar c}{W_{ba}^2 - E^2}\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{m}\,|a\rangle, \qquad (60)$$

$$h_2 \equiv \frac{2c}{3\omega}\operatorname{Re}\sum_b \frac{W_{ba}}{W_{ba}^2 - E^2}\langle a|\,\boldsymbol{p}\,|b\rangle\cdot\langle b|\,\boldsymbol{m}\,|a\rangle, \qquad (61)$$

g_1 and g_2 by

$$g_1 \equiv -h_1 + ih_2, \qquad (62)$$

$$g_2 \equiv -h_1 - ih_2, \qquad (63)$$

we find, using (43) and (53)–(58):

$$\overline{\alpha_{\alpha\beta}}^{\omega} = g_0\,\delta_{\alpha\beta}, \qquad (64)$$

$$\overline{\alpha_{\alpha\beta\gamma}}^{\omega} = g_1\,\delta_{\alpha\beta\gamma}, \qquad (65)$$

$$\overline{\alpha_{\alpha\beta\gamma}'}^{\omega} = 0, \qquad (66)$$

$$\overline{\alpha_{\alpha\beta}'}^{\omega} = ik\,g_2\,\delta_{\alpha\beta}. \qquad (67)$$

We note that according to (62) and (63)

$$g_2 = g_1^*. \qquad (68)$$

Anticipating some results that will subsequently be obtained we would like to make the following remarks:

Firstly, Condon *a priori* neglects in the expressions for the induced moments the terms containing $\rho_{\alpha\beta\gamma}^{pq}$, $\rho_{\alpha\beta\gamma}^{qp}$, $\sigma_{\alpha\beta\gamma}^{pq}$ and $\sigma_{\alpha\beta\gamma}^{qp}$, (cf. (43b), (43c), (45) and (46)), saying that "they give a small correction, of the order of a few parts in a million, to the ordinary connection between mean refractive index and the electric dipole moment and so will be neglected". This is not correct, since these terms are of the same order of magnitude as the other terms contributing to $\boldsymbol{p}^{(1)-}$ and $\boldsymbol{q}^{(0)-}$. In the special case of isotropic media, how-

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ever, the terms containing the tensors $\rho_{\alpha\beta\gamma}^{pq}$, $\rho_{\alpha\beta\gamma}^{qp}$, $\sigma_{\alpha\beta\gamma}^{pq}$ and $\sigma_{\alpha\beta\gamma}^{qp}$ do not give any contribution at all to the optical rotatory power, as will be shown later on, due to the fact that their orientational averages vanish (cf. (55)).

Secondly, since we have assumed the molecule as a whole to be electrically neutral, the electric dipole moment, and therefore also g_0, given by (59), is independent of the choice of the reference point r'. According to (20) and (22) the r'- dependent parts of h_1 and h_2 (cf. (60) and (61)) are

$$- \tfrac{2}{3} \operatorname{Im} \sum_b \frac{\hbar c}{W_{ba}^2 - E^2} \langle a| \sum_k e_k r_k |b\rangle \cdot \Big\langle b \Big| \frac{1}{2c} \sum_l e_l \, r' \times \dot{r}_l \Big| a \Big\rangle$$

and

$$- \frac{2c}{3\omega} \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| \sum_k e_k r_k |b\rangle \cdot \Big\langle b \Big| \frac{1}{2c} \sum_l e_l \, r' \times \dot{r}_l \Big| a \Big\rangle$$

respectively. We note that

$$- \langle a| \sum_k e_k \, r_k |b\rangle \cdot \Big\langle b \Big| \frac{1}{2c} \sum_l e_l \, r' \times \dot{r}_l \Big| a \Big\rangle$$

is a real quantity. Indeed we have

$$\Big(- \sum_{k,l} e_k e_l \langle a| r_{k\alpha} |b\rangle \, \delta_{\alpha\beta\gamma} \frac{1}{2c} r_\beta' \langle b| \dot{r}_{l\gamma} |a\rangle \Big)^* =$$

$$= \Big(- \sum_{k,l} e_k e_l \langle a| r_{k\alpha} |b\rangle \delta_{\alpha\beta\gamma} \frac{1}{2c} r_\beta' \frac{i}{\hbar} W_{ba} \langle b| r_{l\gamma} |a\rangle \Big)^* =$$

$$= \sum_{k,l} e_k e_l \langle a| r_{l\gamma} |b\rangle \, \delta_{\alpha\beta\gamma} \frac{1}{2c} r_\beta' \frac{i}{\hbar} W_{ba} \langle b| r_{k\alpha} |a\rangle =$$

$$= - \sum_{k,l} e_k e_l \langle a| r_{l\gamma} |b\rangle \, \delta_{\gamma\beta\alpha} \frac{1}{2c} r_\beta' \frac{i}{\hbar} W_{ba} \langle b| r_{k\alpha} |a\rangle.$$

Consequently h_1 is independent of the choice of r', but not so h_2. In fact, r' could be chosen in such a way as to make h_2 vanish. Thus one might ask whether our final results would be considerably modified by a small change of the position of the reference point. In our final results the measurable quantities relating to optical rotatory power will contain, when expressed in terms of the molecular constants g_1 and g_2, only the combination $(g_1 + g_2)$, *i.e.* only h_1 (cf. (62) and (63)). In other words, a small change in r' does not affect our results at all. From this it should not be inferred, however, that the choice of r' is completely arbitrary. When a charge distribution is expanded in terms of multipole moments with respect to a certain reference point, one should, if one wishes to break off the expansion after a certain number of terms, ensure a sufficiently rapid convergence of the series by a favorable choice of the reference point.

Thirdly, Hoek found upon calculating g_1 and g_2 for Born's model (a spatial distribution of coupled oscillators) that $g_1 = g_2$. As we shall show in Chapter III, this is in accordance with (68) since in Born's model $h_2 \equiv 0$.

§ 3. *The secondary radiation field of a molecule*. As we have seen a molecule acquires under the influence of an external field of frequency ω electric and magnetic moments oscillating with the same frequency (in the linear approximation). Our next task is to determine the secondary field radiated by the molecule.

We have assumed the region of space corresponding to values of the molecular wave function appreciably different from zero to be of order d (in linear dimensions). Let the wave function for configurations outside this region fall off rapidly to zero, then we may enclose virtually the entire molecule in a sphere with diameter of the order d, setting the molecular wave function for configurations falling outside this sphere equal to zero. In other words, we consider a continuous charge and current distribution, $\rho_e(\xi, t)$, $j(\xi, t)$ occupying a region of linear dimensions of the order d. The radiation field E, B of this distribution is described by the well known basic equations of the theory of electrons:

$$\left.\begin{array}{c} \operatorname{div} B = 0 \\[2mm] \operatorname{rot} E + \dfrac{1}{c} \dot{B} = 0 \\[2mm] \operatorname{div} E = 4\pi\rho_e \\[2mm] \operatorname{rot} B - \dfrac{1}{c} \dot{E} = \dfrac{4\pi}{c} j \end{array}\right\} \tag{69}$$

One can describe the radiation field with the potentials φ and A, from which E and B follow according to

$$B = \operatorname{rot} A, \tag{70a}$$

$$E = -\operatorname{grad} \varphi - \frac{1}{c} \frac{\partial A}{\partial t}, \tag{70b}$$

where φ and A can be made to obey the Lorentz-condition

$$\operatorname{div} A + \frac{1}{c} \frac{\partial \varphi}{\partial t} = 0. \tag{70c}$$

Since ρ_e and j are not independent of each other (equation of continuity) one can describe the radiation source with a single vector $\tilde{p}(\xi, t)$, the polari-

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zation vector, with

$$\rho_e = - \operatorname{div} \widetilde{\boldsymbol{p}}, \tag{71a}$$

$$\boldsymbol{j} = \frac{\partial \widetilde{\boldsymbol{p}}}{\partial t}. \tag{71b}$$

Similarly, φ and $\boldsymbol{A}$ being connected by the Lorentz-condition, one can advantageously describe the radiation field with a single vector potential, the Hertzvector $\boldsymbol{Z}(\boldsymbol{r}, t)$, with

$$\varphi = - \operatorname{div} \boldsymbol{Z}, \tag{72a}$$

$$\boldsymbol{A} = \frac{1}{c} \frac{\partial \boldsymbol{Z}}{\partial t}, \tag{72b}$$

so that $\boldsymbol{B}$ and $\boldsymbol{E}$ follow from $\boldsymbol{Z}$ according to

$$\boldsymbol{B} = \frac{1}{c} \frac{\partial}{\partial t} \operatorname{rot} \boldsymbol{Z}, \tag{73a}$$

$$\boldsymbol{E} = \operatorname{rot} \operatorname{rot} \boldsymbol{Z} - 4\pi \widetilde{\boldsymbol{p}}, \tag{73b}$$

the latter equation reducing outside the source to

$$\boldsymbol{E} = \operatorname{rot} \operatorname{rot} \boldsymbol{Z}. \tag{73c}$$

$\boldsymbol{Z}$ has to satisfy the equation

$$\left(\Delta - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \boldsymbol{Z} = - 4\pi \widetilde{\boldsymbol{p}}. \tag{74}$$

A solution of (74) is the retarded Hertzvector

$$\boldsymbol{Z}(\boldsymbol{r}, t) = \int \frac{\widetilde{\boldsymbol{p}}(\boldsymbol{\xi}, t_R)}{|\boldsymbol{r} - \boldsymbol{\xi}|} \, d\boldsymbol{\xi}, \tag{75}$$

where the retarded time t_R is given by

$$c(t - t_R) = |\boldsymbol{r} - \boldsymbol{\xi}|. \tag{76}$$

Since we are dealing with an oscillating charge and current distribution, let us write

$$\rho_e(\boldsymbol{\xi}, t) = \operatorname{Re} \rho^-(\boldsymbol{\xi}) \, e^{-i\omega t}, \tag{77a}$$

$$\boldsymbol{j}(\boldsymbol{\xi}, t) = \operatorname{Re} \boldsymbol{j}^-(\boldsymbol{\xi}) \, e^{-i\omega t}, \tag{77b}$$

$$\widetilde{\boldsymbol{p}}(\boldsymbol{\xi}, t) = \operatorname{Re} \widetilde{\boldsymbol{p}}^-(\boldsymbol{\xi}) \, e^{-i\omega t}, \tag{77c}$$

$$\boldsymbol{Z}(\boldsymbol{r}, t) = \operatorname{Re} \boldsymbol{Z}^-(\boldsymbol{r}) \, e^{-i\omega t}. \tag{77d}$$

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Then we have, according to (71a), (71b) and (75)

$$\rho_e^-(\boldsymbol{\xi}) = -\operatorname{div} \tilde{\boldsymbol{p}}^-(\boldsymbol{\xi}),\tag{78a}$$

$$\boldsymbol{j}^-(\boldsymbol{\xi}) = -i\omega\tilde{\boldsymbol{p}}^-(\boldsymbol{\xi}),\tag{78b}$$

$$\boldsymbol{Z}^-(\boldsymbol{r}) = \int \frac{\tilde{\boldsymbol{p}}^-(\boldsymbol{\xi})\, e^{ik|\boldsymbol{r}-\boldsymbol{\xi}|}}{|\boldsymbol{r}-\boldsymbol{\xi}|}\, d\boldsymbol{\xi}.\tag{79}$$

Let $\boldsymbol{r}'$ be again a fixed centre inside the charge distribution. Let $|\boldsymbol{r}-\boldsymbol{r}'| = R$, $|\boldsymbol{\xi}-\boldsymbol{r}'| = R_1$ and the angle between $\boldsymbol{r}-\boldsymbol{r}'$ and $\boldsymbol{\xi}-\boldsymbol{r}'$ be γ. Then for $R > R_1$ the following expansion holds [14]

$$\frac{e^{ik|\boldsymbol{r}-\boldsymbol{\xi}|}}{|\boldsymbol{r}-\boldsymbol{\xi}|} = ik \sum_{n=0}^{\infty} (2n+1)\, P_n(\cos\gamma)\, j_n(kR_1)\, h_n^{(1)}(kR),\tag{80}$$

where $P_n(\cos\gamma)$ are Legendre-polynomials, $j_n(kR_1)$ and $h_n^{(1)}(kR)$ spherical Bessel functions and Hankel functions respectively. Choosing R larger than the radius of the sphere containing the entire charge distribution, we have

$$\boldsymbol{Z}^-(\boldsymbol{r}) = ik \sum_{n=0}^{\infty} (2n+1)\, h_n^{(1)}(kR) \int \tilde{\boldsymbol{p}}^-(\boldsymbol{\xi})\, j_n(kR_1)\, P_n(\cos\gamma)\, d\boldsymbol{\xi}.\tag{81}$$

As we have assumed $d/\lambda \ll 1$, it follows that $kR_1 \ll 1$ for all values of R_1 inside the charge distribution. Now, since

$$j_n(x) = 2^n x^n \sum_{m=0}^{\infty} \frac{(-1)^m (n+m)!}{m!(2n+2m+1)!}\, x^{2m} \qquad (n=0, 1, \dots),\tag{82}$$

we have to first order in kR_1:

$$\left.\begin{aligned} j_0(kR_1) &= 1 \\ j_1(kR_1) &= \tfrac{1}{3}kR_1 \\ j_m(kR_1) &= 0 \qquad m=2, 3, \dots \end{aligned}\right\}\tag{83}$$

Furthermore

$$P_0(\cos\gamma) = 1,\tag{84a}$$

$$P_1(\cos\gamma) = \cos\gamma,\tag{84b}$$

$$h_0^{(1)}(kR) = -\frac{1}{kR}\, e^{ikR},\tag{85a}$$

$$h_1^{(1)}(kR) = -\frac{1}{kR}\left(1 + \frac{i}{kR}\right) e^{ikR},\tag{85b}$$

so that we find, to first order in kR_1:

$$Z_\alpha^-(\boldsymbol{r}) = \frac{e^{ikR}}{R} \int \tilde{p}_\alpha^-(\boldsymbol{\xi})\, d\boldsymbol{\xi} - \left(\frac{\partial}{\partial x_\mu} \frac{e^{ikR}}{R}\right) \int \tilde{p}_\alpha^-(\boldsymbol{\xi})\, (\xi_\mu - x_\mu')\, d\boldsymbol{\xi} + \dots\tag{86}$$

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Using (78a) we find

$$\int \tilde{p}_\alpha(\xi, t)\, d\xi = \int \rho_e(\xi, t)\, (\xi_\alpha - x'_\alpha)\, d\xi. \tag{87a}$$

Since $\rho_e(\xi, t)$ is the quantum mechanical charge density the integral in the right hand side of (87a) is the expectation value of the electric dipole moment operator, so that we may rewrite (87a) as follows, using (77c) and (24),

$$\int \tilde{p}_\alpha^-(\xi)\, d\xi = p_\alpha^-. \tag{87b}$$

Similarly, upon splitting $\int \tilde{p}_\alpha^-(\xi)\, (\xi_\mu - x'_\mu)\, d\xi$ into a symmetric and an antisymmetric part, we find, using (78), (24b) and (24c)

$$\int \tilde{p}_\alpha^-(\xi)\, (\xi_\mu - x'_\mu)\, d\xi = \tfrac{1}{2} \int \rho_e^-(\xi)\, (\xi_\alpha - x'_\alpha)\, (\xi_\mu - x'_\mu)\, d\xi -$$

$$- \frac{1}{2i\omega} \int [(\xi_\mu - x'_\mu)\, j_\alpha^-(\xi) - (\xi_\alpha - x'_\alpha)\, j_\mu^-(\xi)]\, d\xi =$$

$$= q_{\alpha\mu}^- - \frac{1}{ik}\, \delta_{\gamma\mu\alpha}\, m_\gamma^-. \tag{88}$$

Combining (86)–(88) we obtain (cf. (26b)):

$$Z_\alpha^-(r) = \frac{e^{ikR}}{R}\, p_\alpha^- + \left(\frac{\partial}{\partial x_\mu}\, \frac{e^{ikR}}{R}\right)\left(- q_{\alpha\mu}^- + \frac{1}{ik}\, \delta_{\gamma\mu\alpha}\, m_\gamma^-\right) + \dots \tag{89}$$

We now recall that in § 2 we showed that p^-, q^- and m^- could be expanded in series of terms of increasing order in d/λ. We found to first order in d/λ (cf. (28), (29), (44)–(47))

$$Z_\alpha^-(r) = Z_\alpha^{(0)-}(r) + Z_\alpha^{(1)-}(r), \tag{90}$$

with

$$Z_\alpha^{(0)-}(r) = \frac{e^{ikR}}{R}\, \alpha_{\alpha\beta}\, E_\beta^-, \tag{91a}$$

$$Z_\alpha^{(1)-}(r) = \frac{e^{ikR}}{R}\, \alpha_{\alpha\beta\gamma}\, E_{\beta\gamma}^- + \left(\frac{\partial}{\partial x_\mu}\, \frac{e^{ikR}}{R}\right)\left(- \alpha'_{\alpha\mu\beta}\, E_\beta^- + \frac{1}{ik}\, \delta_{\gamma\mu\alpha}\, \alpha'_{\gamma\beta}\, E_\beta^-\right). \tag{91b}$$

Using the abbreviations

$$S(r, r') \equiv \frac{e^{ikR}}{R}; \quad \frac{\partial^{(n)}}{\partial x_\mu\, \partial x_\nu \dots}\, S \equiv S_{\mu\nu\dots}, \tag{92}$$

$$\alpha_{\alpha\beta}^{}_{\mu} \equiv - \alpha'_{\alpha\mu\beta} + \frac{1}{ik}\, \delta_{\gamma\mu\alpha}\, \alpha'_{\gamma\beta}, \tag{93}$$

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we can write, according to (90) and (91)

$$Z_\alpha^-(\mathbf{r}) = S\,\alpha_{\alpha\beta}\,E_\beta^- + S\alpha_{\alpha\beta\gamma}\,E_{\beta\gamma}^- + S_\mu\underset{\mu}{\alpha_{\alpha\beta}}\,E_\beta^-. \tag{94}$$

We note that according to (66) and (67) the orientational average of $\underset{\mu}{\alpha_{\alpha\beta}}$ is given by

$$\overline{\underset{\mu}{\alpha_{\alpha\beta}}}^\omega = g_2\,\delta_{\alpha\beta\mu}. \tag{95}$$

Formula (94) forms the starting point in Hoek's work on optical rotatory power. Whereas Hoek simply assumes (94) to hold for an arbitrary molecule, we have given a rigorous derivation on the basis of Rosenfeld's quantum mechanical treatment for a general molecule consisting of point charges. In doing so, we obtained at the same time explicit expressions in terms of matrix elements for the tensors $\alpha_{\alpha\beta}$, $\alpha_{\alpha\beta\gamma}$ and $\underset{\mu}{\alpha_{\alpha\beta}}$. These tensors, called by Hoek "generalized polarizability tensors", depend on the kind of molecule under consideration (in a specific case), its orientation and the frequency of the external field.

§ 4. *The equations for dynamical equilibrium.* Consider now a medium consisting of N identical particles. Let the positions of the centres of the molecules be $\mathbf{r}_i(i = 1, 2, ..., N)$. The secondary radiation field Re $\mathbf{E}^-$ $e^{-i\omega t}$ emitted by molecule j, when it undergoes the influence of a field Re $\mathbf{E}'^-$ $e^{-i\omega t}$, is, according to (73c) and (94):

$$E_\alpha^-(\mathbf{r}) = T_{\alpha\beta}(\mathbf{r})\,Z_\beta^-(\mathbf{r}) = T_{\alpha\beta}(\mathbf{r})\,S(\mathbf{r}, \mathbf{r}_j)\,\alpha_{\beta\gamma}\,E_\gamma'^-(\mathbf{r}_j) +$$
$$+ T_{\alpha\beta}(\mathbf{r})\,S(\mathbf{r}, \mathbf{r}_j)\,\alpha_{\beta\gamma\delta}\,E_{\gamma\delta}'^-(\mathbf{r}_j) + T_{\alpha\beta}(\mathbf{r})\,S_\mu(\mathbf{r}, \mathbf{r}_j)\,\underset{\mu}{\alpha_{\beta\gamma}}\,E_\gamma'^-(\mathbf{r}_j), \tag{96}$$

where, as usual, we dropped the factor $e^{-i\omega t}$ and where we introduced the abbreviation

$$T_{\alpha\beta}(\mathbf{r}) \equiv (\text{rot rot})_{\alpha\beta}. \tag{97}$$

Since the operator $T_{\alpha\beta}$ will always act upon quantities A satisfying the wave equation

$$(\Delta + k^2)\,A = 0, \tag{98}$$

we have

$$T_{\alpha\beta}(\mathbf{r}) = \nabla_\alpha\nabla_\beta + k^2\delta_{\alpha\beta}. \tag{97a}$$

From now on we shall omit the minus sign denoting the complex amplitudes associated with the time factor $e^{-i\omega t}$. Let the external field, *i.e.* the field of the light-wave, be Re $\mathbf{E}^0$ $e^{-i\omega t}$. The "exciting field" at the centre of molecule i, Re $\mathbf{E}_i$ $e^{-i\omega t}$, is then the sum of the external field and the second-

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ary radiation fields from all the other molecules:

$$E_{i\alpha} = E_{\alpha}^0(\mathbf{r}_i) + \sum_{j \neq i} T_{\alpha\beta}(\mathbf{r}_i) \, S(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma} +$$

$$+ \sum_{j \neq i} T_{\alpha\beta}(\mathbf{r}_i) \, S(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma\delta}(j) \, E_{j\gamma\delta} + \sum_{j \neq i} T_{\alpha\beta}(\mathbf{r}_i) \, S_\mu(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma}. \qquad (99)$$

For the derivatives $E_{j\gamma\delta}$, occurring in the right hand side of (99) we have accordingly

$$E_{i\alpha\varepsilon} = E_{\alpha\varepsilon}^0(\mathbf{r}_i) + \sum_{j \neq i} T_{\alpha\beta}(\mathbf{r}_i) \, S_\varepsilon(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma}, \qquad (100)$$

where we have neglected the terms of first order in d/λ, since $E_{i\alpha\varepsilon}$ will only be needed in (99), where it appears in a term which is itself of first order in d/λ.

We note that we have assumed the generalized polarizability tensors to depend only on the kind of molecule under consideration, its orientation and the frequency of the external field, whereas in reality they will also depend on the positions and orientations of all molecules [5] [15] [16]).

§ 5. *The integral equations for the statistical averages.* In accordance with the foregoing we now regard our system of N identical molecules as consisting of N particles with positions $\mathbf{r}_i$, orientations $\boldsymbol{\omega}_i$ and canonically conjugated momenta. Their internal structure is contained in the characteristic polarizability tensors $\alpha_{\alpha\beta}$, $\alpha_{\alpha\beta\gamma}$ and $\alpha_{\alpha\beta}^{\mu}$. We take the system to be in thermal equilibrium. For the configuration distribution function f that we use to describe the system we may take the distribution function in the absence of the external field, since we are throughout this investigation interested in the linear approximation for the induced electric effects. Then f is a function of $\mathbf{r}^N$, $\boldsymbol{\omega}^N$ only. We assume it to be normalized to 1:

$$\langle f \rangle_{\omega, \, \mathbf{r}} = 1, \qquad (101)$$

$\langle \ldots \rangle_{\omega, \, \mathbf{r}}$ denoting an integration over position and orientation coordinates. We define the $\boldsymbol{\omega}_i$ in such a way that

$$\int \mathrm{d}\omega = 1, \qquad (102)$$

the integration extending over all orientations.

We confine ourselves to the case of "spherical" molecules, *i.e.* we assume that the interaction-energy of a pair of molecules in the absence of the external field does not depend on their orientations. Then the configuration distribution function depends only on the position coordinates,

$$f = f(\mathbf{r}^N), \qquad (103)$$

with, according to (101) and (102),

$$\langle f \rangle_{\mathbf{r}} = 1. \qquad (104)$$

Let the number density be uniform:

$$\sum_{i=1}^{N} \langle \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} = \sum_{i=1}^{N} \langle \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\mathbf{r}} = \rho = \frac{N}{V}, \tag{105}$$

V being the total volume of the system.

The average of $\mathbf{E}_i$, when molecule i is at $\mathbf{r}$, the positions of all other molecules being arbitrary, is given by

$$\overline{E_{i\alpha}}(\mathbf{r}) = \frac{\langle E_{i\alpha} \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}}}{\langle \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}}}. \tag{106}$$

The molecules being identical, we have

$$\overline{E_{i\alpha}}(\mathbf{r}) = \overline{E_{j\alpha}}(\mathbf{r}) = \overline{E_\alpha}(\mathbf{r}). \tag{107}$$

The average exciting field per unit volume, $\mathscr{E}_\alpha(\mathbf{r})$, is

$$\mathscr{E}_\alpha(\mathbf{r}) = \sum_i \langle E_{i\alpha} \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} = \rho \overline{E_\alpha}(\mathbf{r}). \tag{108}$$

Similarly, the average per unit volume of the derivative of the exciting field is

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) = \sum_i \langle E_{i\alpha\varepsilon} \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} = \rho \overline{E_{\alpha\varepsilon}}(\mathbf{r}). \tag{109}$$

We note that in general $\mathscr{E}_{\alpha\varepsilon}^{(1)} \neq (\partial/\partial x_\varepsilon) \, \mathscr{E}_\alpha(\mathbf{r})$, *i.e.* the average of the derivative of the exciting field is not the same as the derivative of the average exciting field, since according to (108)

$$\frac{\partial}{\partial x_\varepsilon} \mathscr{E}_\alpha(\mathbf{r}) = - \sum_i \left\langle E_{i\alpha} \left\{ \frac{\partial}{\partial x_{i\varepsilon}} \delta(\mathbf{r}_i - \mathbf{r}) \right\} f \right\rangle_{\omega, \mathbf{r}} =$$

$$= \sum_i \langle E_{i\alpha\varepsilon} \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} + \sum_i \left\langle E_{i\alpha} \delta(\mathbf{r}_i - \mathbf{r}) \frac{\partial f}{\partial x_{i\varepsilon}} \right\rangle_{\omega, \mathbf{r}} =$$

$$= \mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) + \sum_i \left\langle E_{i\alpha} \delta(\mathbf{r}_i - \mathbf{r}) \frac{\partial f}{\partial x_{i\varepsilon}} \right\rangle_{\omega, \mathbf{r}}. \tag{110}$$

In § 6, where $\mathscr{E}_{\alpha\varepsilon}^{(1)}$ will be calculated in terms of $\mathscr{E}_\alpha$, this statement will be made more precise (cf. (144)).

Substitution of (99) and (100) into (108) and (109) yields

$$\mathscr{E}_\alpha(\mathbf{r}) = \rho E_\alpha^0(\mathbf{r}) + \sum_{\substack{i, j \\ j \neq i}} \langle [T_{\alpha\beta}(\mathbf{r}_i) \, S(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma}] \, \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} +$$

$$+ \sum_{\substack{i, j \\ j \neq i}} \langle [T_{\alpha\beta}(\mathbf{r}_i) \, S(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma\delta}(j) \, E_{j\gamma\delta}] \, \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}} +$$

$$+ \sum_{\substack{i, j \\ j \neq i}} \langle [T_{\alpha\beta}(\mathbf{r}_i) \, S_\mu(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma}]_\mu \, \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}}, \tag{111}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) = \rho E_{\alpha\varepsilon}^0(\mathbf{r}) + \sum_{\substack{i, j \\ j \neq i}} \langle [T_{\alpha\beta}(\mathbf{r}_i) \, S_\varepsilon(\mathbf{r}_i, \mathbf{r}_j) \, \alpha_{\beta\gamma}(j) \, E_{j\gamma}] \, \delta(\mathbf{r}_i - \mathbf{r}) f \rangle_{\omega, \mathbf{r}}. \tag{112}$$

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Performing the integration over the orientation coordinates, neglecting orientational correlations [18] between the polarizability tensors and the exciting fields, we have, using (64), (65) and (95):

$$\mathscr{E}_\alpha(\mathbf{r}) = \rho E_\alpha^0(\mathbf{r}) + \sum_{\substack{i,j \\ j \neq i}} g_0 \langle [T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) E_{j\beta}] \delta(\mathbf{r}_i - \mathbf{r}) f \rangle +$$

$$+ \sum_{j \neq i} g_1 \langle [T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\delta} E_{j\gamma\delta}] \delta(\mathbf{r}_i - \mathbf{r}) f \rangle +$$

$$+ \sum_{j \neq i} g_2 \langle [T_{\alpha\beta}(\mathbf{r}_i) S_\mu(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\mu} E_{j\gamma}] \delta(\mathbf{r}_i - \mathbf{r}) f \rangle, \tag{113}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) = \rho E_{\alpha\varepsilon}^0(\mathbf{r}) + \sum_{\substack{i,j \\ j \neq i}} g_0 \langle [T_{\alpha\beta}(\mathbf{r}_i) S_\varepsilon(\mathbf{r}_i, \mathbf{r}_j) E_{j\beta}] \delta(\mathbf{r}_i - \mathbf{r}) f \rangle. \tag{114}$$

Here and in what follows $\langle \ldots \rangle$ denotes an integration over position coordinates. We note that formally we arrive at the same result by taking as basic equations

$$E_{i\alpha} = E_\alpha^0(\mathbf{r}_i) + \sum_{j \neq i} g_0 T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) E_{j\beta} +$$

$$+ \sum_{j \neq i} g_1 T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\delta} E_{j\gamma\delta} + \sum_{j \neq i} g_2 T_{\alpha\beta}(\mathbf{r}_i) S_\mu(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\mu} E_{j\gamma}, \tag{115}$$

$$E_{i\alpha\varepsilon} = E_{\alpha\varepsilon}^0(\mathbf{r}_i) + \sum_{j \neq i} g_0 T_{\alpha\beta}(\mathbf{r}_i) S_\varepsilon(\mathbf{r}_i, \mathbf{r}_j) E_{j\beta}, \tag{116}$$

so that the fields do not depend on ω^N.

In order to simplify the notation, let us write

$$\left. \begin{aligned}
T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) &\equiv A_{\alpha\beta}^{(0)}(\mathbf{r}_i, \mathbf{r}_j) \\
T_{\alpha\beta}(\mathbf{r}_i) S(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\delta} &\equiv A_{\alpha\gamma\delta}^{(1)}(\mathbf{r}_i, \mathbf{r}_j) \\
T_{\alpha\beta}(\mathbf{r}_i) S_\mu(\mathbf{r}_i, \mathbf{r}_j) \delta_{\beta\gamma\mu} &\equiv A_{\alpha\gamma}^{(2)}(\mathbf{r}_i, \mathbf{r}_j) \\
T_{\alpha\beta}(\mathbf{r}_i) S_\varepsilon(\mathbf{r}_i, \mathbf{r}_j) &\equiv B_{\alpha\varepsilon\beta}^{(0)}(\mathbf{r}_i, \mathbf{r}_j).
\end{aligned} \right\} \tag{117}$$

We can then write for (113) and (114)

$$\mathscr{E}_\alpha(\mathbf{r}) = \rho E_\alpha^0(\mathbf{r}) + \sum_{\substack{i,j \\ j \neq i}} g_0 \int^V \mathrm{d}\mathbf{r}' \langle A_{\alpha\beta}^{(0)}(\mathbf{r}_i, \mathbf{r}_j) \overline{E}_\beta(\mathbf{r}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') f \rangle +$$

$$+ \sum_{\substack{i,j \\ j \neq i}} g_2 \int^V \mathrm{d}\mathbf{r}' \langle A_{\alpha\beta}^{(2)}(\mathbf{r}_i, \mathbf{r}_j) \overline{E}_\beta(\mathbf{r}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') f \rangle +$$

$$+ \sum_{\substack{i,j \\ j \neq i}} g_1 \int^V \mathrm{d}\mathbf{r}' \langle A_{\alpha\gamma\delta}^{(1)}(\mathbf{r}_i, \mathbf{r}_j) \overline{E}_{\gamma\delta}(\mathbf{r}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') f \rangle +$$

$$+ J_\alpha(\mathbf{r}), \tag{118}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) = \rho E_{\alpha\varepsilon}^0(\mathbf{r}) + \sum_{\substack{i,j \\ j \neq i}} g_0 \int^V \mathrm{d}\mathbf{r}' \langle B_{\alpha\varepsilon\beta}^{(0)}(\mathbf{r}_i, \mathbf{r}_j) \overline{E}_\beta(\mathbf{r}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\mathbf{r}_j - \mathbf{r}') f \rangle +$$

$$+ J_{\alpha\varepsilon}^{(1)}(\mathbf{r}), \tag{119}$$

with the "fluctuation"-terms

$$
J_\alpha(r) = \sum_{\substack{i,j \\ j \neq i}} g_0 \int^V dr' \langle A^{(0)}_{\alpha\beta}(r_i, r_j) (E_{j\beta} - \overline{E_\beta}) \delta(r_i - r) \delta(r_j - r') f \rangle +
$$

$$
+ \sum_{\substack{i,j \\ j \neq i}} g_2 \int^V dr' \langle A^{(2)}_{\alpha\beta}(r_i, r_j) (E_{j\beta} - \overline{E_\beta}) \delta(r_i - r) \delta(r_j - r') f \rangle +
$$

$$
+ \sum_{\substack{i,j \\ j \neq i}} g_1 \int^V dr' \langle A^{(1)}_{\alpha\gamma\delta}(r_i, r_j) (E_{j\gamma\delta} - \overline{E_{\gamma\delta}}) \delta(r_i - r) \delta(r_j - r') f \rangle. \tag{120}
$$

$$
J^{(1)}_{\alpha\varepsilon}(r) = \sum_{\substack{i,j \\ j \neq i}} g_0 \int^V dr' \langle B^{(0)}_{\alpha\varepsilon\beta}(r_i, r_j) (E_{j\beta} - \overline{E_\beta}) \delta(r_i - r) \delta(r_j - r') f \rangle. \tag{121}
$$

Using the definition of the pair distribution function

$$
\rho^2 g(r, r') = \sum_{\substack{i,j \\ j \neq i}} \langle \delta(r_i - r) \delta(r_j - r') f \rangle, \tag{122}
$$

we can write (120) and (121) as follows:

$$
\mathscr{E}_\alpha(r) = \rho E^0_\alpha(r) + G_0 \int^V dr' A^{(0)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') g(r, r') +
$$

$$
+ G_2 \int^V dr' A^{(2)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') g(r, r') +
$$

$$
+ G_1 \int^V dr' A^{(1)}_{\alpha\gamma\delta}(r, r') \mathscr{E}^{(1)}_{\gamma\delta}(r') g(r, r') + J_\alpha(r), \tag{123}
$$

$$
\mathscr{E}^{(1)}_{\alpha\varepsilon}(r) = \rho E^0_{\alpha\varepsilon}(r) + G_0 \int^V dr' B^{(0)}_{\alpha\varepsilon\beta}(r, r') \mathscr{E}_\beta(r') g(r, r') +
$$

$$
+ J^{(1)}_{\alpha\varepsilon}(r), \tag{124}
$$

where

$$
\rho g_i \equiv G_i \qquad (i = 1, 2, 3). \tag{125}
$$

Using the fact that due to the strong repulsion between particles at very small distances $g(r, r') \to 0$ for $r' \to r$ we may in the integrals occurring in (123) and (124) exclude a little sphere of volume $v(r)$, centered around r, from the region of integration. Then, writing $g(r, r') \equiv 1 + \{g(r, r') - 1\}$ the upper limit of the integral containing $\{g(r, r') - 1\}$ may be taken to be ∞ if we assume the linear dimensions of our system to be large compared with the correlation length between molecules, i.e. large compared with the linear dimensions of the region where $g(r, r')$ is appreciably different from 1. Thus we have, e.g. for the integral with $A^{(0)}_{\alpha\beta}$

$$
\int^V_{v(r)} dr' A^{(0)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') g(r, r') = \int^\infty_{v(r)} dr' A^{(0)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') g(r, r') =
$$

$$
= \int^V_{v(r)} dr' A^{(0)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') + \int^\infty_{v(r)} dr' A^{(0)}_{\alpha\beta}(r, r') \mathscr{E}_\beta(r') \{g(r, r') - 1\}. \tag{126}
$$

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Introducing the following abbreviations:

$$\mathscr{E}_\alpha^d(\boldsymbol{r}) = G_0 \int\limits_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\beta(\boldsymbol{r}') +$$

$$+ G_2 \int\limits_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(2)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\beta(\boldsymbol{r}') + G_1 \int\limits_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta\gamma}^{(1)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_{\beta\gamma}^{(1)}(\boldsymbol{r}'), \qquad (127)$$

$$\mathscr{E}_{\alpha\beta}^{(1)d}(\boldsymbol{r}) = G_0 \int\limits_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, B_{\alpha\beta\gamma}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\gamma(\boldsymbol{r}'), \qquad (128)$$

we can then write for (123) and (124):

$$\mathscr{E}_\alpha(\boldsymbol{r}) = \rho E_\alpha^0(\boldsymbol{r}) + \mathscr{E}_\alpha^d(\boldsymbol{r}) + G_0 \int\limits_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\beta(\boldsymbol{r}')\,\{g(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ G_2 \int\limits_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(2)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\beta(\boldsymbol{r}')\,\{g(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ G_1 \int\limits_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta\gamma}^{(1)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_{\beta\gamma}^{(1)}(\boldsymbol{r}')\,\{g(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ J_\alpha(\boldsymbol{r}), \qquad (129)$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\boldsymbol{r}) = \rho E_{\alpha\varepsilon}^0(\boldsymbol{r}) + \mathscr{E}_{\alpha\varepsilon}^{(1)d}(\boldsymbol{r}) +$$

$$+ G_0 \int\limits_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, B_{\alpha\varepsilon\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\, \mathscr{E}_\beta(\boldsymbol{r}')\,\{g(\boldsymbol{r},\,\boldsymbol{r}') - 1\} + J_{\alpha\varepsilon}^{(1)}(\boldsymbol{r}). \qquad (130)$$

One now clearly sees the influence of statistical effects: they are embodied in what we shall call the "correlation terms", consisting of integrals with $\{g(\boldsymbol{r},\,\boldsymbol{r}') - 1\}$ in the integrand, and in the terms $J_\alpha(\boldsymbol{r})$ and $J_{\alpha\varepsilon}^{(1)}(\boldsymbol{r})$, to which we shall refer as "fluctuation terms", since they find their origin in the fluctuations of $E_{J\alpha}$ and $E_{J\alpha\beta}$ around their averages $\overline{E_\alpha}$ and $\overline{E_{\alpha\beta}}$. When these statistical effects are completely neglected, i.e. when we put $g(\boldsymbol{r},\,\boldsymbol{r}') \equiv$ $\equiv 1$, $J_\alpha \equiv 0$ and $J_{\alpha\varepsilon}^{(1)} \equiv 0$, (129) and (130) reduce to Hoek's equations, which he obtained by averaging over physically infinitesimal volume elements. We shall go one step further. We note that (129) and (130) are rigorous to first order in d/λ. The "main" terms, i.e. the non-statistical terms $\mathscr{E}_\alpha^d$ and $\mathscr{E}_{\alpha\varepsilon}^{(1)d}$, as well as the statistical correction terms may be classified as being of zeroth or first order (in d/λ) according to whether they contain g_0 or either one of g_1 and g_2 respectively. Now the main terms of first order are very small compared to the main terms of zeroth order. The first order statistical correction terms are correspondingly very small compared to the zeroth order statistical terms. On the other hand the statistical correction terms of zeroth order are very small compared to the zeroth order main terms. We therefore make the following approximation: we dropp all first order statistical terms, i.e. we take the statistical effects into account only in so far as they occur in the zeroth order theory, the theory of the refractive

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index of non-polar, isotropic media. Thus in (129) we retain only those correlation and fluctuation terms containing G_0. Furthermore we shall neglect, for the sake of simplicity, the correlation and fluctuation terms in (130), since $\mathscr{E}_{\alpha\varepsilon}^{(1)}(r)$ is needed only in the small contribution to $\mathscr{E}_{\alpha}^{d}(r)$ containing G_1 (cf. (127)) *). We then have:

$$\mathscr{E}_\alpha(r) = \rho E_\alpha^0(r) + \mathscr{E}_\alpha^d(r) + G_0 \int\limits_{v(r)}^{\infty} dr' \, A_{\alpha\beta}^{(0)}(r, r') \, \mathscr{E}_\beta(r') \, \{g(r, r') - 1\} +$$
$$+ J_\alpha(r), \tag{131}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(r) = \rho E_{\alpha\varepsilon}^0(r) + \mathscr{E}_{\alpha\varepsilon}^{(1)d}(r), \tag{132}$$

with

$$J_\alpha(r) = \sum_{\substack{i, j \\ j \neq i}} g_0 \int\limits^{V} dr' \, \langle A_{\alpha\beta}^{(0)}(r_i, r_j) \, (E_{j\beta} - \overline{E_\beta}) \, \delta(r_i - r) \, \delta(r_j - r') f \rangle. \tag{133}$$

It can be shown [5]) that $J_\alpha(r)$ may be written as

$$J_\alpha(r) = \int\limits^{V} dr' \, K_{\alpha\beta}(r, r') \, [\rho E_\beta^0(r') + \mathscr{E}_\beta^d(r') +$$
$$+ g_0 \int\limits_{v(r)}^{\infty} dr'' \, A_{\beta\gamma}^{(0)}(r', r'') \, \mathscr{E}_\gamma(r'') \, \{g(r', r'') - 1\}], \tag{134}$$

where the kernel $K_{\alpha\beta}(r, r')$ is a symmetric tensor such that

$$\int K_{\alpha\beta}(r, r') \, dr' = \delta_{\alpha\beta} \, \varphi(\rho, T, \omega), \tag{135}$$

with φ a function of density, temperature and frequency only. One obtains for $K_{\alpha\beta}(r, r')$ to second order in g_0:

$$K_{\alpha\beta}(r, r') = \rho^2 g_0^2 \int\limits^{V} dr'' \, A_{\alpha\gamma}^{(0)}(r, r'') \, A_{\gamma\beta}^{(0)}(r'', r') \, \{g(r, r'', r') -$$
$$- g(r, r'') \, g(r'', r')\} +$$
$$+ \rho g_0^2 \int\limits^{V} dr'' \, A_{\alpha\gamma}^{(0)}(r, r'') \, A_{\gamma\beta}^{(0)}(r'', r') \, \{g(r, r'') \, \delta(r - r')\}, \tag{136}$$

where $\rho^3 g(r, r'', r')$ is the distribution function for three particles, defined by

$$\rho^3 g(r, r'', r') = \sum_{\substack{i, k, l \\ k \neq i, \, l \neq k, \, l \neq i}} \langle \delta(r_i - r) \, \delta(r_k - r'') \, \delta(r_l - r') f \rangle. \tag{137}$$

Thus we can write for (131):

$$\mathscr{E}_\alpha(r) = \rho E_\alpha^0(r) + \mathscr{E}_\alpha^d(r) + G_0 \int\limits_{v(r)}^{\infty} dr' \, A_{\alpha\beta}^{(0)}(r, r') \, \mathscr{E}_\beta(r') \, \{g(r, r') - 1\} +$$
$$+ \int\limits^{V} dr' \, K_{\alpha\beta}(r, r') \, [\rho E_\beta^0(r') + \mathscr{E}_\beta^d(r') +$$
$$+ G_0 \int\limits_{v(r')}^{\infty} dr'' \, A_{\beta\gamma}^{(0)}(r', r'') \, \mathscr{E}_\beta(r'') \, \{g(r', r'') - 1\}]. \tag{138}$$

(138) and (132) are the desired integral equations.

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*) See, however, the discussion after formula (157).

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One might ask whether these equations would be essentially modified if the first order statistical effects, neglected in the transition from (129) and (130) to (131) and (132) had been taken into account. In order to show that this is not the case, we derive in appendix A the full integral equations resulting from (129) and (130). Obviously these equations are more complicated than (138) and (132). However, they display the same structure as the latter equations and could in principle be treated by the same methods that will be applied to (138) and (132) in the following.

§ 6. *Computation of the optical rotatory power.* We shall now show that (138) and (132) have a solution satisfying

$$\Delta \mathscr{E} + k^2 n^2 \, \mathscr{E} = 0, \tag{139}$$

$$\text{div } \mathscr{E} = 0, \tag{140}$$

$$\Delta \mathscr{E}^{(1)}_{\alpha\beta} + k^2 n^2 \, \mathscr{E}^{(1)}_{\alpha\beta} = 0. \tag{141}$$

In order to prove this we assume (139)–(141) to hold and show that n can be chosen in such a way that (138) and (132) become identities. Finally n will be identified with the physical refractive index of the medium.

With (141) one can show (cf. appendix B) that, providing $n^2 \neq 1$, (132) can be written as

$$\mathscr{E}^{(1)}_{\alpha\varepsilon}(\boldsymbol{r}) = \rho E^0_{\alpha\varepsilon}(\boldsymbol{r}) + G_0 \left[\frac{4\pi}{5} \left\{ \frac{\partial \mathscr{E}_\alpha}{\partial x_\varepsilon} + \frac{\partial \mathscr{E}_\varepsilon}{\partial x_\alpha} + \delta_{\alpha\varepsilon} \, \text{div } \mathscr{E} \right\} + \right.$$

$$+ \frac{4\pi}{k^2(n^2 - 1)} \frac{\partial^2}{\partial x_\alpha \, \partial x_\varepsilon} \, \text{div } \mathscr{E} + \frac{4\pi}{n^2 - 1} \frac{\partial \mathscr{E}_\alpha}{\partial x_\varepsilon} \left. \right] +$$

$$+ G_0 \frac{1}{k^2(n^2 - 1)} \, T_{\alpha\beta}(\boldsymbol{r}) \int^\Sigma \mathrm{d}\boldsymbol{r}' \left[\mathscr{E}_\beta(\boldsymbol{r}') \frac{\partial}{\partial v} S_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') - S_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') \frac{\partial}{\partial v} \mathscr{E}_\beta(\boldsymbol{r}') \right], \tag{142}$$

where the integration extends over the bounding surface Σ of the system and where $\partial/\partial v$ denotes a differentiation in the direction of the outward normal to Σ. The terms in (142) can be divided into two groups, each group satisfying a different wave equation. Hence each group of terms must vanish separately. This leads to an equation describing the extinction of the field $E^0_{\alpha\varepsilon}$, i.e. the derivative of the external field,

$$\rho E^0_{\alpha\varepsilon}(\boldsymbol{r}) + G_0 \frac{1}{k^2(n^2 - 1)} \, T_{\alpha\beta}(\boldsymbol{r}) \int^\Sigma \mathrm{d}\boldsymbol{r}' \left[\mathscr{E}_\beta(\boldsymbol{r}') \frac{\partial}{\partial v} S_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') - \right.$$

$$\left. - S_\varepsilon(\boldsymbol{r}, \boldsymbol{r}') \frac{\partial}{\partial v} \mathscr{E}_\beta(\boldsymbol{r}') \right] = 0 \tag{143}$$

and to an equation expressing $\mathscr{E}_{\alpha\varepsilon}^{(1)}$ in terms of $\mathscr{E}_\alpha$:

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r}) = G_0 \left[\frac{4\pi}{5} \left\{ \frac{\partial \mathscr{E}_\alpha}{\partial x_\varepsilon} + \frac{\partial \mathscr{E}_\varepsilon}{\partial x_\alpha} + \delta_{\alpha\varepsilon} \operatorname{div} \mathscr{E} \right\} + \frac{4\pi}{k^2(n^2-1)} \frac{\partial^2}{\partial x_\alpha \partial x_\varepsilon} \operatorname{div} \mathscr{E} + \right.$$

$$\left. + \frac{4\pi}{n^2-1} \frac{\partial \mathscr{E}_\alpha}{\partial x_\varepsilon} \right]. \tag{144}$$

According to (140) the terms in (144) containing div $\mathscr{E}$ are zero. We then obtain from (144)

$$\delta_{\alpha\beta\gamma} \mathscr{E}_{\beta\gamma}^{(1)} = - G_0 \frac{4\pi}{n^2-1} \operatorname{rot}_\alpha \mathscr{E}. \tag{145}$$

These relations explicitly show the difference between the average of the derivative of the exciting field strength, $\mathscr{E}_{\alpha\varepsilon}^{(1)}(\mathbf{r})$, on the one hand, and the derivative of the average exciting field strength, $(\partial/\partial x_\varepsilon) \mathscr{E}_\alpha(\mathbf{r})$, on the other hand. (cf. the discussion after formula (109)).

Let us choose for $\mathscr{E}$ a solution of (139) and (140) representing a transverse plane wave propagated in an arbitrary direction. We then have

$$\mathscr{E}(\mathbf{r'}) = \mathscr{E}(\mathbf{r}) \, e^{ink \cdot (\mathbf{r'}-\mathbf{r})}, \tag{146}$$

where the vector $\mathbf{k}$ is the product of k and the unit vector in the direction of propagation. Then the integral equation (138) may be brought into the form

$$\{1 + G_0 D(1 + R)\} \mathscr{E}_\alpha(\mathbf{r}) = \rho E_\alpha^0(\mathbf{r}) + \mathscr{E}_\alpha^d(\mathbf{r}) + $$

$$+ \int\limits^V d\mathbf{r'} \, K_{\alpha\beta}(\mathbf{r}, \mathbf{r'}) \left[\rho E_\beta^0(\mathbf{r'}) + \mathscr{E}_\beta^d(\mathbf{r'}) \right], \tag{147}$$

with the definitions

$$D(\rho, T, \omega) = - \int\limits_{v(\mathbf{r})}^{\infty} d\mathbf{r'} \, n_\alpha A_{\alpha\beta}^{(0)}(\mathbf{r}, \mathbf{r'}) \, n_\beta \, e^{ink \cdot (\mathbf{r'}-\mathbf{r})} \{ g(\mathbf{r}, \mathbf{r'}) - 1 \}, \tag{148}$$

$$R(\rho, T, \omega) = \int\limits^V d\mathbf{r'} \, n_\alpha \, K_{\alpha\beta}'(\mathbf{r}, \mathbf{r'}) \, n_\beta \, e^{ink \cdot (\mathbf{r'}-\mathbf{r})}, \tag{149}$$

where $\mathbf{n}$ denotes the unit vector in a direction perpendicular to $\mathbf{k}(\mathbf{k} \cdot \mathbf{n} = 0)$. With (139), (140) and (145) one can show (cf. Appendix B) that

$$\mathscr{E}_\alpha^d(\mathbf{r}) = G_0 \frac{4\pi}{3} \frac{n^2+2}{n^2-1} \mathscr{E}_\alpha(\mathbf{r}) - G_2 \frac{4\pi}{n^2-1} \operatorname{rot}_\alpha \mathscr{E}(\mathbf{r}) -$$

$$- G_1 G_0 \frac{4\pi}{3} \frac{n^2+2}{n^2-1} \frac{4\pi}{n^2-1} \operatorname{rot}_\alpha \mathscr{E}(\mathbf{r}) +$$

$$+ G_0 \frac{1}{k^2(n^2-1)} T_{\alpha\beta}(\mathbf{r}) \int\limits^\Sigma d\mathbf{r'} \left[\mathscr{E}_\beta(\mathbf{r'}) \frac{\partial}{\partial \nu} S(\mathbf{r}, \mathbf{r'}) - \right.$$

$$\left. - S(\mathbf{r}, \mathbf{r'}) \frac{\partial}{\partial \nu} \mathscr{E}_\beta(\mathbf{r'}) \right] +$$

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$$+ G_2 \frac{1}{k^2(n^2-1)} T_{\alpha\beta}(\mathbf{r})\, \delta_{\beta\gamma\delta} \int^{\Sigma} \mathrm{d}\mathbf{r}' \left[\mathscr{E}_\gamma(\mathbf{r}') \frac{\partial}{\partial\nu} S_\delta(\mathbf{r}, \mathbf{r}') - \right.$$

$$\left. - S_\delta(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial\nu} \mathscr{E}_\gamma(\mathbf{r}') \right] +$$

$$+ G_1 G_0 \frac{1}{k^2(n^2-1)} \frac{4\pi}{n^2-1} T_{\alpha\beta}(\mathbf{r}) \int^{\Sigma} \mathrm{d}\mathbf{r}' \left[\mathrm{rot}_\beta\, \mathscr{E}(\mathbf{r}') \frac{\partial}{\partial\nu} S(\mathbf{r}, \mathbf{r}') - \right.$$

$$\left. - S(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial\nu} \mathrm{rot}_\beta\, \mathscr{E}(\mathbf{r}') \right]. \tag{150}$$

Combining (147) and (150) we obtain once again an equation containing two groups of terms each satisfying a different wave equation. This yields an equation describing the extinction of $\mathbf{E}^0$ itself,

$$\rho E_\alpha^0(\mathbf{r}) + G_0 \frac{1}{k^2(n^2-1)} T_{\alpha\beta}(\mathbf{r}) \int^{\Sigma}\mathrm{d}\mathbf{r}' \left[\mathscr{E}_\beta(\mathbf{r}') \frac{\partial}{\partial\nu} S(\mathbf{r}, \mathbf{r}') - S(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial\nu} \mathscr{E}_\beta(\mathbf{r}') \right] +$$

$$+ G_2 \frac{1}{k^2(n^2-1)} T_{\alpha\beta}(\mathbf{r})\, \delta_{\beta\gamma\delta} \int^{\Sigma}\mathrm{d}\mathbf{r}' \left[\mathscr{E}_\gamma(\mathbf{r}') \frac{\partial}{\partial\nu} S_\delta(\mathbf{r}, \mathbf{r}') - S_\delta(\mathbf{r}, \mathbf{r}') \frac{\partial}{\partial\nu} \mathscr{E}_\gamma(\mathbf{r}') \right] +$$

$$+ G_1 G_0 \frac{1}{k^2(n^2-1)} \frac{4\pi}{n^2-1} T_{\alpha\beta}(\mathbf{r}) \int^{\Sigma}\mathrm{d}\mathbf{r}' \left[\mathrm{rot}_\beta\, \mathscr{E}(\mathbf{r}') \frac{\partial}{\partial\nu} S(\mathbf{r}, \mathbf{r}') - S(\mathbf{r}, \mathbf{r}') \cdot \right.$$

$$\left. \cdot \frac{\partial}{\partial\nu} \mathrm{rot}_\beta \mathscr{E}(\mathbf{r}') \right] = 0, \tag{151}$$

and a generalization of H o e k's corresponding formula:

$$\mathscr{E}(\mathbf{r}) = \frac{1+R}{1 + G_0 D(1+R)} \left[G_0 \frac{4\pi}{3} \frac{n^2+2}{n^2-1} \mathscr{E}(\mathbf{r}) - \right.$$

$$\left. - G_2 \frac{4\pi}{n^2-1} \mathrm{rot}\, \mathscr{E}(\mathbf{r}) - G_1 G_0 \frac{4\pi}{3} \frac{n^2+2}{n^2-1} \frac{4\pi}{n^2-1} \mathrm{rot}\, \mathscr{E}(\mathbf{r}) \right]. \tag{152}$$

We still have to identify n with the refractive index. For this purpose we evaluate the average field $\mathbf{E}(\mathbf{r})$ in an arbitrary point of the medium:

$$E_\alpha(\mathbf{r}) = E_\alpha^0(\mathbf{r}) + \sum_j \langle T_{\alpha\beta}(\mathbf{r})\, S(\mathbf{r}, \mathbf{r}_j)\, \alpha_{\beta\gamma}(j)\, E_{j\gamma}\, \nmid\rangle_{\omega, \mathbf{r}} +$$

$$+ \sum_j \langle T_{\alpha\beta}(\mathbf{r})\, S_\mu(\mathbf{r}, \mathbf{r}_j)\, \alpha_{\beta\gamma}(j)\, E_{j\gamma}\, \nmid\rangle_{\omega, \mathbf{r}} +$$

$$+ \sum_j \langle T_{\alpha\beta}(\mathbf{r})\, S(\mathbf{r}, \mathbf{r}_j)\, \alpha_{\beta\gamma\delta}(j)\, E_{j\gamma\delta}\, \nmid\rangle_{\omega, \mathbf{r}} =$$

$$= E_\alpha^0(\mathbf{r}) + g_0 \int^V \mathrm{d}\mathbf{r}'\, T_{\alpha\beta}(\mathbf{r})\, S(\mathbf{r}, \mathbf{r}')\, \mathscr{E}_\beta(\mathbf{r}') +$$

$$+ g_2 \int^V \mathrm{d}\mathbf{r}'\, T_{\alpha\beta}(\mathbf{r})\, S_\mu(\mathbf{r}, \mathbf{r}')\, \delta_{\beta\gamma\mu}\, \mathscr{E}_\gamma(\mathbf{r}') +$$

$$+ g_1 \int^V \mathrm{d}\mathbf{r}'\, T_{\alpha\beta}(\mathbf{r})\, S(\mathbf{r}, \mathbf{r}')\, \delta_{\beta\gamma\delta}\, \mathscr{E}_{\gamma\delta}^{(1)}(\mathbf{r}'). \tag{153}$$

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Using the definition (127) of $\mathcal{E}^d(\boldsymbol{r})$ we may write

$$\rho E_\alpha(\boldsymbol{r}) = \rho E_\alpha^0(\boldsymbol{r}) + \mathcal{E}_\alpha^d(\boldsymbol{r}) + G_0 \overset{v(r)}{\int} \mathrm{d}\boldsymbol{r}'\, T_{\alpha\beta}(\boldsymbol{r})\, S(\boldsymbol{r}, \boldsymbol{r}')\, \mathcal{E}_\beta(\boldsymbol{r}') +$$
$$+ G_2 \overset{v(r)}{\int} \mathrm{d}\boldsymbol{r}'\, T_{\alpha\beta}(\boldsymbol{r})\, S_\mu(\boldsymbol{r}, \boldsymbol{r}')\, \delta_{\beta\gamma\mu}\, \mathcal{E}_\gamma(\boldsymbol{r}') +$$
$$+ G_1 \overset{v(r)}{\int} \mathrm{d}\boldsymbol{r}'\, T_{\alpha\beta}(\boldsymbol{r})\, S(\boldsymbol{r}, \boldsymbol{r}')\, \delta_{\beta\gamma\delta}\, \mathcal{E}_{\gamma\delta}^{(1)}(\boldsymbol{r}'), \qquad (154)$$

where the integrals extend over a small sphere centered around $\boldsymbol{r}$. Evaluating these integrals explicitly in the limit of an infinitely small sphere (cf. Appendix B) one obtains, using (150) and (151),

$$\rho E(\boldsymbol{r}) = G_0 \frac{4\pi}{n^2 - 1}\, \mathcal{E}(\boldsymbol{r}) - G_2 \frac{4\pi}{n^2 - 1}\, \mathrm{rot}\; \mathcal{E}(\boldsymbol{r}) -$$

$$- G_1 G_0 \frac{4\pi}{3} \frac{n^2 + 2}{n^2 - 1} \frac{4\pi}{n^2 - 1}\, \mathrm{rot}\; \mathcal{E}(\boldsymbol{r}) + \frac{4\pi}{3} G_1 \frac{4\pi}{n^2 - 1}\, \mathrm{rot}\; \mathcal{E}(\boldsymbol{r}). \quad (155)$$

This relation shows that E is propagated with the same velocity as $\mathcal{E}$, which establishes the interpretation of n as the refractive index of the medium.

Going back to eq. (152) we shall now investigate the propagation of a light-wave through the medium. In the zeroth order theory, *i.e.* when $G_1 = G_2 = 0$, (152) yields the well known generalized Lorentz-Lorenz equation for an isotropic medium consisting of non-polar molecules with constant polarizabilities [5])

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} \frac{G_0(1 + R)}{1 + G_0 D(1 + R)}, \qquad (156)$$

which, in the absence of statistical effects ($R \equiv 0, D \equiv 0$) takes the familiar form

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} G_0. \qquad (157)$$

Let us now consider the first order theory. We may advantageously use the results of the zeroth order theory to simplify the third term in the right hand side of (152). We note that this term arises from the partial contribution from $\mathcal{E}_{\alpha\varepsilon}^{(1)}$ to $\mathcal{E}^d$ (cf. (127), (145), (150) and appendix B). Now we recall that we have, for the sake of simplicity, neglected the zeroth order statistical effects in $\mathcal{E}_{\alpha\varepsilon}^{(1)}$ (cf. (132) and the discussion preceding (131)). As a result the term under consideration should contain no statistical effects. If we had *not* neglected those zeroth order statistical effects (which would have led to tedious calculations), we would accordingly use for the reduction of the term the zeroth order results *with* statistical effects, *i.e.* (156), but since we *have* neglected the zeroth order statistical effects we now use for the reduction the zeroth order results *without* statistical effects, *i.e.* (157). This

procedure, if not equivalent to the rigorous treatment, is quite adequate for the present purpose, the simplification of the term in (152) containing G_1, and leads at most to a negligible error. Now the customary approximation [4]) consists in replacing the factor $4\pi\, G_0(n^2 + 2)/3(n^2 - 1)$ in the term with G_1 by the corresponding expression of the zeroth order theory, $4\pi G_0(n_0^2 + 2)/3(n_0^2 - 1)$. If we then, in accordance with the above discussion apply (157), we see that this factor equals 1 so that (152) reduces to

$$\mathscr{E}(\boldsymbol{r}) = \frac{1+R}{1+G_0\,D(1+R)}\left[G_0\frac{4\pi}{3}\frac{n^2+2}{n^2-1}\,\mathscr{E}(\boldsymbol{r}) - \frac{4\pi}{n^2-1}\,(G_1+G_2)\,\mathrm{rot}\,\mathscr{E}(\boldsymbol{r})\right].$$
(158)

Now let the direction of propagation of the plane wave be the z-direction. Then we have

$$\mathscr{E}_x(\boldsymbol{r}) = \mathscr{E}_x\,e^{iknz},\ \mathscr{E}_y(\boldsymbol{r}) = \mathscr{E}_y\,e^{iknz},\ \mathscr{E}_z(\boldsymbol{r}) = 0.$$
(159)

Substitution into (158) yields two equations for $\mathscr{E}_x$ and $\mathscr{E}_y$. Setting the coefficient determinant equal to zero gives the condition

$$1 - \frac{1+R}{1+G_0\,D(1+R)}\frac{4\pi}{3}\,G_0\frac{n^2+2}{n^2-1} = \pm\frac{1+R}{1+G_0\,D(1+R)}\frac{4\,\pi nk}{n^2-1}\,(G_1+G_2),$$
(160)

with solutions $\mathscr{E}_x \mp i\mathscr{E}_y = 0$, the $-(+)$ sign corresponding to a right (left) circularly polarized wave with refractive index $n_r(n_l)$. Multiplying (160) by $n^2 - 1$ we find

$$\left[1 - \frac{1+R}{1+G_0(1+R)}\frac{4\pi}{3}\,G_0\right](n_r^2 - n_l^2) =$$

$$= \frac{1+R}{1+G_0\,D(1-R)}\,4\pi k(G_1+G_2)\,(n_r + n_l),$$
(161)

which according to (156) reduces to

$$n_r - n_l = \frac{1+R}{1+G_0\,D(1+R)}\,4\pi k\,\frac{n_0^2+2}{3}\,(G_1+G_2).$$
(162)

Combining (162) with Fresnel's formula (1) we finally obtain

$$\varphi = -\frac{8\pi^3}{\lambda^2}\frac{1+R}{1+G_0\,D(1+R)}\,\frac{n_0^2+2}{3}\,(G_1+G_2).$$
(163)

In the absence of statistical effects (163) reduces to Hoek's formula

$$\varphi = -\frac{8\pi^3}{\lambda^2}\frac{n_0^2+2}{3}\,(G_1+G_2).$$
(164)

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Since in the absence of statistical effects we have, according to (157),

$$\frac{n_0^2 + 2}{3} = \frac{n_0^2 - 1}{4\pi G_0},$$

(165)

(164) may also be written as

$$\varphi = -\frac{8\pi^3}{\lambda^2}\frac{n_0^2 - 1}{4\pi G_0}(G_1 + G_2).$$

(166)

This way of writing Hoek's equation has the advantage that the form of the equation remains unaltered in going over to our statistical treatment. Indeed, (163) may, according to (156), be written as (166), the only difference being that in Hoek's case the factor $(n_0^2 - 1)/4\pi G_0$ contains no statistical effects, whereas in our case it does.

One can show [3]) that if the wavelength of the incident radiation is large compared to the correlation length between molecules, as is the case for visible light and gases at moderate densities, in first approximation D may be neglected and R, given to second order in g_0 by (149) and (136), reduces to the corresponding static expression with $k = 0$, say $S_2(\rho, T, \omega)$. For a quantitative discussion of $S_2(\rho, T, \omega)$ we refer to [8]).

§ 7. *Connection with the macroscopic theory of optical activity.* We shall now deduce the equations which give a macroscopic description of optical activity. To this end we first express the macroscopic moment densities in terms of $\mathscr{E}_\alpha$ and $\mathscr{E}_{\alpha\beta}^{(1)}(r)$. We have

$$P(r, t) \equiv \operatorname{Re} P(r)\, e^{-i\omega t}; \quad P(r) = \sum_i \langle p_i^- \delta(r_i - r) \, \rangle_{\omega, r} \quad (167)$$

$$Q(r, t) \equiv \operatorname{Re} Q(r)\, e^{-i\omega t}; \quad Q(r) = \sum_i \langle q_i^- \delta(r_i - r) \, \rangle_{\omega, r} \quad (168)$$

$$M(r, t) \equiv \operatorname{Re} M(r)\, e^{-i\omega t}; \quad M(r) = \sum_i \langle m_i^- \delta(r_i - r) \, \rangle_{\omega, r}. \quad (169)$$

Upon substituting (44)–(47) we find, using (64)–(67), (108) and (109),

$$P_\alpha(r) = g_0 \mathscr{E}_\alpha(r) + g_1\, \delta_{\alpha\beta\gamma}\, \mathscr{E}_{\beta\gamma}^{(1)}(r),$$

(170)

$$Q_{\alpha\beta}(r) = 0,$$

(171)

$$M_\alpha(r) = ik\, g_2\, \mathscr{E}_\alpha(r).$$

(172)

Macroscopically the system is described by the Maxwell equations

$$\left.\begin{aligned}
\operatorname{div} B &= 0 \\
-c\operatorname{rot} E &= \dot{B} \\
\operatorname{div} D &= 0 \\
c\operatorname{rot} H &= \dot{D}
\end{aligned}\right\},$$

(173)

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where E and B are the average electric resp. magnetic field strengths in an arbitrary point of the medium and where D and H are defined by

$$D = E + 4\pi(P - \text{Div } Q), \tag{174}$$

$$B = H + 4\pi\, M. \tag{175}$$

(for a derivation of the Maxwell equations on a molecular basis see ref. [15]).

Our task is to determine the relation of the fields D and H to the fields B and E. Clearly this is to be achieved by eliminating the auxiliary quantities $\mathscr{E}_\alpha$ and $\mathscr{E}_{\alpha\varepsilon}^{(1)}$. For this purpose we will need eq. (145), which gives the connection between $\mathscr{E}_{\alpha\varepsilon}^{(1)}$ and $\mathscr{E}_\alpha$, eq. (152), which determines the value of the index of refraction, and eq. (155), which gives the connection between E and $\mathscr{E}$.

Let us first treat the zeroth order case (the theory of the refractive index). (170) and (172) then reduce to

$$P(r) = g_0\, \mathscr{E}(r), \tag{176}$$

$$M(r) = 0, \tag{177}$$

(145) need not be considered, whereas (152) and (155) take the form

$$1 + s = G_0\, \frac{4\pi}{3}\, \frac{n_0^2 + 2}{n_0^2 - 1}, \tag{178}$$

$$\rho E(r) = G_0\, \frac{4\pi}{3}\, \frac{n_0^2 + 2}{n_0^2 - 1}\, \mathscr{E}(r) - \frac{4\pi}{3}\, G_0\, \mathscr{E}(r), \tag{179}$$

where we introduced the abbreviation

$$1 + s \equiv \frac{1 + G_0\, D(1 + R)}{1 + R}, \tag{180}$$

so that s vanishes in the absence of statistical effects. Using (176) and (178), (179) can be written as

$$\mathscr{E}(r) = \frac{\rho}{1 + s}\left(E(r) + \frac{4\pi}{3}\, P(r)\right). \tag{181}$$

Introducing this expression into (176) we find

$$P(r) = \frac{G_0 E(r)}{(1 + s) - \dfrac{4\pi}{3}\, G_0}, \tag{182}$$

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which leads to (cf. (174) and (171))

$$D = \varepsilon_0 E, \tag{183}$$

with

$$\varepsilon_0 \equiv \frac{(1+s) + \dfrac{8\pi}{3} G_0}{(1+s) - \dfrac{4\pi}{3} G_0} = n_0^2, \tag{184}$$

where in the last equality (178) has been used. Furthermore, in view of (177), (175) takes the form

$$B = H. \tag{185}$$

We now turn to the first order theory, where we proceed in an entirely analogous fashion. Using (145), (170) can be written as

$$P(r) = g_0 \, \mathscr{E}(r) - g_1 \, G_0 \, \frac{4\pi}{n^2 - 1} \, \text{rot} \, \mathscr{E}(r), \tag{186}$$

whereas (155), upon using (152) and (186) takes the form

$$\mathscr{E}(r) = \frac{\rho}{1+s} \left(E(r) + \frac{4\pi}{3} P(r) \right). \tag{187}$$

Using the same approximation which led to (158) we rewrite (186) as

$$P(r) = g_0 \, \mathscr{E}(r) - g_1 \left(\frac{3}{n_0^2 + 2} \right) \text{rot} \, \mathscr{E}(r). \tag{188}$$

Eliminating $\mathscr{E}(r)$ from (187) and (188) we find

$$P(r) = \frac{G_0 E(r)}{(1+s) - \dfrac{4\pi}{3} G_0} - G_1 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s} \, \text{rot} \, E(r), \tag{189}$$

where it should be remembered that throughout our investigation terms non linear in g_1 and g_2 have been discarded (cf. (100)). Similarly we obtain, using (172), (187) and (188),

$$M(r) = ik \, G_2 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s} \, E(r). \tag{190}$$

From (171), (189), (190) and (184) we see that (174) and (175) may be written as

$$D = \varepsilon_0 \, E - 4\pi \, G_1 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s} \, \text{rot} \, E, \tag{191}$$

$$B = H + ik \, 4\pi \, G_2 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s} \, E, \tag{192}$$

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or alternatively, expressing $G_1 = \rho g_1$ and $G_2 = \rho g_2$ in terms of h_1 and h_2 (cf. (62) and (63), using (173) and the fact that the fields oscillate with frequence ω,

$$D = \varepsilon_0 E + vB + w\dot{B}, \tag{193}$$

$$B = H + vE - w\dot{E}, \tag{194}$$

where

$$v \equiv k \, 4\pi \, h_2 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s}, \tag{195}$$

$$w \equiv - \frac{1}{c} \, 4\pi \, h_1 \left(\frac{n_0^2 + 2}{3} \right) \frac{1}{1+s}. \tag{196}$$

As has been shown by Rosenfeld, (193) and (194), together with the Maxwell equations (173), lead again to (163).

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OPTICAL ROTATORY POWER OF AN ISOTROPIC TWO-COMPONENT SYSTEM

Synopsis

The theory of the foregoing chapter is extended to the case of an isotropic two-component system. A generalized Lorentz-Lorenz formula is obtained as well as an expression for the optical rotatory power and, in the case of a solution of an optically active substance in an inactive solvent, an expression containing the non-specific influence of the solvent.

§ 1. *Introduction.* We shall now generalize the results of the foregoing chapter to the case of a medium consisting of a mixture of arbitrary molecules, eventually specializing to the case that has been studied in an extensive way experimentally, namely that of the optical rotatory power of a solution of an optically active substance in an inactive solvent. This will lead to an expression for what Kuhn [1]) calls the non-specific influence of the solvent, *i.e.* the influence which persists in the absence of specific effects such as the formation of chemical compounds or of association products between the various molecules.

In § 2 we derive the integral equations for the statistical averages of the field strengths for a medium consisting of *s* components. Whereas for the one-component system one obtains 2 coupled equations, the statistical correlation and fluctuation effects provide an additional coupling between the partial contributions from each molecular species, thus yielding a system of $2s$ intricately coupled equations.

In § 3 the case of a two-component system is treated along the same lines as the one-component system. This results in a generalized Lorentz-Lorenz formula, an expression for the optical rotatory power and, in the case of an inactive solvent, an expression containing the non-specific influence of the solvent.

§ 2. *The integral equations for the statistical averages in a s-component system.* We consider a mixture of *s* components. Let the number of molecules of species *m* be $N_m(m = 1, 2, ..., s)$ and let the total number of molecules

be N, $\sum\limits_{m=1}^{s} N_m = N$. The molecules of species m are labelled $(m1)$, $(m2)$, ..., (mN_m). Let the positions of the centres of the molecules be $\boldsymbol{r}_{mi}$.

The equations for dynamical equilibrium (cf. (I. 99) and (I. 100)) can now be written as

$$E_{mi\alpha} = E_\alpha^0(\boldsymbol{r}_{mi}) + \sum_{m'i' \neq mi} T_{\alpha\beta}(\boldsymbol{r}_{mi})\, S(\boldsymbol{r}_{mi}, \boldsymbol{r}_{m'i'})\, \alpha_{\beta\gamma}(m'i')\, E_{m'i\gamma} +$$

$$+ \sum_{m'i' \neq mi} T_{\alpha\beta}(\boldsymbol{r}_{mi})\, S(\boldsymbol{r}_{mi}, \boldsymbol{r}_{m'i'})\, \alpha_{\beta\gamma\delta}(m'i')\, E_{m'i'\gamma\delta} +$$

$$+ \sum_{m'i' \neq mi} T_{\alpha\beta}(\boldsymbol{r}_{mi})\, S_\mu(\boldsymbol{r}_{mi}, \boldsymbol{r}_{m'i'})\, \alpha_{\alpha\gamma}(m'i')\, E_{m'i'\gamma}, \tag{1}$$

$$E_{mi\alpha\varepsilon} = E_{\alpha\varepsilon}^0(\boldsymbol{r}_{mi}) + \sum_{m'i' \neq mi} T_{\alpha\beta}(\boldsymbol{r}_{mi})\, S_\varepsilon(\boldsymbol{r}_{mi}, \boldsymbol{r}_{m'i'})\, \alpha_{\beta\gamma}(m'i')\, E_{m'i'\gamma}. \tag{2}$$

Assuming the interaction energy of any pair of molecules to be independent of their orientations, in the absence of an external field, we can describe the system with a configuration distribution function depending on position coordinates only (cf. I § 5). Let the number density of each species be uniform,

$$\sum_{i=1}^{N_m} \langle \delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\, f \rangle_{\omega, r} = \sum_{i=1}^{N_m} \langle \delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\, f \rangle_r = \rho_m = \frac{N_m}{V},$$

$$(m = 1, 2, ..., s) \tag{3}$$

$$\sum_{m=1}^{s} \rho_m = \rho = \frac{N}{V}, \tag{4}$$

where V is the total volume of the system. The contribution from the molecules of species m to the average exciting field per unit volume, $\mathscr{E}_\alpha(m, \boldsymbol{r})$, and their contribution to the average derivative of the exciting field per unit volume $\mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \boldsymbol{r})$, are

$$\mathscr{E}_\alpha(m, \boldsymbol{r}) = \sum_{i=1}^{N_m} \langle E_{mi\alpha}\, \delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\, f \rangle_{\omega, r} = \rho_m\, \overline{E_\alpha}(m, \boldsymbol{r}), \tag{5}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \boldsymbol{r}) = \sum_{i=1}^{N_m} \langle E_{mi\alpha\varepsilon}\, \delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\, f \rangle_{\omega, r} = \rho_m\, \overline{E_{\alpha\varepsilon}}(m, \boldsymbol{r}). \tag{6}$$

Substituting (1) and (2) into (5) and (6), performing the orientational averaging, using the same approximation as in the one-component case, with the notations (cf. (I.64), (I. 65) and (I. 95)):

$$\left.\begin{array}{c} \overline{\alpha_{\alpha\beta}}^{\,\omega}(m) = g_0(m)\, \delta_{\alpha\beta} \\[4pt] \overline{\alpha_{\alpha\beta\gamma}}^{\,\omega}(m) = g_1(m)\, \delta_{\alpha\beta\gamma} \\[4pt] \overline{\alpha_{\alpha\beta}}^{\,\omega}_{\mu}(m) = g_2(m)\, \delta_{\alpha\beta\mu} \end{array}\right\} \tag{7}$$

and using the abbreviations (I. 117), we have

$$\mathscr{E}_\alpha(m, \mathbf{r}) = \rho_m E_\alpha^0(\mathbf{r}) +$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m') \langle A_{\alpha\beta}^{(0)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta} \delta(\mathbf{r}_{mi} - \mathbf{r}) f \rangle +$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_2(m') \langle A_{\alpha\beta}^{(2)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta} \delta(\mathbf{r}_{mi} - \mathbf{r}) f \rangle +$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_1(m') \langle A_{\alpha\beta\gamma}^{(1)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta\gamma} \delta(\mathbf{r}_{mi} - \mathbf{r}) f \rangle, \tag{8}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \mathbf{r}) = \rho_m E_{\alpha\varepsilon}^0(\mathbf{r}) +$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m') \langle B_{\alpha\varepsilon\beta}^{(0)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta} \delta(\mathbf{r}_{mi} - \mathbf{r}) f \rangle. \tag{9}$$

We note that formally we could have performed the orientational averaging in (1) and (2), *i.e.* we could have taken as basic equations

$$E_{mi\alpha} = E_\alpha^0(\mathbf{r}_{mi}) + \sum_{m'i' \neq mi} g_0(m') A_{\alpha\beta}^{(0)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta} +$$

$$+ \sum_{m'i' \neq mi} g_2(m') A_{\alpha\beta}^{(2)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta} +$$

$$+ \sum_{m'i' \neq mi} g_1(m') A_{\alpha\beta\gamma}^{(1)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta\gamma}, \tag{10}$$

$$E_{mi\alpha\varepsilon} = E_{\alpha\varepsilon}^0(\mathbf{r}_{mi}) + \sum_{m'i' \neq mi} g_0(m') B_{\alpha\varepsilon\beta}^{(0)}(\mathbf{r}_{mi}, \mathbf{r}_{m'i'}) E_{m'i'\beta}. \tag{11}$$

We now transform (8) and (9) in exactly the same way as (I. 113) and (I. 114). First we write $E_{m'i'\beta}$ and $E_{m'i'\beta\gamma}$ as $\overline{E_{m'i'\beta}} + (E_{m'i'\beta} - \overline{E_{m'i'\beta}})$ and $\overline{E_{m'i'\beta\gamma}} + (E_{m'i'\beta\gamma} - \overline{E_{m'i'\beta\gamma}})$, *i.e.* we split off the contributions to $\mathscr{E}_\alpha(m, \mathbf{r})$ and $\mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \mathbf{r})$ due to statistical fluctuations around the average values. We call these "fluctuation terms" $J_\alpha(m, \mathbf{r})$ and $J_{\alpha\varepsilon}^{(1)}(m, \mathbf{r})$ respectively. Using the definition of the pair distribution functions
  i) for two molecules of different species

$$\rho_m \rho_{m'} g^{(m, m')}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_m} \sum_{i'=1}^{N_{m'}} \langle \delta(\mathbf{r}_{mi} - \mathbf{r}) \delta(\mathbf{r}_{m'i'} - \mathbf{r}') f \rangle, \tag{12}$$

  ii) for two molecules of the same species

$$\rho_m \rho_m g^{(m, m)}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N_m} \sum_{\substack{i'=1 \\ i' \neq i}}^{N_m} \langle \delta(\mathbf{r}_{mi} - \mathbf{r}) \delta(\mathbf{r}_{mi'} - \mathbf{r}') f \rangle, \tag{13}$$

as well as the properties of the pair correlation functions (cf. (I. 126)), and

using also the abbreviations

$$\mathscr{E}_\alpha^d(\boldsymbol{r}) = \sum_m g_0\,(m) \int_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m,\,\boldsymbol{r}') +$$

$$+ \sum_m g_2\,(m) \int_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(2)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m,\,\boldsymbol{r}') +$$

$$+ \sum_m g_1\,(m) \int_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta\gamma}^{(1)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_{\beta\gamma}^{(1)}(m,\,\boldsymbol{r}'), \tag{14}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)d}(\boldsymbol{r}) = \sum_m g_0\,(m) \int_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, B_{\alpha\varepsilon\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m,\,\boldsymbol{r}'), \tag{15}$$

we find

$$\mathscr{E}_\alpha(m,\,\boldsymbol{r}) = \rho_m E_\alpha^0(\boldsymbol{r}) + \rho_m\,\mathscr{E}_\alpha^d(\boldsymbol{r}) +$$

$$+ \rho_m \sum_{m'} g_0(m') \int_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m',\,\boldsymbol{r}')\,\{g^{(m,\,m')}(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ \rho_m \sum_{m'} g_2\,(m') \int_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta}^{(2)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m',\,\boldsymbol{r}')\,\{g^{(m,\,m')}(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ \rho_m \sum_{m'} g_1\,(m') \int_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, A_{\alpha\beta\gamma}^{(1)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_{\beta\gamma}^{(1)}(m',\,\boldsymbol{r}')\,\{g^{(m,\,m')}(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ J_\alpha(m,\,\boldsymbol{r}), \tag{16}$$

$$\mathscr{E}_{\alpha\varepsilon}^{(1)}(m,\,\boldsymbol{r}) = \rho_m E_{\alpha\varepsilon}^0(\boldsymbol{r}) + \rho_m\,\mathscr{E}_{\alpha\varepsilon}^{(1)d}(\boldsymbol{r}) +$$

$$+ \rho_m \sum_{m'} g_0(m') \int_{v(r)}^{\infty} \mathrm{d}\boldsymbol{r}'\, B_{\alpha\varepsilon\beta}^{(0)}(\boldsymbol{r},\,\boldsymbol{r}')\,\mathscr{E}_\beta(m',\,\boldsymbol{r}')\,\{g^{(m,\,m')}(\boldsymbol{r},\,\boldsymbol{r}') - 1\} +$$

$$+ J_{\alpha\varepsilon}^{(1)}(m,\,\boldsymbol{r}), \tag{17}$$

where $J_\alpha(m,\,\boldsymbol{r})$ and $J_{\alpha\varepsilon}^{(1)}(m,\,\boldsymbol{r})$ are given by:

$$J_\alpha(m,\,\boldsymbol{r}) = \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m') \cdot$$

$$\cdot \int^{V} \mathrm{d}\boldsymbol{r}'\, \langle A_{\alpha\beta}^{(0)}(\boldsymbol{r}_{mi},\,\boldsymbol{r}_{m'i'})(E_{m'i'\beta} - \overline{E_{m'i'\beta}})\,\delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\,\delta(\boldsymbol{r}_{m'i'} - \boldsymbol{r}')\, f\rangle +$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_2(m') \cdot$$

$$\cdot \int^{V} \mathrm{d}\boldsymbol{r}'\, \langle A_{\alpha\beta}^{(2)}(\boldsymbol{r}_{mi},\,\boldsymbol{r}_{m'i'})(E_{m'i'\beta} - \overline{E_{m'i'\beta}})\,\delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\,\delta(\boldsymbol{r}_{m'i'} - \boldsymbol{r}')\, f\rangle$$

$$+ \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_1(m') \cdot$$

$$\cdot \int^{V} \mathrm{d}\boldsymbol{r}'\, \langle A_{\alpha\beta\gamma}^{(1)}(\boldsymbol{r}_{mi},\,\boldsymbol{r}_{m'i'})(E_{m'i'\beta\gamma} - \overline{E_{m'i'\beta\gamma}})\,\delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\,\delta(\boldsymbol{r}_{m'i'} - \boldsymbol{r}')f\rangle, \tag{18}$$

$$J_{\alpha\varepsilon}^{(1)}(m,\,\boldsymbol{r}) = \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m') \int^{V} \mathrm{d}\boldsymbol{r}' \cdot$$

$$\cdot \langle B_{\alpha\varepsilon\beta}^{(0)}(\boldsymbol{r}_{mi},\,\boldsymbol{r}_{m'i'})(E_{m'i'\beta} - \overline{E_{m'i'\beta}})\,\delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\,\delta(\boldsymbol{r}_{m'i'} - \boldsymbol{r}')\, f\rangle. \tag{19}$$

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The statistical effects in (17) and (18) are contained in the fluctuation terms $J_\alpha(m, r)$ and $J_{\alpha\varepsilon}^{(1)}(m, r)$ and in what we have called (cf. I § 5)) "correlation terms", consisting of integrals with the factor $\{g^{(m, m')}(r, r') - 1\}$ in the integrand. Upon neglecting these statistical correction terms alltogether, (17) and (18) reduce to

$$\mathscr{E}_\alpha(m, r) = \rho_m E_\alpha^{(0)}(r) + \rho_m \mathscr{E}_\alpha^d(r), \tag{20}$$

$$\mathscr{E}_\alpha^{(1)}(m, r) = \rho_m E_{\alpha\varepsilon}^{(0)}(r) + \rho_m \mathscr{E}_{\alpha\varepsilon}^{(1)d}(r). \tag{21}$$

It follows that $\overline{E_\alpha}(m, r) = [\mathscr{E}_\alpha(m, r)]/\rho_m$ and $\overline{E_{\alpha\varepsilon}}(m, r) = [\mathscr{E}_{\alpha\varepsilon}^{(1)}(m, r)]/\rho_m$ are then independent of m, so that (20) and (21) can be written, using (14) and (15)

$$\overline{E_\alpha}(r) = E_\alpha^{(0)}(r) + G_0 \int\limits_{v(r)}^{V} dr' \, A_{\alpha\beta}^{(0)}(r, r') \, \overline{E_\beta}(r') +$$

$$+ G_2 \int\limits_{v(r)}^{V} dr' \, A_{\alpha\beta}^{(2)}(r, r') \, \overline{E_\beta}(r') +$$

$$+ G_1 \int\limits_{v(r)}^{V} dr' \, A_{\alpha\beta\gamma}^{(1)}(r, r') \, \overline{E_{\beta\gamma}}(r'), \tag{22}$$

$$\overline{E_{\alpha\varepsilon}}(r) = E_{\alpha\varepsilon}^0(r) + G_0 \int\limits_{v(r)}^{V} dr' \, B_{\alpha\varepsilon\beta}^{(0)}(r, r') \, \overline{E_\beta}(r'), \tag{23}$$

where

$$\sum_m \rho_m g_i(m) = G_i, \qquad (i = 0, 1, 2). \tag{24}$$

Eqs. (22) and (23) are the two coupled integral equations which Hoek [2]) obtained by averaging over physically infinitesimal volume elements.

However, (14) and (15) as they stand form a set of $2s$ intricately coupled equations, since the statistical effects provide an additional coupling between the partial contributions from each molecular species to the average fields. Rather than take all these statistical effects into account, we shall use the same approximations as in the one-component case (cf. the discussion after formula (I. 130)). Firstly we drop all first order correlation and fluctuation terms in (16) so that this relation reduces to

$$\mathscr{E}_\alpha(m, r) = \rho_m E_\alpha^0(r) + \rho_m \mathscr{E}_\alpha^d(r) +$$

$$+ \rho_m \sum_{m'} g_0(m') \int\limits_{v(r)}^{\infty} dr' \, A_{\alpha\beta}^{(0)}(r, r') \, \mathscr{E}_\beta(m', r') \{g^{(m, m')}(r, r') - 1\} +$$

$$+ J_\alpha(m, r), \tag{25}$$

where $J_\alpha(m, r)$ is now given by

$$J_\alpha(m, r) =$$

$$= \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m') \int\limits^{V} dr' \, \langle A_{\alpha\beta}^{(0)}(r_{mi}, r_{m'i'})(E_{m'i'\beta} - \overline{E_{m'i'\beta}}) \cdot$$

$$\cdot \delta(r_{mi} - r) \, \delta(r_{m'i'} - r') \, |\rangle. \tag{26}$$

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Secondly we neglect the influence of zeroth order statistical effects in the small partial contribution to $\mathscr{E}^d(\boldsymbol{r})$ containing g_1(cf. (14)), *i.e.* we take $\mathscr{E}^{(1)}_{\beta\gamma}(m, \boldsymbol{r}')$ to satisfy Hoek's equation (21). The other first order partial contribution to $\mathscr{E}^d_\alpha(\boldsymbol{r})$, *i.e.* the term containing g_2, can now by using the same approximation also be simplified. Since in the absence of statistical effects we have

$$\sum_m g_2(m)\, \mathscr{E}_\alpha(m, \boldsymbol{r}) = \sum_m \frac{G_2}{G_0}\, g_0(m)\, \mathscr{E}_\alpha(m, \boldsymbol{r}), \tag{27}$$

we write with negligible error for the partial contribution to $\mathscr{E}^d_\alpha(\boldsymbol{r})$ containing g_2:

$$\sum_m \frac{G_2}{G_0}\, g_0(m) \int\limits_{v(r)}^{V} \mathrm{d}\boldsymbol{r}'\, A^{(2)}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}')\, \mathscr{E}_\beta(m, \boldsymbol{r}'). \tag{28}$$

Note the difference with the one-component case: in the many-component system the approximation of neglecting zeroth order statistical effects in the first order contributions to $\mathscr{E}^d_\alpha(\boldsymbol{r})$ implies neglecting the statistical coupling of the partial contributions, to the averages of the fields, from each molecular species, so that this approximation affects both first order contributions to $\mathscr{E}^d_\alpha(\boldsymbol{r})$, whereas in the one-component system, where the statistical coupling between contributions from different species is absent, the approximation affects only the first order contribution to $\mathscr{E}^d_\alpha(\boldsymbol{r})$ containing g_1.

We shall now show that $J_\alpha(m, \boldsymbol{r})$ can be written as

$$J_\alpha(m, \boldsymbol{r}) = \sum_{m'} \int^V \mathrm{d}\boldsymbol{r}'\, K_{\alpha\beta}(m, m'; \boldsymbol{r}, \boldsymbol{r}')\, [\rho_{m'}\, E^0_\beta(\boldsymbol{r}') + \rho_{m'}\mathscr{E}^d_\beta(\boldsymbol{r}') +$$

$$+ \rho_{m'} \sum_{m''} g_0(m'') \int\limits_{v(r')}^{\infty} \mathrm{d}\boldsymbol{r}''\, A^{(0)}_{\beta\gamma}(\boldsymbol{r}', \boldsymbol{r}'')\, \mathscr{E}_\gamma(m'', \boldsymbol{r}'')\, \{g^{(m', m'')}(\boldsymbol{r}', \boldsymbol{r}'') - 1\}] \tag{29}$$

where the kernel $K(m, m'; \boldsymbol{r}, \boldsymbol{r}')$ is a symmetric tensor such that

$$\int K_{\alpha\beta}(m, m'; \boldsymbol{r}, \boldsymbol{r}')\, \mathrm{d}\boldsymbol{r}' = \delta_{\alpha\beta}\, \varphi(m, m'; \rho_1, ..., \rho_s, T, \omega). \tag{30}$$

In order to prove this we introduce a quantity $\boldsymbol{E}^*(m, \boldsymbol{r})$ defined by

$$E^*_\alpha(m, \boldsymbol{r}) = E^0_\alpha(\boldsymbol{r}) + \frac{1}{\rho_m} \sum_{i=1}^{N_m} \sum_{m'i' \neq mi} g_0(m')\, \langle A^{(0)}_{\alpha\beta}(\boldsymbol{r}_{mi}, \boldsymbol{r}_{m'i'})\, \overline{E_{m'i'\beta}}\, \delta(\boldsymbol{r}_{mi} - \boldsymbol{r})\, f\rangle =$$

$$= E^0_\alpha(\boldsymbol{r}) + \sum_{m'} g_0(m') \int^V \mathrm{d}\boldsymbol{r}'\, A^{(0)}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}')\, \mathscr{E}_\beta(m', \boldsymbol{r}')\, g^{(m, m')}(\boldsymbol{r}, \boldsymbol{r}'). \tag{31}$$

Let $\boldsymbol{E}_{mi}(\boldsymbol{r}_{mi} = \boldsymbol{r})$ be the $\boldsymbol{E}_{mi}$, as given by (10), corresponding to the confi-

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guration $(\boldsymbol{r}_{11}, ..., \boldsymbol{r}_{1N_1}, ..., \boldsymbol{r}_{mi} = \boldsymbol{r}, ..., \boldsymbol{r}_{sN_s})$. Then we have:

$$E_{mi\alpha}(\boldsymbol{r}_{mi} = \boldsymbol{r}) = E_\alpha^*(m, \boldsymbol{r}) + \sum_{m'i' \neq mi} g_0(m') A_{\alpha\beta}^{(0)}(\boldsymbol{r}, \boldsymbol{r}_{m'i'}) E_{m'i'\beta}(\boldsymbol{r}_{mi} = \boldsymbol{r}) -$$

$$- \frac{1}{\rho m} \sum_{j=1}^{N_m} \sum_{m''j'' \neq mj} g_0(m'') \langle A_{\alpha\beta}^{(0)}(\boldsymbol{r}_{mj}, \boldsymbol{r}_{m''j''}) \overline{E_{m''j''\beta}}(\boldsymbol{r}_{m''j''}) \delta(\boldsymbol{r}_{mj} - \boldsymbol{r}) f \rangle. \quad (32)$$

Furthermore

$$\overline{E_{mi\alpha}}(\boldsymbol{r}) = E_\alpha^*(m, \boldsymbol{r}) +$$

$$+ \frac{1}{\rho m} \sum_{j=1}^{N_m} \sum_{m''j'' \neq mj} g_0(m'') \langle A_{\alpha\beta}^{(0)}(\boldsymbol{r}_{mj}, \boldsymbol{r}_{m''j''}) (E_{m''j''\beta} - \overline{E_{m''j''\beta}}) \delta(\boldsymbol{r}_{mj} - \boldsymbol{r}) f \rangle. \quad (33)$$

Substituting (32) and (33) into (26) one obtains an expression which can by iterative use of (32) and (33) be transformed into a series. The expression becomes proportional to $\boldsymbol{E}^*$ and, in view of the definition (31) may be written as in (29). For $K(m, m'; \boldsymbol{r}, \boldsymbol{r}')$ one finds, to second order in the $g_0(m)$,

$$K_{\alpha\beta}(m, m'; \boldsymbol{r}, \boldsymbol{r}') = \sum_{m''} \int^V \mathrm{d}\boldsymbol{r}'' g_0(m'') A_{\alpha\gamma}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') g_0(m') A_{\gamma\beta}^{(0)}(\boldsymbol{r}'', \boldsymbol{r}').$$

$$\rho m \rho m'' \{g^{(m, m'', m')}(\boldsymbol{r}, \boldsymbol{r}'', \boldsymbol{r}') - g^{(m, m'')}(\boldsymbol{r}, \boldsymbol{r}'') g^{(m'', m')}(\boldsymbol{r}'', \boldsymbol{r}')\} +$$

$$+ \sum_{m''} \int^V \mathrm{d}\boldsymbol{r}'' g_0(m'') A_{\alpha\gamma}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') g_0(m') A_{\gamma\beta}^{(0)}(\boldsymbol{r}'', \boldsymbol{r}') \cdot$$

$$\cdot \delta_{m'm} \rho m'' g^{(m, m'')}(\boldsymbol{r}, \boldsymbol{r}'') \delta(\boldsymbol{r} - \boldsymbol{r}'), \quad (34)$$

where the distribution function for three particles, *e.g.* for three particles of different species is defined as

$$\rho m \rho m' \rho m'' g^{(m, m', m'')}(\boldsymbol{r}, \boldsymbol{r}', \boldsymbol{r}'') = \sum_{i=1}^{N_m} \sum_{i'=1}^{N_{m'}} \sum_{i''=1}^{N_{m''}} \langle \delta(\boldsymbol{r}_{mi} - \boldsymbol{r}) \delta(\boldsymbol{r}_{m'i'} - \boldsymbol{r}') \cdot$$

$$\cdot \delta(\boldsymbol{r}_{m''i''} - \boldsymbol{r}'') f \rangle. \quad (35)$$

§ 3. *Computation of the optical rotatory power in a two-component system.* We shall now prove that (25) and (21) have a solution satisfying

$$\Delta \mathscr{E}(m, \boldsymbol{r}) + k^2 n^2 \mathscr{E}(m, \boldsymbol{r}) \qquad = 0, \qquad (m = 1, 2, ..., s) \quad (36)$$

$$\mathrm{div}\ \mathscr{E}(m, \boldsymbol{r}) = 0, \qquad (m = 1, 2, ..., s) \quad (37)$$

$$\Delta \mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \boldsymbol{r}) + k^2 n^2 \mathscr{E}_{\alpha\varepsilon}^{(1)}(m, \boldsymbol{r}) = 0, \qquad (m = 1, 2, ..., s) \quad (38)$$

by assuming (36)–(38) to hold, and showing that n can then be chosen so that (25) and (21) become identities. Finally n can be identified with the physical refractive index.

With (21), (37) and (38) one shows (cf. (I. 145)):

$$\delta_{\alpha\beta\gamma} \mathscr{E}_{\beta\gamma}^{(1)}(m, \boldsymbol{r}) = - \rho m \sum_{m'} g_0(m') \frac{4\pi}{n^2 - 1}\ \mathrm{rot}_\alpha\ \mathscr{E}(m', \boldsymbol{r}). \quad (39)$$

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Choosing for $\mathscr{E}(m, \boldsymbol{r})$ a solution of (36) and (37) representing a transverse plane wave propagated in an arbitrary direction, so that

$$\mathscr{E}(m, \boldsymbol{r}') = e^{ink\cdot(\boldsymbol{r}'-\boldsymbol{r})}\,\mathscr{E}(m, \boldsymbol{r}), \qquad (m = 1, 2, ..., s) \qquad (40)$$

where the vector $\boldsymbol{k}$ is the product of k and the unit vector in the direction of propagation, we can write for (25):

$$\sum_{m'} \{\delta_{mm'} + \rho_m D_{mm'}\, g_0(m') + \sum_{m''} R_{mm''}\rho_{m''}\, D_{m''m'}\, g_0(m')\}\, \mathscr{E}_\alpha(m', \boldsymbol{r}) =$$

$$= \rho_m E^0_\alpha(\boldsymbol{r}) + \rho_m \mathscr{E}^d_\alpha(\boldsymbol{r}) + \sum_{m'} \int^V d\boldsymbol{r}'\, K_{\alpha\beta}(m, m'; \boldsymbol{r}, \boldsymbol{r}')\, [\rho_{m'}\, E^0_\beta(\boldsymbol{r}') + \rho_{m'}\mathscr{E}^d_\beta(\boldsymbol{r}')]$$

$$(41)$$

with the definitions

$$-D_{mm'} \equiv \int^V d\boldsymbol{r}'\, n_\alpha\, A^{(0)}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{r}')\, n_\beta\, e^{ink\cdot(\boldsymbol{r}'-\boldsymbol{r})}\, \{g^{(m, m')}(\boldsymbol{r}, \boldsymbol{r}') - 1\}, \qquad (42)$$

$$R_{mm'} \equiv \int^V d\boldsymbol{r}'\, n_\alpha K_{\alpha\beta}(m, m'; \boldsymbol{r}, \boldsymbol{r}')\, n_\beta\, e^{ink\cdot(\boldsymbol{r}'-\boldsymbol{r})}, \qquad (43)$$

$\boldsymbol{n}$ being a unit vector orthogonal to $\boldsymbol{k}$.

With (36), (37) and (40) one can show, using (14) and (28), that (41) leads to two equations, one describing the extinction of the field E^0, the other (cf. (152)) determining the parameter n,

$$\sum_{m'} \{\delta_{mm'} + \rho_m D_{mm'}\, g_0(m') + \sum_{m''} R_{mm''}\rho_{m''}D_{m''m'}\, g_0(m')\}\, \mathscr{E}_\alpha(m', \boldsymbol{r}) =$$

$$= \sum_{m'} \{(\rho_m + \sum_{m''} R_{mm''}\rho_{m''})\, g_0(m')\}\frac{4\pi}{3}\frac{n^2+2}{n^2-1}\,\mathscr{E}_\alpha(m', \boldsymbol{r}) -$$

$$- \sum_{m'} \{(\rho_m + \sum_{m''} R_{mm''}\rho_{m''})\, g_0(m')\}\frac{G_2}{G_0}\frac{4\pi}{n^2-1}\, \mathrm{rot}_\alpha\,\mathscr{E}(m', \boldsymbol{r}) -$$

$$- \sum_{m'} \{(\rho_m + \sum_{m''} R_{mm''}\rho_{m''})\, g_0(m')\}\, G_1\frac{4\pi}{3}\frac{n^2+2}{n^2-1}\frac{4\pi}{n^2-1}\, \mathrm{rot}_\alpha\,\mathscr{E}(m', \boldsymbol{r}).$$

$$(44)$$

Finally the interpretation of n as the refractive index of the medium can be established in complete analogy to the one-component case.

We shall now investigate the propagation of the light through the medium. Let us write (44) in a more compact form by introducing a matrix notation. Let $\mathscr{E}_\alpha(\boldsymbol{r})$ be a "vector" with s components $\mathscr{E}_\alpha(m, \boldsymbol{r})$, $(m = 1, 2, ..., s)$ and let U, V and W be square matrices with elements

$$U_{mm'} \equiv \delta_{mm'}, \qquad (45)$$

$$V_{mm'} \equiv (\rho_m D_{mm'} + \sum_{m''} R_{mm''}\, \rho_{m''}D_{m''m'})\, g_0(m'), \qquad (46)$$

$$W_{mm'} \equiv (\rho_m + \sum_{m''} R_{mm''}\rho_{m''})\, g_0(m'). \qquad (47)$$

Then we can write (44) as

$$\left(U + V - \frac{4\pi}{3} \frac{n^2 + 2}{n^2 - 1} W \right) \cdot \mathscr{E}_\alpha =$$

$$- \frac{4\pi}{n^2 - 1} \left(\frac{G_2}{G_0} + \frac{4\pi}{3} \frac{n^2 + 2}{n^2 - 1} G_1 \right) W \cdot \mathrm{rot}_\alpha \, \mathscr{E}. \qquad (48)$$

For the sake of simplicity we now specialize to a two-component system ($s = 2$). In zeroth order (*i.e.* setting $g_1(m) = g_2(m) = 0$, $(m = 1, 2)$), we obtain the generalized Lorentz-Lorenz equation for an isotropic two-component consisting of non-polar molecules with constant polarizabilities:

$$\det \left(U + V - \frac{4\pi}{3} \frac{n_0^2 + 2}{n_0^2 - 1} W \right) = 0. \qquad (49)$$

Since we have, according to (47),

$$\det W = 0, \qquad (50)$$

(49) reduces to

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} \frac{g_0(1) \det F^{(1)} + g_0(2) \det F^{(2)}}{\det (U + V)}, \qquad (51)$$

with the definitions

$$F^{(1)} \equiv \begin{vmatrix} \dfrac{1}{g_0(1)} W_{11} & V_{12} \\ \dfrac{1}{g_0(1)} W_{21} & 1 + V_{22} \end{vmatrix}, \quad F^{(2)} \equiv \begin{vmatrix} 1 + V_{11} & \dfrac{1}{g_0(2)} W_{12} \\ V_{21} & \dfrac{1}{g_0(2)} W_{22} \end{vmatrix}. \qquad (52)$$

Upon neglecting statistical effects, we have $V = 0$, $\det F^{(1)} = \rho_1$, $\det F^{(2)} = \rho_2$, so that (51) reduces to

$$\frac{n_0^2 - 1}{n_0^2 + 2} = \frac{4\pi}{3} G_0, \qquad (53)$$

where (24) has been used.

Let us now turn to the first order theory. As in the one-component case (cf. the discussion after formula (I. 157)) we replace in the right hand side of (48) the factor $4\pi(n^2 + 2)/3(n^2 - 1)$ by $4\pi(n_0^2 + 2)/3(n_0^2 - 1)$ and then substitute eq. (53). We obtain

$$\left(U + V - \frac{4\pi}{3} \frac{n^2 + 2}{n^2 - 1} W \right) \cdot \mathscr{E}_\alpha = - \frac{4\pi}{n^2 - 1} \left(\frac{G_2 + G_1}{G_0} \right) W \cdot \mathrm{rot}_\alpha \, \mathscr{E}. \qquad (54)$$

Let the direction of propagation of the plane waves be the z-direction. Then we have

$$\mathscr{E}_x(m, r) = \mathscr{E}_x(m) \, e^{iknz}; \quad \mathscr{E}_y(m, r) = \mathscr{E}_y(m) \, e^{iknz}; \quad \mathscr{E}_z(m, r) = 0. \qquad (55)$$

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Substitution into (54) yields 4 equations for $\mathscr{E}_x(1)$, $\mathscr{E}_y(1)$, $\mathscr{E}_x(2)$ and $\mathscr{E}_y(2)$. Denoting

$$\left(U + V - \frac{4\pi}{3}\frac{n^2+2}{n^2-1}W\right) \text{ by A and } \frac{4\pi}{n^2-1}\left(\frac{G_2+G_1}{G_0}\right)W \text{ by B}$$

we find, upon setting the coefficient determinant equal to zero and using (50)

$$\det A = \pm\left\{\begin{vmatrix} A_{11} & B_{12} \\ A_{21} & B_{22} \end{vmatrix} + \begin{vmatrix} B_{11} & A_{12} \\ B_{21} & A_{22} \end{vmatrix}\right\}, \tag{56}$$

with solutions $\mathscr{E}_x(m) \mp i\mathscr{E}_y(m) = 0$, $(m = 1, 2)$, the $-$ $(+)$ sign corresponding to a right (left) circularly polarized wave with refractive index $n_r(n_l)$. In terms of the matrices U, V, $F^{(1)}$ and $F^{(2)}$ relation (56) takes the form

$$\det (U + V) - \frac{4\pi}{3}\frac{n^2+2}{n^2-1}\{g_0(1)\det F^{(1)} + g_0(2)\det F^{(2)}\} =$$

$$\pm \frac{4\pi k n}{n^2-1}\left(\frac{G_1+G_2}{G_0}\right)\{g_0(1)\det F^{(1)} + g_0(2)\det F^{(2)}\}. \tag{57}$$

Multiplication of (57) by $n^2 - 1$ and subtraction of the second equation (with the $-$ sign) form the first yields, using (51):

$$n_r - n_l = 4\pi k\left(\frac{G_1+G_2}{G_0}\right)\frac{\{g_0(1)\det F^{(1)} + g_0(2)\det F^{(2)}\}}{\det (U+V)-\{g_0(1)\det F^{(1)} + g_0(2)\det F^{(2)}\}} \tag{58}$$

According to (51) this relation may then be written as

$$n_r - n_l = 4\pi k\left(\frac{G_1+G_2}{G_0}\right)\frac{n_0^2+2}{3}\frac{\{g_0(1)\det F^{(1)} + g_0(2)\det F^{(2)}\}}{\det (U+V)} \tag{59}$$

or, alternatively

$$n_r - n_l = 4\pi k(G_1+G_2)\frac{n_0^2-1}{4\pi G_0}. \tag{60}$$

Substitution into Fresnel's formula (I. 1) yields

$$\varphi = -\frac{8\pi^3}{\lambda^2}\frac{n_0^2-1}{4\pi G_0}(G_1+G_2), \tag{61}$$

which is the desired generalization of (I. 166).

Finally we note that in the case of a solution of an optically active substance in an optically inactive solvent $(g_1(2) = g_2(2) = 0)$ the non-specific influence of the solvent is contained in the factor

$$f(n_0) = \frac{n_0^2-1}{4\pi G_0}. \tag{62}$$

This is an extension of H o e k's result. He obtained

$$f(n_0) = \frac{n_0^2 + 2}{3}, \tag{63}$$

which is correct only in the absence of statistical effects, as can be seen from (51) and (55) (cf. the discussion after formula (I. 166)).

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BORN'S COUPLED OSCILLATORS MODEL

Synopsis

The molecular constants occurring in the general theory of optical rotatory power are calculated for Born's molecular model, a spatial distribution of coupled oscillators. Born's method of the relative electric moment is discussed.

§ 1. *Introduction.* Born [1]) and Oseen [4]) were the first to give the correct interpretation of optical activity on a molecular basis. Using as molecular model a spatial distribution of coupled oscillators they showed that the essential feature of a theoretical treatment of optical activity consists in taking into account the finiteness of the ratio of the molecular diameter to the wavelength of the light. A similar approach was made by de Malleman [5]), whereas Kuhn [6]) gave an extensive treatment of the most simple case of the coupled oscillators model to show activity. These early calculations on classical models have the great merit of giving direct insight into the mechanism of optical activity. They have however several shortcomings. Apart from the fact that in this early work statistical effects were not included, the detailed treatment contains some obscurities and inconsistencies, which have given rise to a certain amount of confusion and controversy.

The general formalism that we have developed in the two preceding chapters not only takes into account zeroth order statistical effects but settles the controversial points as well.

Firstly there has been a discrepancy in the expression derived for the factor $f(n_0)$ (cf. (II. 62) and (II. 63)). We note that the question as to what $f(n_0)$ should be is of a general nature, *i.e.* independent of the molecular model that is used. Now Hoek gave an unambiguous derivation of the correct factor $f(n_0)$ in the absence of statistical effects (cf. (II. 63)) whereas we have shown how this result can be extended when zeroth order statistical effects are taken into account (cf. (II. 62)).

The second important controversial point has been the role of the induced magnetic dipole moment. Born, in his first paper [1]) dealing with isotropic media, uses the electric moment only, neglecting the magnetic

moment. In a second paper [2]) he introduces instead of the electric moment the socalled "relative" electric moment. Finally in his "Optik" [3]) he adds to the relative electric moment the magnetic moment. Kooy [7]) then showed that if one uses the method of the relative electric moment, the magnetic moment has to be omitted. Hoek [8]) concluded that the result obtained by the method of the relative electric moment is correct (provided the right procedure, leading to the correct expression for $f(n_0)$ is followed). However, he erroneously assumed that in his own treatment the magnetic moment has been neglected.

We note that the question whether or not the induced magnetic dipole moment should be taken into account is again independent of the particular molecular model that is used. Now as we have shown a consistent first order (in d/λ) theory requires taking into account not only the induced electric dipole moment but the electric quadrupole moment and magnetic dipole moment as well. In isotropic media the quadrupole moment vanishes upon orientational averaging and can therefore be left out of consideration. Thus it is immediately clear that Born's first treatment, where he takes only the electric dipole moment into account, is incomplete. In order to be able to discuss the method of the relative electric moment we have to consider Born's model in more detail. To this end we first calculate, in § 2, the molecular constants for this particular model, in a similar way as Condon [9]) has done for Kuhn's simple model. By the nature of the model the results obtained by a quantum mechanical treatment are identical with those obtained by a classical treatment. Then, in § 3, we shall show that the method of the relative electric moment is intrinsically wrong, even though it yields the correct expression for the optical rotatory power.

§ 2. *Calculation of the molecular constants in Born's model.* We consider a molecule consisting of s particles with charges e_k and masses m_k ($k = 1$, 2, ..., s). Let r' be a fixed centre, and let the fixed equilibrium positions of the particles be r_k. Denoting the displacements of the particles from their equilibrium positions by u_k, we assume the potential energy to be given by

$$U = \tfrac{1}{2} \sum_{k,l=1}^{s} f_{\alpha\beta}^{kl} u_{k\alpha} u_{l\beta},$$ (1)

where, as usual, the summation convention is used for *greek* indices. The kinetic energy is given by

$$T = \tfrac{1}{2} \sum_{k=1}^{s} m_k \dot{u}_{k\alpha} \dot{u}_{k\alpha}.$$ (2)

Transforming to normal coordinates Q_i through

$$\sqrt{m_k}\, u_{k\alpha} = \sum_{i=1}^{3s} \xi_{k\alpha}^i Q_i,$$ (3)

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where $\xi_{k\alpha}^i$ satisfies the relations

$$\sum_i \xi_{k\alpha}^i \xi_{l\beta}^i = \delta_{kl}\, \delta_{\alpha\beta}; \ \sum_k \xi_{k\alpha}^i \xi_{k\alpha}^j = \delta_{ij}, \tag{4}$$

T and U become

$$T = \tfrac{1}{2} \sum_i \dot{Q}_i^2, \ \ U = \tfrac{1}{2} \sum_i \omega_i^2 Q_i^2, \tag{5}$$

where ω_i is the ith normal mode frequency. When the particles are acted upon by a harmonic force of frequency ω, $\boldsymbol{F}\, e^{-i\omega t}$, the equations of motion are, in normal coordinates,

$$\ddot{Q}_i + \omega_i^2 Q_i = F_i\, e^{-i\omega t}, \tag{6}$$

where (denoting the force acting on particle k by $\boldsymbol{F}_k$)

$$F_i = \sum_k \xi_{k\alpha}^i \frac{F_{k\alpha}}{\sqrt{m_k}}. \tag{7}$$

The solution of (10), $Q_i\, e^{-i\omega t}$, where

$$Q_i = \frac{F_i}{\omega_i^2 - \omega^2}, \tag{8}$$

can be expressed in terms of the old coordinates, using (3), (4) and (7). One obtains $u_{k\alpha}\, e^{-i\omega t}$ with

$$u_{k\alpha} = \sum_l A_{\alpha\beta}^{kl} F_{l\beta}, \tag{9}$$

where

$$A_{\alpha\beta}^{kl} = \sum_i \frac{\xi_{k\alpha}^i \xi_{l\beta}^i}{\omega_i^2 - \omega^2} \frac{1}{\sqrt{m_k m_l}}. \tag{10}$$

We note that

$$A_{\alpha\beta}^{kl} = A_{\beta\alpha}^{lk}. \tag{11}$$

When the particles are acted upon by an electromagnetic field of frequency ω, the force $\boldsymbol{F}_k$ is the Lorentz force on particle k. Confining oneself to the region where the displacements are linear in terms of the field strengths one may neglect the action of the magnetic field and write for (9)

$$u_{k\alpha} = \sum_l A_{\alpha\beta}^{kl} e_l E_\beta(\boldsymbol{r}_l). \tag{12}$$

We now proceed to calculate g_0, g_1 and g_2, defined by (I. 59)–(1.63). According to (5) the Hamiltonian is

$$H = \tfrac{1}{2}\sum_i (P_i^2 + \omega_i^2 Q_i^2), \tag{13}$$

where $P_i = \dot{Q}_i$, i.e. the Hamiltonian of $3s$ independent harmonic oscillators. As is well known, the eigenfunctions are products of $3s$ single oscillator

eigenfunctions,

$$|n_1 \dots n_{3s}\rangle = |n_1\rangle |n_2\rangle \dots |n_{3s}\rangle. \tag{14}$$

Corresponding to the eigenvalue

$$E_{n_1 \dots n_s} = \sum_i (n_i + \tfrac{1}{2}) \hbar\omega_i, \quad (n_i = 0, 1, 2, \dots). \tag{15}$$

We have to calculate the matrix elements of the operators

$$p_\alpha = \sum_k e_k u_{k\alpha} =$$

$$= \sum_k \frac{e_k}{\sqrt{m_k}} \sum_i \xi_{k\alpha}^i Q_i \tag{16}$$

and (neglecting the term of second order in the small displacements $u_{k\alpha}$)

$$m_\alpha = \frac{1}{2c} \sum_k e_k (\mathbf{r}_k \times \dot{\mathbf{u}}_k)_\alpha =$$

$$= \frac{1}{2c} \delta_{\alpha\beta\gamma} \sum_k \frac{e_k}{\sqrt{m_k}} r_{k\beta} \sum_i \xi_{k\gamma}^i \dot{Q}_i. \tag{17}$$

The matrix elements that will be needed are

$$\langle n_1 \dots n_{3s} | Q_i | n_1' \dots n_{3s}' \rangle =$$

$$= \left(\frac{\hbar}{\omega_i}\right)^{\frac{1}{2}} \left[\left(\frac{n_i + 1}{2}\right)^{\frac{1}{2}} \delta_{n' i n_i + 1} + \left(\frac{n_i}{2}\right)^{\frac{1}{2}} \delta_{n' i n_i - 1} \right] \prod_{j \neq i} \delta_{n_j n'_j} \tag{18}$$

$$\langle n_1 \dots n_{3s} | P_i | n_1' \dots n_{3s}' \rangle = i(\hbar\omega_i)^{\frac{1}{2}}.$$

$$\left[\left(\frac{n_i}{2}\right)^{\frac{1}{2}} \delta_{n' i n_i - 1} - \left(\frac{n_i + 1}{2}\right)^{\frac{1}{2}} \delta_{n' i n_i + 1} \right] \prod_{j \neq i} \delta_{n_j n'_j}. \tag{19}$$

Now let $|a\rangle$ stand for $|n_1 \dots n_{3s}\rangle$. Then we have

$$\sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| Q_i |b\rangle \langle b| Q_j |a\rangle = \tfrac{1}{2} \frac{1}{\omega_i^2 - \omega^2} \delta_{ij}, \tag{20}$$

$$\sum_b \frac{\hbar c}{W_{ba}^2 - E^2} \langle a| P_i |b\rangle \langle b| Q_j |a\rangle = \frac{i}{2} \frac{c}{\omega_i^2 - \omega^2} \delta_{ij}, \tag{21}$$

where $E = \hbar\omega$ and $W_{ba} = E_b - E_a$.

For g_0, defined by

$$g_0 = \tfrac{2}{3} \operatorname{Re} \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \langle a| p_\alpha |b\rangle \langle b| p_\alpha |a\rangle \tag{22}$$

we find, using (10), (16) and (20),

$$g_0 = \tfrac{1}{3} \sum_{k, l} e_k e_l A_{\alpha\alpha}^{kl}. \tag{23}$$

h_2, defined by

$$h_2 = \frac{2c}{3\omega} \, \mathrm{Re} \, \sum_b \frac{W_{ba}}{W_{ba}^2 - E^2} \, \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, m_\alpha \, |a\rangle, \tag{24}$$

vanishes, since according to (16), (17) and (18) $\langle a| \, p_\alpha \, |b\rangle \, \langle b| \, m_\alpha \, |a\rangle$ is an imaginary quantity.

For h_1, defined by

$$h_1 = \tfrac{2}{3} \, \mathrm{Im} \, \sum_b \frac{\hbar c}{W_{ba}^2 - E^2} \, \langle a| \, p_\alpha \, |b\rangle \, \langle b| \, m_\alpha \, |a\rangle \tag{25}$$

we find, using (16), (17) and (21)

$$h_1 = - \tfrac{1}{6} \sum_{k,\,l} e_k \, e_l \, A_{\alpha\beta}^{kl} \, r_{l\gamma} \, \delta_{\alpha\beta\gamma}. \tag{26}$$

As $h_2 = 0$, we have $g_1 = g_2 = - h_1$, so that we find:

$$g_1 = g_2 = \tfrac{1}{6} \sum_{k,\,l} e_k \, e_l \, A_{\alpha\beta}^{kl} \, r_{l\gamma} \, \delta_{\alpha\beta\gamma} \tag{27}$$

(cf. the remark at the end of I § 2).

§ 3. *The method of the relative electric moment.* In his second paper [2]) B o r n defines the relative electric moment in the following way

$$p_\alpha^{\mathrm{rel}} = \sum_k e_k \, u_{k\alpha} \, e^{-ik \cdot (r_k - r')}, \tag{28}$$

where the exciting field varies inside the molecule as

$$E_\alpha(r_k) = E_\alpha(r') \, e^{ik \cdot (r_k - r')}. \tag{29}$$

Using (11) and (12) one finds

$$p_\alpha^{\mathrm{rel}} = \sum_{k,\,l} e_k \, e_l \, A_{\alpha\beta}^{kl} \, E_\beta(r') + \sum_{k,\,l} e_k \, e_l \, A_{\alpha\beta}^{kl} \, (r_{l\gamma} - r_{k\gamma}) \, E_{\beta\gamma}(r'). \tag{30}$$

Defining the polarization as

$$P = \sum_i \langle p_i^{\mathrm{rel}} \, \delta(r_i - r) \, f \rangle_{\omega,\,r}, \tag{31}$$

we find, using the definitions (I. 108) and (I. 109) of the average exciting field $\mathscr{E}_\alpha(r)$ and the average of its derivative, $\mathscr{E}_{\alpha e}^{(1)}(r)$,

$$P_\alpha = (\tfrac{1}{3} \sum_{k,\,l} e_k \, e_l \, A_{\alpha'\alpha}^{kl}) \, \mathscr{E}_\alpha +$$
$$+ (\tfrac{1}{3} \sum_{k,\,l} e_k \, e_l \, A_{\alpha'\beta'}^{kl} \, r_{l\gamma'} \, \delta_{\alpha'\beta'\gamma'}) \, \delta_{\alpha\beta\gamma} \, \mathscr{E}_{\beta\gamma}^{(1)} \tag{32}$$

or, using (23) and (27),

$$P_\alpha = g_0 \mathscr{E}_\alpha + (g_1 + g_2) \, \delta_{\alpha\beta\gamma} \, \mathscr{E}_{\beta\gamma}^{(1)}. \tag{33}$$

Now the correct expression for the polarization P_α in terms of $\mathscr{E}_\alpha$ and $\mathscr{E}_{\alpha e}^{(1)}$

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is (cf. (I. 170))

$$P_\alpha(\mathbf{r}) = g_0 \mathscr{E}_\alpha(\mathbf{r}) + g_1 \delta_{\alpha\beta\gamma} \mathscr{E}_{\beta\gamma}^{(1)}(\mathbf{r}), \tag{34}$$

whereas the magnetization M_α is given by (cf. (I. 172))

$$M_\alpha(\mathbf{r}) = ik\, g_2\, \mathscr{E}_\alpha(\mathbf{r}). \tag{35}$$

The resulting optical rotatory power was shown to be (cf. (I. 164))

$$\varphi = - \frac{8\pi^3}{\lambda^2}\, \frac{n_0^2 + 2}{3}\, (G_1 + G_2), \tag{36}$$

where

$$G_i = \rho g_i \qquad (i = 0, 1, 2). \tag{37}$$

From (36) and (37) it is immediately clear that a theory with g_1' and g_2', where $g_1' \equiv g_1 + g_2$ and $g_2' \equiv 0$, leads to the same expression for the optical rotatory power as the theory with g_1 and g_2. Now according to (33) and (34) Born has replaced g_1 by $g_1' \equiv g_1 + g_2$. Thus one can *a posteriori* say that Born's method of the relative electric moment leads to the correct expression for the optical rotatory power if and only if the induced magnetic moment is neglected ($g_2' \equiv 0$). We note however that Born's method, even though it yields the correct optical rotatory power, may, when applied to other electromagnetic phenomena, lead to erroneous conclusions. When we consider *e.g.* the distribution of the light scattered by the medium it is not at all clear that Born's method of the relative electric moment will yield the correct result, since the secondary radiation field emitted by a particle is in his treatment quite different from the secondary field as obtained by a rigorous treatment, including explicitly the induced magnetic moment. Thus in each particular case the applicability of the method of the relative electric moment has to be investigated since the method has no *a priori* justification.

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Appendix A

For the sake of completeness we shall derive the "full" integral equations resulting from (I. 129) and (I. 130), *i.e.* the equations rigorous to first order in d/λ. To this end we first show that $J_\alpha(r)$ and $J_{\alpha\varepsilon}^{(1)}(r)$ can be written as

$$J_\alpha(r) = \int^V dr' \, K_{\alpha\beta}^{(1)}(r, r') \, [\rho E_\beta^0(r') + G_0 \int^V dr'' \, A_{\beta\gamma}^{(0)}(r, r'') \, \mathscr{E}_\gamma(r'') \, g(r', r'') +$$

$$+ G_2 \int^V dr'' \, A_{\beta\gamma}^{(2)}(r', r'') \, \mathscr{E}_\gamma(r'') \, g(r', r'') +$$

$$+ G_1 \int^V dr'' \, A_{\beta\gamma\delta}^{(1)}(r, r'') \, \mathscr{E}_{\gamma\delta}^{(1)}(r'') \, g(r', r'')] +$$

$$+ \int^V dr' \, K_{\alpha\beta\varepsilon}^{(2)}(r, r') \, [\rho E_{\beta\varepsilon}^0(r') + G_0 \int^V dr'' B_{\beta\varepsilon\gamma}^{(0)}(r', r'') \, \mathscr{E}_\gamma(r'') \, g(r', r'')], \qquad (A. 1)$$

$$J_{\alpha\varepsilon}^{(1)}(r) = \int^V dr' \, K_{\alpha\varepsilon\beta}^{(3)}(r, r') \, [\rho E_\beta^0(r') + G_0 \int^V dr'' \, A_{\beta\gamma}^{(0)}(r', r'') \, \mathscr{E}_\gamma(r'') \, g(r', r'') +$$

$$+ G_2 \int^V dr'' \, A_{\beta\gamma}^{(2)}(r', r'') \, \mathscr{E}_\gamma(r'') \, g(r', r'') +$$

$$+ G_1 \int^V dr'' \, A_{\beta\gamma\delta}^{(1)}(r', r'') \, \mathscr{E}_{\gamma\delta}^{(1)}(r'') \, g(r', r'')] +$$

$$+ \int^V dr' \, K_{\alpha\varepsilon\beta\gamma}^{(4)}(r, r') \, [\rho E_{\beta\gamma}^0(r') + G_0 \int^V dr'' \, B_{\beta\gamma\delta}^{(0)}(r', r'') \, \mathscr{E}_\delta(r'') \, g(r', r'')], \qquad (A. 2)$$

where the components of the tensors $K^{(i)}(r, r')$ $(i = 1, 2, 3, 4)$ fall off rapidly to zero for $|r - r'| \to \infty$.

For this purpose we define

$$E_\alpha^*(r) = E_\alpha^0(r) + \frac{1}{\rho} \sum_{\substack{i, j \\ j \neq i}} g_0 \, \langle A_{\alpha\beta}^{(0)}(r_i, r_j) \, \overline{E}_\beta(r_j) \, \delta(r_i - r) \, f\rangle +$$

$$+ \frac{1}{\rho} \sum_{\substack{i, j \\ j \neq i}} g_2 \langle A_{\alpha\beta}^{(2)}(r_i, r_j) \, \overline{E}_\beta(r_j) \, \delta(r_i - r) \, f\rangle +$$

$$+ \frac{1}{\rho} \sum_{\substack{i, j \\ j \neq i}} g_1 \langle A_{\alpha\beta\gamma}^{(1)}(r_i, r_j) \, \overline{E}_{\beta\gamma}(r_j) \, \delta(r_i - r) \, f\rangle \qquad (A. 3a)$$

$$= E_\alpha^0(r) + g_0 \int^V dr' \, A_{\alpha\beta}^{(0)}(r, r') \, \mathscr{E}_\beta(r') \, g(r, r') +$$

$$+ g_2 \int^V dr' \, A_{\alpha\beta}^{(2)}(r, r') \, \mathscr{E}_\beta(r') \, g(r, r') +$$

$$+ g_1 \int^V dr' \, A_{\alpha\beta\gamma}^{(1)}(r, r') \, \mathscr{E}_{\beta\gamma}^{(1)}(r') \, g(r, r'), \qquad (A. 3b)$$

$$E_{\alpha\varepsilon}^*(r) = E_{\alpha\varepsilon}^0(r) + \frac{1}{\rho} \sum_{\substack{i, j \\ j \neq i}} g_0 \langle B_{\alpha\varepsilon\beta}^{(0)}(r_i, r_j) \, \overline{E}_\beta(r_j) \, \delta(r_i - r) \, f\rangle \qquad (A. 4a)$$

$$= E_{\alpha\varepsilon}^0(r) + g_0 \int^V dr' \, B_{\alpha\varepsilon\beta}^{(0)}(r, r') \, \mathscr{E}_\beta(r') \, g(r, r'). \qquad (A. 4b)$$

Let us write $E_{i\alpha}(r_i = r)$ and $E_{i\alpha\varepsilon}(r_i = r)$ for the $E_{i\alpha}$ and $E_{i\alpha\varepsilon}$ corresponding with the configuration $(r_1, r_2, ..., r_i = r, ..., r_N)$, where $E_{i\alpha}$ and $E_{i\alpha\varepsilon}$ are defined by (I. 115) and (I. 116). Then we have

$$E_{i\alpha}(r_i = r) = E_\alpha^*(r) + g_0 \sum_{j \neq i} A_{\alpha\beta}^{(0)}(r, r_j) E_{j\beta}(r_i = r) +$$

$$+ g_2 \sum_{j \neq i} A_{\alpha\beta}^{(2)}(r, r_j) E_{j\beta}(r_i = r) +$$

$$+ g_1 \sum_{j \neq i} A_{\alpha\beta\gamma}^{(1)}(r, r_j) E_{j\beta\gamma}(r_i = r) -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle A_{\alpha\beta}^{(0)}(r_k, r_l) \overline{E_{l\beta}}(r_l) \delta(r_k - r) f \rangle -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_2 \langle A_{\alpha\beta}^{(2)}(r_k, r_l) \overline{E_{l\beta}}(r_l) \delta(r_k - r) f \rangle -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_1 \langle A_{\alpha\beta\gamma}^{(1)}(r_k, r_l) \overline{E_{l\beta\gamma}}(r_l) \delta(r_k - r) f \rangle, \tag{A. 5}$$

$$E_{i\alpha\varepsilon}(r_i = r) = E_{\alpha\varepsilon}^*(r) + g_0 \sum_{j \neq i} B_{\alpha\varepsilon\beta}^{(0)}(r, r_j) E_{j\beta}(r_i = r) -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle B_{\alpha\varepsilon\beta}^{(0)}(r_k, r_l) \overline{E_{l\beta}}(r_l) \delta(r_k - r) f \rangle. \tag{A. 6}$$

Furthermore

$$\overline{E_\alpha}(r) = E_\alpha^*(r) + \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle A_{\alpha\beta}^{(0)}(r_k, r_l) \{E_{l\beta} - \overline{E_\beta}(r_l)\} \delta(r_k - r) f \rangle +$$

$$+ \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_2 \langle A_{\alpha\beta}^{(2)}(r_k, r_l) \{E_{l\beta} - \overline{E_\beta}(r_l)\} \delta(r_k - r) f \rangle +$$

$$+ \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_1 \langle A_{\alpha\beta\gamma}^{(1)}(r_k, r_l) \{E_{l\beta\gamma} - \overline{E_{\beta\gamma}}(r_l)\} \delta(r_k - r) f \rangle, \tag{A. 7}$$

$$\overline{E_{\alpha\varepsilon}}(r) = E_{\alpha\varepsilon}^*(r) + \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle B_{\alpha\varepsilon\beta}^{(0)}(r_k, r_l) \{E_{l\beta} - \overline{E_\beta}(r_l)\} \delta(r_k - r) f \rangle. \tag{A. 8}$$

Substitution of (A. 5)–(A. 8) into (I. 120) yields

$$J_\alpha(r) = \sum_{\substack{i, j \\ j \neq i}}^V \int dr' \langle [g_0 A_{\alpha\beta}^{(0)}(r_i, r_j) + g_2 A_{\alpha\beta}^{(2)}(r_i, r_j)] \cdot$$

$$[g_0 \sum_{k \neq j} A_{\beta\gamma}^{(0)}(r', r_k) E_{k\gamma}(r_j = r') +$$

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$$+ g_2 \sum_{k \neq j} A^{(2)}_{\beta\gamma}(\mathbf{r}', \mathbf{r}_k)\, E_{k\gamma}(\mathbf{r}_j = \mathbf{r}') +$$

$$+ g_1 \sum_{k \neq j} A^{(1)}_{\beta\gamma\delta}(\mathbf{r}', \mathbf{r}_k)\, E_{k\gamma\delta}(\mathbf{r}_j = \mathbf{r}') -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle A^{(0)}_{\beta\gamma}(\mathbf{r}_k, \mathbf{r}_l)\, E_{l\gamma}\, \delta(\mathbf{r}_k - \mathbf{r}')\, f \rangle -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_2 \langle A^{(2)}_{\beta\gamma}(\mathbf{r}_k, \mathbf{r}_l)\, E_{l\gamma}\, \delta(\mathbf{r}_k - \mathbf{r}')\, f \rangle -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_1 \langle A^{(1)}_{\beta\gamma\delta}(\mathbf{r}_k, \mathbf{r}_l)\, E_{l\delta}\, \delta(\mathbf{r}_k - \mathbf{r}')\, f \rangle].$$

$$\cdot \delta(\mathbf{r}_i - \mathbf{r})\, \delta(\mathbf{r}_j - \mathbf{r}')\, f \rangle$$

$$+ \sum_{\substack{i, j \\ j \neq i}} \int^V d\mathbf{r}' \, \langle g_1 A^{(1)}_{\alpha\beta\gamma}(\mathbf{r}_i, \mathbf{r}_j)\, [g_0 \sum_{k \neq j} B^{(0)}_{\beta\gamma\delta}(\mathbf{r}', \mathbf{r}_k)\, E_{k\delta}(\mathbf{r}_j = \mathbf{r}') -$$

$$- \frac{1}{\rho} \sum_{\substack{k, l \\ l \neq k}} g_0 \langle B^{(0)}_{\beta\gamma\delta}(\mathbf{r}_k, \mathbf{r}_l)\, E_{l\delta}\, \delta(\mathbf{r}_k - \mathbf{r}')\, f \rangle] \cdot$$

$$\cdot \delta(\mathbf{r}_i - \mathbf{r})\, \delta(\mathbf{r}_j - \mathbf{r}')\, f \rangle. \tag{A. 9}$$

By making repeated use of (A. 5) and (A. 6) one obtains a series for $J_\alpha(\mathbf{r})$. The series can be broken off after an arbitrary number of iterations by replacing all remaining E_α by E^*_α and $E_{\alpha\beta}$ by $E^*_{\alpha\beta}$. The integrand then consists of a part proportional to E^*_α and a part proportional to $E^*_{\alpha\beta}$. Thus one sees, recalling the definitions (A. 3b) and (A. 4b), that $J_\alpha(\mathbf{r})$ can indeed be written as in (A. 1). A first approximation to $K^{(1)}(\mathbf{r}, \mathbf{r}')$ and $K^{(2)}(\mathbf{r}, \mathbf{r}')$ is obtained from (A. 9) by replacing $E_{k\gamma}$ and $E_{l\gamma}$ by E^*_γ, $E_{k\gamma\delta}$ and $E_{l\gamma\delta}$ by $E^*_{\gamma\delta}$. One finds, using the definition (I. 137) of the distribution function for three particles,

$$K^{(1)}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \rho^2 \int^V d\mathbf{r}''\, [\{g_0 A^{(0)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') + g_2 A^{(2)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'')\} \{g_0 A^{(0)}_{\gamma\beta}(\mathbf{r}'', \mathbf{r}') +$$

$$+ g_2 A^{(2)}_{\gamma\beta}(\mathbf{r}'', \mathbf{r}')\} + g_1 A^{(1)}_{\alpha\gamma\delta}(\mathbf{r}, \mathbf{r}'')\, g_0 B^{(0)}_{\gamma\delta\beta}(\mathbf{r}'', \mathbf{r}')]\, [g(\mathbf{r}, \mathbf{r}'', \mathbf{r}') -$$

$$- g(\mathbf{r}, \mathbf{r}'')\, g(\mathbf{r}'', \mathbf{r}')] +$$

$$+ \rho \int^V d\mathbf{r}''\, [\{g_0 A^{(0)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') + g_2 A^{(2)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'')\} \{g_0 A^{(0)}_{\gamma\beta}(\mathbf{r}'', \mathbf{r}') + g_2 A^{(2)}_{\gamma\beta}(\mathbf{r}'', \mathbf{r}')\} +$$

$$+ g_1 A^{(1)}_{\alpha\gamma\delta}(\mathbf{r}, \mathbf{r}'')\, g_0 B^{(0)}_{\gamma\delta\beta}(\mathbf{r}'', \mathbf{r}')]\, g(\mathbf{r}, \mathbf{r}'')\, \delta(\mathbf{r} - \mathbf{r}'), \tag{A. 10}$$

$$K^{(2)}_{\alpha\beta\varepsilon}(\mathbf{r}, \mathbf{r}') = \rho^2 \int^V d\mathbf{r}''\, \{g_0 A^{(0)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') + g_2 A^{(2)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'')\}\, g_1 A^{(1)}_{\gamma\beta\varepsilon}(\mathbf{r}'', \mathbf{r}')$$

$$\{g(\mathbf{r}, \mathbf{r}'', \mathbf{r}') - g(\mathbf{r}, \mathbf{r}'')\, g(\mathbf{r}'', \mathbf{r}')\} +$$

$$+ \rho \int^V d\mathbf{r}''\, \{g_0 A^{(0)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') + g_2 A^{(2)}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'')\}\, g_1 A^{(1)}_{\gamma\beta\varepsilon}(\mathbf{r}'', \mathbf{r}') \cdot$$

$$\cdot g(\mathbf{r}, \mathbf{r}'')\, \delta(\mathbf{r} - \mathbf{r}'). \tag{A. 11}$$

Similarly one finds in first approximation for $K_{\alpha\varepsilon\beta}^{(3)}$ and $K_{\alpha\varepsilon\beta\gamma}^{(4)}$

$$K_{\alpha\varepsilon\beta}^{(3)}(\boldsymbol{r}, \boldsymbol{r}') = \rho^2 \int^V \mathrm{d}\boldsymbol{r}'' \, g_0 \, B_{\alpha\varepsilon\gamma}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') \, \{g_0 \, A_{\gamma\beta}^{(0)}(\boldsymbol{r}'', \boldsymbol{r}') + g_2 \, A_{\gamma\beta}^{(2)}(\boldsymbol{r}'', \boldsymbol{r}')\} \cdot$$
$$\cdot \{g(\boldsymbol{r}, \boldsymbol{r}'', \boldsymbol{r}') - g(\boldsymbol{r}, \boldsymbol{r}'') \, g(\boldsymbol{r}'', \boldsymbol{r}')\} +$$
$$+ \rho \int^V \mathrm{d}\boldsymbol{r}'' \, g_0 \, B_{\alpha\varepsilon\gamma}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') \, \{g_0 \, A_{\gamma\beta}^{(0)}(\boldsymbol{r}'', \boldsymbol{r}') + g_2 \, A_{\gamma\beta}^{(2)}(\boldsymbol{r}'', \boldsymbol{r}')\} \cdot$$
$$\cdot g(\boldsymbol{r}, \boldsymbol{r}'') \, \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad \text{(A. 12)}$$

$$K_{\alpha\varepsilon\beta\gamma}^{(4)}(\boldsymbol{r}, \boldsymbol{r}') = \rho^2 \int^V \mathrm{d}\boldsymbol{r}'' \, g_0 \, B_{\alpha\varepsilon\delta}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') \, g_1 \, A_{\delta\beta\gamma}^{(1)}(\boldsymbol{r}'', \boldsymbol{r}') \, \{g(\boldsymbol{r}, \boldsymbol{r}'', \boldsymbol{r}') -$$
$$- g(\boldsymbol{r}, \boldsymbol{r}'') \, g(\boldsymbol{r}'', \boldsymbol{r}')\} +$$
$$+ \rho \int^V \mathrm{d}\boldsymbol{r}'' \, g_0 \, B_{\alpha\varepsilon\delta}^{(0)}(\boldsymbol{r}, \boldsymbol{r}'') \, g_1 \, A_{\delta\gamma\beta}^{(1)}(\boldsymbol{r}'', \boldsymbol{r}') \, g(\boldsymbol{r}, \boldsymbol{r}'') \, \delta(\boldsymbol{r} - \boldsymbol{r}'). \qquad \text{(A. 13)}$$

This completes the proof of (A. 1) and (A. 2).

Substitution of (A. 1) and (A. 2) into (I. 129) and (I. 130) yields the full integral equations. Comparing these equations with the integral equations (I. 138) and (I. 122), in which first order statistical effects have been neglected, one sees that the full integral equations, though more complicated, display essentially the same structure as (I. 138) and (I. 122) (cf. the remark at the end of I § 5).

Consider the function

$$S(r, r') = S(R) = \frac{e^{ikR}}{R},$$ (B. 1)

where $R = |r - r'|$. The following equations hold:

$$\frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial x_\beta} \cdots S(r, r') = \left(-\frac{\partial}{\partial x_\alpha'}\right)\left(-\frac{\partial}{\partial x_\beta'}\right) \cdots S(r, r'),$$ (B. 2)

$$\frac{\partial S}{\partial x_\alpha} = (x_\alpha - x_\alpha') \left(\frac{1}{R} \frac{d}{dR}\right) S,$$ (B. 3)

$$\frac{\partial^2 S}{\partial x_\alpha \partial x_\beta} = (x_\alpha - x_\alpha')(x_\beta - x_\beta')\left(\frac{1}{R}\frac{d}{dR}\right)^2 S + \delta_{\alpha\beta}\left(\frac{1}{R}\frac{d}{dR}\right)S,$$ (B. 4)

$$(\Delta + k^2)\, S = 0,$$ (B. 5)

$$S(R) = \frac{1}{R} + ik + \frac{(ik)^2}{2} R + \cdots,$$ (B. 6)

$$\frac{dS}{dR} = -\frac{1}{R^2} + \frac{(ik)^2}{2} + \cdots,$$ (B. 7)

$$\left(\frac{1}{R}\frac{d}{dR}\right)^2 S = \frac{3}{R^5} - \frac{(ik)^2}{2}\frac{1}{R^3} + \cdots.$$ (B. 8)

Defining the unit vector v from r to r',

$$v_\alpha = \frac{x_\alpha' - x}{R},$$ (B. 9)

and denoting the average of a quantity A over a spherical surface $s(r)$ of radius a, centered around r, by $\bar{A} \equiv 1/4\pi a^2 \int^{s(r)} A\, dr'$, we have

$$\left.\begin{array}{l}
\overline{v_\alpha} = 0 \\[4pt]
\overline{v_\alpha v_\beta} = \tfrac{1}{3}\delta_{\alpha\beta} \\[4pt]
\overline{v_\alpha v_\beta v_\gamma} = 0 \\[4pt]
\overline{v_\alpha v_\beta v_\gamma v_\delta} = \tfrac{1}{15}\left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right)
\end{array}\right\}$$ (B. 10)

Let $v(r)$ be a sphere of radius a around r; let the surface of $v(r)$ be $s(r)$. Then we have

$$\frac{\partial}{\partial x_\alpha} \int_{v(r)}^{V} S(r, r')\, F(r')\, dr' = \int_{v(r)}^{V} \frac{\partial}{\partial x_\alpha}\, S(r, r')\, F(r')\, dr' -$$

$$- \int^{s(r)} S(r, r')\, F(r')\, v_\alpha\, dr'.$$ (B. 11)

In the limit $a \to 0$ the surface integral vanishes as can be seen by expanding $F(r')$ in a Taylor series around r, and (B. 11) reduces to

$$\frac{\partial}{\partial x_\alpha} \int\limits_{v(r)}^{V} S(r, r') \, F(r') \, dr' = \int\limits_{v(r)}^{V} \frac{\partial}{\partial x_\alpha} S(r, r') \, F(r') \, dr'. \qquad \text{(B. 12)}$$

Similarly we find, in the limit $a \to 0$, using (B. 11) with $\partial S/\partial x_\alpha$ and $\partial^2 S/\partial x_\alpha \partial x_\beta$ instead of S, and applying (B. 3), (B. 7), (B. 9) and (B. 10):

$$\frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} \int\limits_{v(r)}^{V} S(r, r') \, F(r') \, dr' = \int\limits_{v(r)}^{V} \frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} S(r, r') \, F(r') \, dr' -$$

$$- \frac{4\pi}{3} \, \delta_{\alpha\beta} \, F(r), \qquad \text{(B. 13)}$$

$$\frac{\partial^3}{\partial x_\alpha \, \partial x_\beta \, \partial x_\gamma} \int\limits_{v(r)}^{V} S(r, r') \, F(r') \, dr' = \int\limits_{v(r)}^{V} \frac{\partial^3}{\partial x_\alpha \, \partial x_\beta \, \partial x_\gamma} S(r, r') \, F(r') \, dr' -$$

$$- \frac{4\pi}{5} \left\{ \delta_{\alpha\beta} \frac{\partial F(r)}{\partial x_\gamma} + \text{cycl.} \right\}. \qquad \text{(B. 14)}$$

Now let F be a vector with components F_α. From (B. 13) we obtain

$$\frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} \int\limits_{v(r)}^{V} S \, F_\beta \, dr' = \int\limits_{v(r)}^{V} \frac{\partial^2}{\partial x_\beta \, \partial x_\beta} S \, F_\beta \, dr' - \frac{4\pi}{3} \, F_\alpha(r), \qquad \text{(B. 15)}$$

$$\Delta \int\limits_{v(r)}^{V} S \, F_\alpha \, dr' = \int\limits_{v(r)}^{V} \Delta \, S \, F_\alpha \, dr' - 4\pi \, F_\alpha(r), \qquad \text{(B. 16)}$$

According to (B. 5) we may write (B. 16) as

$$(\Delta + k^2) \int\limits_{v(r)} S \, F_\alpha \, dr' = - 4\pi \, F_\alpha(r). \qquad \text{(B. 17)}$$

Combination of (B. 15) and (B. 16) yields

$$T_{\alpha\beta}(r) \int\limits_{v(r)}^{V} S \, F_\beta \, dr' = \int\limits_{v(r)}^{V} T_{\alpha\beta}(r) \, S \, F_\beta \, dr' + \frac{8\pi}{3} \, F_\alpha(r), \qquad \text{(B. 18)}$$

where $T_{\alpha\beta}(r)$ stands for (rot rot)$_{\alpha\beta}$ (cf. (I. 97)).

Now let F satisfy the wave equation

$$(\Delta + n^2 k^2) \, F(r) = 0, \qquad \text{(B. 19)}$$

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with $n^2 \neq 1$. Then we find, using (B. 19) and (B. 5):

$$k^2(n^2 - 1) \int\limits_{v(r)}^{V} S \, F \, \mathrm{d}\boldsymbol{r}' = \int\limits_{v(r)}^{V} (F\Delta S - S\Delta F) \, \mathrm{d}\boldsymbol{r}'. \tag{B. 20}$$

According to Green's theorem the right hand side can be written as the difference of two surface integrals, one over the surface Σ of V, the other one over the surface $s(r)$ of $v(\boldsymbol{r})$,

$$\int^{\Sigma} \left[F(\boldsymbol{r}') \frac{\partial}{\partial v} S(\boldsymbol{r}, \boldsymbol{r}') - S(\boldsymbol{r}, \boldsymbol{r}') \frac{\partial}{\partial v} F(\boldsymbol{r}') \right] \mathrm{d}\boldsymbol{r}' - $$

$$- \int^{s(r)} \left[F(\boldsymbol{r}') \frac{\partial}{\partial v} S(\boldsymbol{r}, \boldsymbol{r}') - S(\boldsymbol{r}, \boldsymbol{r}') \frac{\partial}{\partial v} F(\boldsymbol{r}') \right] \mathrm{d}\boldsymbol{r}', \tag{B. 21}$$

where $\partial/\partial v$ denotes a differentiation along the outward normal (as seen from $\boldsymbol{r}$). The surface integral $s(\boldsymbol{r})$ can be evaluated using the fact that $\partial S/\partial v = \mathrm{d}S/\mathrm{d}R$ and $\partial/\partial v = v_\alpha (\partial/\partial x_\alpha')$. One finds, using (B. 7) and (B. 10):

$$k^2(n^2 - 1) \int\limits_{v(r)}^{V} S \, F \, \mathrm{d}\boldsymbol{r}' = \int^{\Sigma} \left[F \frac{\partial}{\partial v} S - S \frac{\partial}{\partial v} F \right] \mathrm{d}\boldsymbol{r}' + 4\pi \, F(\boldsymbol{r}). \tag{B. 22}$$

We then obtain from (B. 22) and (B. 12)

$$k^2(n^2 - 1) \int\limits_{v(r)}^{V} \frac{\partial}{\partial x_\alpha} S \, F \, \mathrm{d}\boldsymbol{r}' = \int^{\Sigma} \frac{\partial}{\partial x_\alpha} \left[F \frac{\partial S}{\partial v} - S \frac{\partial F}{\partial v} \right] \mathrm{d}\boldsymbol{r}' + 4\pi \frac{\partial F(\boldsymbol{r})}{\partial x_\alpha}, \tag{B. 23}$$

from (B. 22) and (B. 13)

$$k^2(n^2 - 1) \int\limits_{v(r)}^{V} \frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} S \, F \, \mathrm{d}\boldsymbol{r}' = \int^{\Sigma} \frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} \left[F \frac{\partial S}{\partial v} - S \frac{\partial F}{\partial v} \right] \mathrm{d}\boldsymbol{r}' + $$

$$+ \frac{4\pi}{3} k^2(n^2 - 1) \, \delta_{\alpha\beta} \, F(\boldsymbol{r}) + 4\pi \frac{\partial^2 F(\boldsymbol{r})}{\partial x_\alpha \, \partial x_\beta}, \tag{B. 24}$$

and from (B. 22) and (B. 14)

$$k^2(n^2 - 1) \int\limits_{v(r)}^{V} \frac{\partial^3}{\partial x_\alpha \partial x_\beta \partial x_\gamma} S \, F \, \mathrm{d}\boldsymbol{r}' = \int^{\Sigma} \frac{\partial^3}{\partial x_\alpha \partial x_\beta \partial x_\gamma} \left[F \frac{\partial S}{\partial v} - S \frac{\partial F}{\partial v} \right] \mathrm{d}\boldsymbol{r}' + $$

$$+ \frac{4\pi}{5} k^2(n^2 - 1) \left[\delta_{\alpha\beta} \frac{\partial F(\boldsymbol{r})}{\partial x_\gamma} + \text{cycl.} \right] + 4\pi \frac{\partial^3 F(\boldsymbol{r})}{\partial x_\alpha \partial x_\beta \partial x_\gamma}. \tag{B. 25}$$

Expanding $F_\alpha(\boldsymbol{r}')$ in a Taylor series around $\boldsymbol{r}$ and using (B. 6) we find in

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the limit that $a \to 0$

$$\int\limits^{v(r)} S(\mathbf{r}, \mathbf{r}') \, F_\alpha(\mathbf{r}') \, \mathrm{d}\mathbf{r}' = 0. \tag{B. 26}$$

Furthermore, using Gauss' theorem,

$$\int\limits^{v(r)} \frac{\partial}{\partial x_\alpha'} S(\mathbf{r}, \mathbf{r}') \, \mathrm{d}\mathbf{r}' = \int\limits^{s(r)} S(\mathbf{r}, \mathbf{r}') \, \nu_\alpha \, \mathrm{d}\mathbf{r}', \tag{B. 27}$$

we find in the limit $a \to 0$, using (B. 2),

$$\int\limits^{v(r)} \frac{\partial}{\partial x_\alpha} S(\mathbf{r}, \mathbf{r}') \, F_\beta(\mathbf{r}') \, \mathrm{d}\mathbf{r}' = 0, \tag{B. 28}$$

and using (B. 2), (B. 3) and (B. 6):

$$\int\limits^{v(r)} \frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} S(\mathbf{r}, \mathbf{r}') \, F_\gamma(\mathbf{r}') \, \mathrm{d}\mathbf{r}' = - \frac{4\pi}{3} \, \delta_{\alpha\beta} \, F_\gamma(\mathbf{r}). \tag{B. 29}$$

1. Now according to (I. 117), (I. 128) and (I. 132) we have

$$\mathscr{E}_{\alpha\epsilon}^{(1)}(\mathbf{r}) = \rho E_{\alpha\epsilon}^0(\mathbf{r}) + G_0 \int\limits_{v(r)}^{V} \mathrm{d}\mathbf{r}' \, T_{\alpha\beta}(\mathbf{r}) \, S_\epsilon(\mathbf{r}, \mathbf{r}') \, \mathscr{E}_\beta(\mathbf{r}'). \tag{B. 30}$$

Recalling the fact that $T_{\alpha\beta}(\mathbf{r})$, when operating on quantities A satisfying $(\Delta + k^2) \, A = 0$, is given by

$$T_{\alpha\beta}(\mathbf{r}) = \frac{\partial^2}{\partial x_\alpha \, \partial x_\beta} + k^2 \, \delta_{\alpha\beta} \tag{B. 31}$$

and applying (B. 25) and (B. 23) we obtain (I. 142).

2. According to (I. 117) and (I. 127) we have

$$\mathscr{E}_\alpha^d(\mathbf{r}) = G_0 \int\limits_{v(r)}^{V} \mathrm{d}\mathbf{r}' \, T_{\alpha\beta}(\mathbf{r}) \, S(\mathbf{r}, \mathbf{r}') \, \mathscr{E}_\beta(\mathbf{r}') +$$

$$+ G_2 \int\limits_{v(r)}^{V} \mathrm{d}\mathbf{r}' \, T_{\alpha\beta}(\mathbf{r}) \, S_\mu(\mathbf{r}, \mathbf{r}') \, \delta_{\beta\gamma\mu} \, \mathscr{E}_\gamma(\mathbf{r}') +$$

$$+ G_1 \int\limits_{v(r)}^{V} \mathrm{d}\mathbf{r}' \, T_{\alpha\beta}(\mathbf{r}) \, S(\mathbf{r}, \mathbf{r}') \, \delta_{\beta\gamma\delta} \, \mathscr{E}_{\gamma\delta}^{(1)}(\mathbf{r}'). \tag{B. 32}$$

Applying (B. 31), (B. 24) and (B. 22) to the first and third term in the right hand side of (B. 32), (B. 31), (I. 145), (B. 25) and (B. 23) to the second term, we obtain (I. 150).

3. Let us finally consider (I. 154). To the first integral in the right hand side we apply (B. 31), (B. 26) and (B. 29), and obtain $-(4\pi/3) \, G_0 \, \mathscr{E}_0(\mathbf{r})$. As for

the second integral, we note that

$$\frac{\partial^3}{\partial x_\alpha \partial x_\beta \partial x_\gamma} S(\boldsymbol{r}, \boldsymbol{r}') \, \delta_{\beta\gamma\mu} = 0;$$

this, in combination with (B. 28) shows that the second integral vanishes. The third integral is analogous to the first and yields $-(4\pi/3)G_1\delta_{\alpha\gamma\beta}\mathscr{E}^{(1)}_{\gamma\delta}(\boldsymbol{r})$. Combination of these results with (I. 145), (I. 150) and (I. 151) leads to (I. 155).

SAMENVATTING

Wanneer een stuk materie in vacuo getroffen wordt door een mono-chromatische vlakke lichtgolf, zullen in ieder molecuul oscillerende electrische en magnetische momenten geïnduceerd worden, waardoor de moleculen zelf als stralingsbronnen gaan fungeren. Het exacte microscopische stralingsveld dat correspondeert met een bepaalde configuratie van de moleculen is een superpositie van het uitwendige veld van de lichtgolf en de secundaire stralingsvelden van de moleculen. Terwijl deze microscopische velden zich voortplanten met de snelheid van licht in vacuo, c, plant het waarneembare macroscopische veld zich in het medium voort met een snelheid die verschillend is van c.

In dit proefschrift wordt de voortplanting van licht in isotrope optisch actieve media onderzocht. De struktuur van optisch actieve moleculen geeft aanleiding tot circulaire dubbele breking, d.w.z. in het medium planten rechts circulair gepolariseerde vlakke golven zich voort met een andere snelheid dan links circulair gepolariseerde. Dit heeft een draaiing van de polarisatierichting van door het medium vallend lineair gepolariseerd licht ten gevolge. De theorie van de optische activiteit kan beschouwd worden als een uitbreiding van de theorie van de gewone dispersie. Terwijl nl. in laatstgenoemde theorie de verhouding van de lineaire afmetingen van een molecuul t.o.v. de golflengte van het opvallende licht als verwaarloosbaar klein wordt beschouwd, is het essentiële van een theoretische behandeling van de optische activiteit dat deze kleine, maar eindige verhouding, tot op eerste orde in rekening wordt gebracht.

In hoofdstuk I wordt een algemene theorie gegeven van de optische activiteit in een isotroop medium bestaande uit identieke moleculen. Zonder een speciaal molecuul-model aan te nemen, wordt de invloed van een monochromatische vlakke lichtgolf op een molecuul onderzocht. Met behulp van de tijdsafhankelijke quantum mechanische storingsrekening worden uitdrukkingen afgeleid voor de geïnduceerde moleculaire momenten. Vervolgens wordt het secundaire stralingsveld van een molecuul berekend. Met behulp van deze resultaten worden de vergelijkingen opgesteld die in een systeem, bestaande uit N moleculen, het "dynamische evenwicht" beschrijven, d.w.z. de toestand waarbij ieder molecuul de invloed ondergaat

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van het uitwendige veld en de secundaire stralingsvelden van alle overige moleculen. Hieruit worden integraalvergelijkingen afgeleid voor de macroscopische veldgrootheden. In tegenstelling tot vroegere behandelingen van de optische activiteit, waarin de macroscopische grootheden door een ruimtelijke middelingsprocedure uit de microscopische werden verkregen, wordt in dit proefschrift de middelingsprocedure van de statistische mechanica toegepast, en wel worden de macroscopische grootheden gedefiniëerd als ensemblegemiddelden over een kanoniek ensemble. Deze behandelingswijze maakt het mogelijk de tot dusverre bij theoretische beschouwingen over optische activiteit verwaarloosde statistische correlatie- en fluctuatieeffecten in rekening te brengen. Aan de hand van de integraalvergelijkingen voor de gemiddelde veldgrootheden wordt de voortplanting van de lichtgolf door het medium onderzocht. De zgn. uitdovingsstelling, die inhoudt dat een deel van het gemiddelde veld het uitwendige veld compenseert, wordt bewezen. Voorts wordt het verschil tussen de voortplantingssnelheden van links en rechts circulair gepolariseerde vlakke golven berekend.

In hoofdstuk II wordt de algemene theorie uitgebreid voor een twee-componenten systeem.

In hoofdstuk III tenslotte worden de in de algemene theorie optredende moleculaire grootheden berekend voor een speciaal molecuul-model, nl. Borns model van gekoppelde oscillatoren, waarna aan de hand van de in hoofdstuk I en II ontwikkelde algemene theorie een discussie wordt gegeven van de door Born bij de behandeling van zijn model gebruikte methode van het relatieve electrische moment.