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On the Theory of Dispersion

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I. The measured absorption is the difference between absorption and forced emission. This has to be taken into account in the interpretation of measurements in the infrared and the absorption of hot gases, particularly in the sun. II. According to Maxwell's theory, $n^2=\epsilon\mu$. The influence of the magnetic susceptibility on the dispersion is discussed for a gas. The paramagnetic part depends on the frequency formally in the same way as the electric part, but is determined by the magnetic absorption lines. The diamagnetic part is practically independent of the frequency up tc x-ray frequencies.

I. INTRODUCTION

IT has been customary to write the dispersion formula

$$n^2-1=\frac{e^2}{\pi m}\sum_j N_j\sum_s \frac{f_{js}}{\nu_{sj}{}^2-\nu^2}. \tag{1}$$

Here N_j is the number of molecules in the state j per cc, ν the frequency of the incoming light, ν_{sj} the frequency emitted or absorbed in the transition $j\rightarrow s$, f_{js} the "electron number" or strength of the line, positive for an absorption line, negative for an emission line. The connection of f_{js} with the strength of the line comes about in the following manner: Define the absorption coefficient κ of light of frequency ν so that $e^{-\kappa x}$ is the intensity at the depth x in the absorbing medium. If the lines are sufficiently separated that the absorptions do not overlap, then the following relation holds between f and the absorption coefficient integrated over the whole spectral line, i.e., the total absorption in the line:

$$\int \kappa_{js}d\nu=(N\pi e^2/mc)f_{js}. \tag{2}$$

In this paper two points are investigated: The first is connected with pure rotation spectra in gases, the second with the influence of magnetic properties on the refractive index.

II. ROTATION SPECTRUM

It is well known that the "orientation" or "low frequency" part of the dielectric constant is simply the contribution of the pure rotation spectrum. This part of the spectrum is produced not only by the ground state, but also by the highly excited states. If we rewrite (1) by arranging according to lines instead of states and limit ourselves to diatomic molecules, we find the part due to the rotation spectrum in the form

$$n^2-1=\frac{e^2}{\pi m}\sum_j \frac{1}{\nu^2{}_{j,\,j+1}-\nu^2}(f_{j,\,j+1}N_j-f_{j+1,\,j}N_{j+1}). \tag{3}$$

The apparent contribution of the line $j\rightarrow j+1$ to the refractive index is measured therefore by

$$Nf'_{j,\,j+1}=f_{j,\,j+1}N_j-f_{j+1,\,j}N_{j+1}. \tag{4}$$

The question arises then: Is the connection between the strength of an absorption line and its influence on dispersion, which is valid for transitions from the ground state, preserved, that is to say, is

$$c\int \kappa_{j,\,j+1}d\nu=(\pi e^2/m)Nf'_{j,\,j+1}. \tag{5}$$

This is equivalent to asking whether the measured absorption is the difference between true absorption and forced emission to the absorbing state, in other words whether the light emitted in forced emission is coherent.

A little consideration of the classical electrodynamic picture of absorption and dispersion shows that this must be so.[1] In quantum mechanics likewise the coherence follows immediately from the fact that the forced emission is an emission into the eigenstate of the incoming light only; it therefore is not a spherical wave but only increases the amplitude of the original radiation. This means, however, that for a rotation line the total absorption is given by

$$c\int \kappa_{j,\,j+1}d\nu = N\frac{8\pi^3}{3h}p_0^2\frac{2B(j+1)^2}{S}\{e^{-Bhj(j+1)/kT}-e^{-Bh(j+1)(j+2)/kT}\}$$

$$= N\frac{8\pi^3}{3h}p_0^2\frac{2B(j+1)^2}{S}e^{-Bhj(j+1)/kT}(1-e^{-h\nu_j/kT}), \tag{6}$$

where $S=\sum_{j=0}^{\infty}(2j+1)e^{-Bhj(j+1)/kT}$, $B=h/8\pi^2 I$, I = moment of inertia, p_0 = constant electrical dipole moment of the molecule, $\nu_j=2B(j+1)$, and the following formula was used:[2] $e^2 f=(8\pi^2 m/3h)\nu_{j+1,\,j}P^2_{j,\,j+1}$. The dipole moment of the rotator, summed up over all the states belonging to the same energy[3] is given by $P^2_{j,\,j+1}=p_0^2(j+1)$. Similarly, the resultant transition probability is

$$b_{j,\,j+1}-b_{j+1,\,j}=\frac{8\pi^3}{3h^2}p_0^2\frac{j+1}{2j+1}N_j(1-e^{-h\nu_j/kT}). \tag{7}$$

The bracket is a correction to be applied to former calculations. In the case of HCl, $j=5$, it amounts to about $\frac{1}{3}$, which will slightly improve the agreement between theory and experiment[4] as indicated by the following tabulation:

$$b_{\mathrm{exp}}=4.7\cdot 10^{16} \qquad b_{\mathrm{theor\ old}}=1.1\cdot 10^{18} \qquad b_{\mathrm{theor\ new}}=3.6\cdot 10^{17}.$$

The contribution to n^2 due to the rotation spectrum has been developed by Debye[5] and has been shown to go over into the formula for the orientation polarization for $\nu=0$. It is, however, possible to get a simpler insight into the matter if one looks at the rotation spectrum with a spectroscope of such low resolving power that the whole rotation spectrum appears as an unresolved broad band. One sees then even from classical theory that according to the distribution law

$$kT/I\ (\exp.\ -I\nu^2/2kT)\nu d\nu,$$

the average frequency is proportional $T^{1/2}$, $\nu_0^2\sim T$ and that therefore

$$\lim_{\nu=0}\frac{f}{\nu_0^2-\nu^2}\sim\frac{\text{const.}}{T},$$

provided the total absorption in the band is independent of the temperature. That is actually so, but only on account of the negative terms. One finds

$$c\sum_j\int\kappa d\nu = N\frac{16\pi^3}{3h}\frac{p_0^2 B}{S}\sum_j(j+1)^2(e^{-Bhj(j+1)/kT}-e^{-Bh(j+1)(j+2)/kT})$$

$$= N\frac{16\pi^3}{3h}\frac{p_0^2 B}{S}\sum_j e^{-Bhj(j+1)/kT}\{(j+1)^2-j^2\}=\frac{N16\pi^3}{3h}p_0^2 B=\frac{2}{3}N\frac{p_0^2\pi}{I}. \tag{8}$$

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[1] K. F. Herzfeld, Zeits. f. Physik **23**, 341 (1924). R. W. Wood, *Physical Optics*, third edition (New York, 1934), p. 476. See also S. Korff and G. Breit, Rev. Mod. Phys. **4**, 481 (1932) where this is implicitly stated.

[2] A. Sommerfeld, *Wellenmechanischer Ergänzungsband* (Braunschweig, 1929), p. 203.

[3] Reference 2, p. 69.

[4] R. M. Badger, Proc. Nat. Acad. Sci. **13**, 408 (1927).

[5] P. Debye, *Polar Molecules* (New York, 1929), p. 164.

Furthermore, one finds $1/\nu_0^2 = 2\pi^3 I/kT$ which then gives the correct value.

It might be of interest to state here that the disappearance of the usual maxima and minima in the dispersion curve and the appearance of the shape given by Debye[5] are due to a sufficiently large damping. If the denominator of the dispersion formula is written $(\nu_0^2-\nu^2)+\nu^2\nu'^2$, the transition occurs at $\nu' \sim \nu_0$, the exact value depending on the way ν' depends on ν, i.e., on the exact shape of the band.

III. THE INFLUENCE OF MAGNETIC SUSCEPTIBILITY ON n

Maxwell's theory shows that

$$n^2 = \epsilon\mu, \tag{9}$$

where ϵ is the dielectric constant, μ the magnetic susceptibility. While it is always possible to replace for practical purposes μ by 1, it is of interest to investigate the matter closely from a theoretical standpoint. We restrict ourselves to a gas, where both ϵ and μ are nearly 1, and can then write

$$n^2 - 1 = \epsilon - 1 + \mu - 1, \tag{9'}$$

neglecting $(\epsilon-1)(\mu-1)$.

The question is now whether for higher frequencies this can be written in the form (1). This investigation will then yield the dependency of μ on the frequency.

We are going to use Dirac's theory of dispersion.[6, 7] For this purpose we first bring the Hamiltonian in a form suggested by T. Ehrenfest and first used by one of us:[7] One starts with the usual Lagrangian[8]

$$L = (m_i/2)\dot{q}_i^2 - V + (e_i/c)(\dot{q}_i A_i), \tag{10}$$

where the q are the coordinates of the electrons and nuclei, V the internal potential energy of the atom, A the vector potential.

As the equations of motion are deduced by the variation of an integral over L between fixed time limits, it is always possible to add to L a total differential in respect to time. If F_i are components of an arbitrary vector depending on the q_i we can write

$$\begin{aligned} L &= (m_i/2)\dot{q}_i^2 - V + (e_i/c)(\dot{q}_i A_i) - (d/dt)(q_i F_i) \\ &= \frac{m_i}{2}\dot{q}_i^2 - V + \left(\dot{q}_i\left\{\frac{e_i}{c}A_i - \frac{\partial}{\partial q_i}(q_j F_j)\right\}\right) - q_i\left(\frac{\partial F_i}{\partial t}\right). \end{aligned} \tag{11}$$

One finds

$$p_i = \partial L/\partial \dot{q}_i = m_i \dot{q}_i + \varphi_i \tag{12}$$

with the abbreviation

$$\varphi_i = e_i/cA_i - F_i - q_j \partial F_j/\partial q_i, \tag{12'}$$

(on the right side, sum over j, but not over i). H is found in the usual manner as

$$H = p_i\dot{q}_i - L = (1/2m_i)(p_i - \varphi_i)^2 + V + (q_i \partial F_i/\partial t). \tag{13}$$

The Hamiltonian equations, applied to this formula, give the correct equations of motion. We specialize now

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[6] P. Dirac, Proc. Roy. Soc. **A114**, 243, 710 (1927). M. Born and P. Jordan, *Einleitung in die Quantenmechanik* (Berlin, 1930), G. Wentzel, in *Handbuch der Physik*, second edition, Vol. XXIV_1 (Berlin, 1933).

[7] M. Goeppert-Mayer, Ann. d. Physik **9**, 273 (1931).

[8] If an index occurs more than once, one has to sum up over it. $e_i(q_iA_i)$ means therefore $\sum_i e_i(q_iA_i)$.

$$F_i=(e_i/c)A_i \text{ (do not sum over } i\text{)}$$

and have
$$H=\frac{1}{2m_i}p_i^2+V+\frac{e_i}{c}\left(q_i\frac{\partial A_i}{\partial t}\right)+\frac{e_i}{m_ic}\left(p_iq_j\frac{\partial A_j}{\partial q_i}\right)+\frac{e_i^2}{2m_ic^2}\left(\sum_j q_j\frac{\partial A_j}{\partial q_i}\right)^2. \tag{14}$$

The last term is new; the two last terms can be neglected if the variation of the potential within the atom is neglected.

The advantage of this form over the one usually taken lies in the fact that there the second order term $(+(e^2/2mc^2)A^2)$ contributes to dispersion to the same order of magnitude as the first order term, here however, much less.

The total radiation field can now be resolved into its Fourier components. We choose here progressive waves, requiring in place of boundary conditions that the waves repeat themselves periodically in adjacent cubes of volume V. This assures a discreet number of permitted eigenfunctions. We have
$$A=\sum_\alpha(A^\alpha+A^{\alpha+}), \tag{15}$$
where
$$A^\alpha=Q^\alpha V^{-\frac{1}{2}}a_\alpha \exp\left(-\frac{2\pi i\nu_\alpha}{c}(r\sigma_\alpha)\right). \tag{15'}$$

Here a_α and σ_α are two unit vectors, orthogonal to each other. The cross means the conjugate complex for c numbers, for matrices the conjugate complex, transposed matrix.

We then apply the usual method of superquantization which makes Q^α, $Q^{\alpha+}$ noncommutable operators. Q^α has elements corresponding to transitions $N_\alpha\rightarrow N_\alpha-1$ only (N_α number of photons in the vibration α) and $Q^{\alpha+}$, the adjoined matrix, elements corresponding to $N_\alpha\rightarrow N_\alpha+1$ only.

We now assume that light of frequency ν, eigenfunction A^α, falls on the atom and calculate the probability that in the time dt a light quantum has been taken out of the state α and thrown into the state β. The state α (incoming light) is characterized by two unit vectors a (direction of electric field) and σ (direction of propagation). The direction of the light vector in β is b, while the direction of propagation τ lies within the solid angle $d\Omega$. We consider only the case in which the atom has made a double transition from the ground state n elsewhere and back. This is energetically possible only if $\nu_\beta\sim\nu$. After integrating over all frequencies ν_β in the neighborhood of ν we obtain

$$\begin{aligned}w=dt\ V\,d\Omega\frac{4\pi^2\nu^2}{c^7}\Bigg|&\sum_k\frac{1}{h(\nu_{kn}+\nu)}\sum_i\left\{e_iq_i\frac{\partial A_i^\alpha}{\partial t}+\frac{e_i}{m_i}p_iq_j\frac{\partial A_j^\alpha}{\partial q_i}\right\}_{nk}\sum_i\left\{e_iq_i\frac{\partial A_i^{\beta+}}{\partial t}+\frac{e_i}{m_i}p_iq_j\frac{\partial A_j^{\beta+}}{\partial q_i}\right\}_{kn}\\ &+\sum_k\frac{1}{h(\nu_{kn}-\nu)}\sum_i\left\{e_iq_i\frac{\partial A_i^{\beta+}}{\partial t}+\frac{e_i}{m_i}p_iq_j\frac{\partial A_j^{\beta+}}{\partial q_i}\right\}_{nk}\sum_i\left\{e_iq_i\frac{\partial A_i^\alpha}{\partial t}+\frac{e_i}{m_i}p_iq_j\frac{\partial A_j^\alpha}{\partial q_i}\right\}_{kn}\\ &-\left\{\sum_i\frac{e_i^2}{m_i}\left(\sum_j q_j\frac{\partial A_j^\alpha}{\partial q_i}\right)\left(\sum_j q_j\frac{\partial A_j^{\beta+}}{\partial q_i}\right)\right\}_{nn}\Bigg|^2.\end{aligned} \tag{16}$$

From now on, the summation over the particles will not be written explicitly.

Develop now A
$$A^\alpha=Q^\alpha V^{-\frac{1}{2}}a\left\{1-\frac{2\pi i\nu}{c}(r\sigma)-\frac{1}{2}\left(\frac{2\pi\nu}{c}\right)^2(r\sigma)^2\right\}$$
$$\begin{aligned}\frac{e}{c}q_i\frac{\partial A_i}{\partial t}+\frac{e}{mc}p_iq_j\frac{\partial A_j}{\partial q_i}=-Q^\alpha V^{-\frac{1}{2}}e\frac{2\pi i\nu}{c}\Bigg\{&(ra)-\frac{2\pi i\nu}{c}(ra)(r\sigma)\\ &-\frac{1}{2}\left(\frac{2\pi\nu}{c}\right)^2(ra)(r\sigma)^2+\frac{1}{mc}(p\sigma)(ra)-\frac{2\pi i\nu}{c}\frac{1}{mc}\overline{(p\sigma)(r\sigma)}(ra)\Bigg\}.\end{aligned} \tag{17}$$[9]

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[9] $\overline{(p\sigma)(r\sigma)}$ is an abbreviation for $\frac{1}{2}(p\sigma)(r\sigma)+\frac{1}{2}(r\sigma)(p\sigma)$. As σ is normal to a, $(p\sigma)$ commutes with (ra).

One can furthermore write

$$\frac{e}{mc}(p\sigma)(ra)=\frac{e}{c}(\dot{r}\sigma)(ra)=\frac{e}{2c}\left\{(\dot{r}\sigma)(ra)-(r\sigma)(\dot{r}a)+\frac{d}{dt}(r\sigma)(ra)\right\}=M^{\alpha,\sigma}+\frac{e}{2c}\frac{d}{dt}(r\sigma)(ra), \tag{18}$$

where $M^{\alpha,\sigma}$ is the orbital magnetic moment in the direction normal to α and σ, i.e., the direction of the magnetic field. Of course, this is only the orbital part of the moment. If we had added, in the half classical manner, the term (spin moment×magnetic field) to the Hamiltonian function, we would have found added to the orbital magnetic moment the spin moment. Therefore M shall be from now on the resultant moment.

We find then, rearranging,

$$\frac{e}{c}q_i\frac{\partial A_i}{\partial t}+\frac{e}{mc}p_iq_j\frac{\partial A_j}{\partial q_i}=-Q^{\alpha}V^{-\frac{1}{2}}\frac{2\pi i\nu}{c}\left\{e(ra)+M^{\alpha,\sigma}-\frac{2\pi i\nu}{c}e(ra)(r\sigma)+\frac{e}{2c}\frac{d}{dt}(ra)(r\sigma)\right.$$
$$\left.-\frac{e}{2}\left(\frac{2\pi\nu}{c}\right)^2(ra)(r\sigma)^2-\frac{2\pi i\nu}{c}\frac{e}{c}\overline{(\dot{r}\sigma)(r\sigma)}(ra)\right\}. \tag{19}$$

Here, the first term corresponds to the usual electric dipole transitions, the second to transitions of magnetic dipoles, the third and fourth to electric quadrupoles. According to the selection rules[10] there is no allowed transition in common to these three types, so that cross products do not occur. The last two terms are tetraederpole transitions, which should have transitions in common with electric dipole transitions.[10a] These terms, however, are so small that we will only consider cross products with the electrical dipole terms.

The terms which arise from expressions of the type

$$\left\{\frac{e}{2c}\frac{d}{dt}(ra)(r\sigma)-\frac{2\pi i\nu}{c}e(ra)(r\sigma)\right\}_{nk}=-\frac{2\pi i}{c}e\left(\tfrac{1}{2}\nu_{kn}+\nu\right)\{(ra)(r\sigma)\}_{nk}$$

can be transformed

$$4\pi^2\sum_k\left[\left(\frac{1}{2}\nu_{kn}+\nu\right)^2\frac{1}{h(\nu_{kn}+\nu)}\{(ra)(r\sigma)\}_{nk}\{(rb)(r\tau)\}_{kn}\right.$$
$$\left.+\left(\frac{1}{2}\nu_{kn}-\nu\right)^2\frac{1}{h(\nu_{kn}-\nu)}\{(rb)(r\tau)\}_{nk}\{(ra)(r\sigma)\}_{kn}\right]$$
$$=\frac{4\pi^2}{4h}\sum_k\left[\left(\nu_{kn}+\nu+2\nu+\frac{\nu^2}{\nu_{kn}+\nu}\right)\{(ra)(r\sigma)\}_{nk}\{(rb)(r\tau)\}_{kn}\right.$$
$$\left.+\left(\nu_{kn}-\nu-2\nu+\frac{\nu^2}{\nu_{kn}-\nu}\right)\{(rb)(r\tau)\}_{nk}\{(ra)(r\sigma)\}_{kn}\right]$$
$$=\frac{(2\pi\nu)^2}{4h}\sum_k\left[\frac{1}{\nu_{kn}+\nu}\{(ra)(r\sigma)\}_{nk}\{(rb)(r\tau)\}_{kn}+\frac{1}{\nu_{kn}-\nu}\{(rb)(r\tau)\}_{nk}\{(ra)(r\sigma)\}_{kn}\right]$$
$$+\frac{2\pi i}{4h}\sum_k\left[\left\{\frac{d}{dt}(ra)(r\sigma)\right\}_{nk}\{(rb)(r\tau)\}_{kn}-\{(rb)(r\tau)\}_{nk}\left\{\frac{d}{dt}(ra)(r\sigma)\right\}_{kn}\right]. \tag{20}$$

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[10] H. C. Brinkman, Physica **1**, 93 (1933); E. U. Condon, Astrophys. J. **29**, 217 (1934); J. H. Van Vleck, Astrophys. J. **80**, 161 (1934).

[10a] H. M. Taylor, Proc. Camb. Phil. Soc. **31**, 407 (1935).

The last two terms give, with the help of the commutation rules

$$-\frac{1}{4m}\{(ra)(rb)(\sigma\tau)+(r\sigma)(r\tau)(ab)+(ra)(r\tau)(\sigma b)+(rb)(r\sigma)(a\tau)\}_{nn}. \tag{21}$$

This has to be taken together with the last term in (16), namely, the quadratic term of the interaction energy. This latter is, besides a common factor in front of the bracket,

$$-\frac{e^2}{mc^2}(\sigma\tau)\{(ra)(rb)\}_{nn}+\frac{2\pi i\nu}{c}\frac{e^2}{mc^2}(\sigma\tau)\{(ra)(rb)(r,\sigma-\tau)\}_{nn}.$$

We have then as final formula for the transition probability, with N_σ, N_τ as the average number of photons in these states

$$\begin{aligned} w=dt\,d\Omega\,c^{-3}V^{-1}N_\sigma(1+N_\tau)\left(\frac{2\pi\nu}{c}\right)^4\Bigg|&\frac{1}{h}\sum_k\left\{\frac{e^2(ar)_{nk}(br)_{kn}}{\nu_{kn}+\nu}+\frac{e^2(br)_{nk}(ar)_{kn}}{\nu_{kn}-\nu}\right\}\\ &+\frac{1}{h}\sum_k\left\{\frac{M_{nk}{}^{\alpha\sigma}M_{kn}{}^{b\tau}}{\nu_{kn}+\nu}+\frac{M_{nk}{}^{b\tau}M_{kn}{}^{\alpha\sigma}}{\nu_{kn}-\nu}\right\}+\frac{1}{4h}\left(\frac{2\pi\nu}{c}\right)^2e^2\sum_k\Bigg[\frac{1}{\nu_{kn}+\nu}\{(ra)(r\sigma)\}_{nk}\{(rb)(r\tau)\}_{kn}\\ &+\frac{1}{\nu_{kn}-\nu}\{(rb)(r\tau)\}_{nk}\{(ra)(r\sigma)\}_{kn}\Bigg]-\left(\frac{2\pi\nu}{c}\right)^2\frac{e^2}{2h}\sum_k\Bigg\{\frac{1}{\nu_{kn}+\nu}\big[(ar)_{nk}\{(r\tau)^2(rb)\}_{kn}\\ &+\{(r\sigma)^2(ra)\}_{nk}(br)_{kn}\big]+\frac{1}{\nu_{kn}-\nu}\big[(br)_{nk}\{(r\sigma)^2(ra)\}_{kn}+\{(r\tau)^2(rb)\}_{nk}(ar)_{kn}\big]\Bigg\}\\ &+\frac{2\pi i\nu}{c^2}\frac{e^2}{h}\sum_k\Bigg\{\frac{1}{\nu_{kn}+\nu}\big[(ar)_{nk}\{\overline{(\dot r\tau)(r\tau)}(rb)\}_{kn}-\{\overline{(\dot r\sigma)(r\sigma)}(ra)\}_{nk}(br)_{kn}\big]\\ &+\frac{1}{\nu_{kn}-\nu}\big[\{\overline{(\dot r\tau)(r\tau)}(rb)\}_{nk}(ar)_{kn}-(br)_{nk}\{\overline{(\dot r\sigma)(r\sigma)}(ra)\}_{kn}\big]\Bigg\}+\frac{2\pi i\nu}{c}\frac{e^2}{mc^2}\{(ra)(rb)(r,\sigma-\tau)\}_{nn}\\ &-\frac{e^2}{4mc^2}\{3(ra)(rb)(\sigma\tau)-(r\sigma)(r\tau)(ab)-(ra)(r\tau)(b\sigma)-(rb)(r\sigma)(a\tau)\}_{nn}\Bigg|^2. \end{aligned} \tag{22}$$

We have now to build up the secondary plane waves, which are responsible for the refractive index, out of the contributions of a system of molecules.[11] We know that an infinite plane normal to σ, filled uniformly with dipoles of alike character, will give the appropriate plane wave at a distance sufficiently large so that one can neglect the influence of the structure in the plane. Now the dependency on the angle of the contribution of the dipole of strength r to (22) is given by (rb).

If we want to consider quadrupoles instead of dipoles, we can get them by adding another plane of opposite sign but like strength, displaced against the first dipoles in the direction τ by the distance r'. This will give a factor

$$-(2\pi i\nu/c)(r'\tau).$$

On the other hand it is clear that if τ lies in the plane normal to σ there will be no secondary wave, because each dipole has nearby a neighbor of equal strength and opposite sign so that the total polarization of the plane is zero; its structure however does not count at large distances. Therefore, only the component $(r'\sigma)$ affects the secondary wave and the refractive index.[12]

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[11] See for example, R. W. Wood, reference 1.

[12] It may be pointed out that in calculating the refractive index no assumption concerning the reality of the matrices is necessary beyond that involved in the absence of rotatory power.

In applying this consideration, we assume that the material is not optically active so that there is no electric field in the direction $\perp \sigma, \tau$.

We remember furthermore $A_{nk}A_{kn}=|A|_{nk}^2=|A|_{kn}^2$. In the last term in (22), $(\sigma\tau)$ gives the contribution $(\sigma\sigma)=1$, (σb) the contribution $(\sigma a)=0$, $(a\tau)$ gives $(a\sigma)=0$; (ab) corresponds to a dipole of unit strength in the direction a.

In formula (23), n and N on the left side mean the refractive index and the number of molecules per cc; three summation indices are used, nk meaning an electric dipole transition, nm a magnetic dipole transition, nl an electric quadrupole transition.

$$\frac{n^2-1}{4\pi N}=\frac{e^2}{h}\sum_k \frac{2\nu_{kn}}{\nu_{kn}^2-\nu^2}|(ar)_{nk}|^2+\frac{1}{h}\sum_m \frac{2\nu_{mn}}{\nu_{mn}^2-\nu^2}|M_{mn}{}^{\alpha,\sigma}|^2+\left(\frac{2\pi\nu}{c}\right)^2\frac{e^2}{h}\left\{\sum_l \frac{2\nu_{ln}}{\nu_{ln}^2-\nu^2}|\{(ra)(r\sigma)\}_{nl}|^2\right.$$
$$\left.+\sum_k \frac{1}{\nu_{kn}^2-\nu^2}\frac{i}{2\pi}\left[(ar)_{nk}\{(r\sigma)^2(\dot{r}a)\}_{kn}-\{(r\sigma)^2(\dot{r}a)\}_{nk}(ar)_{kn}\right]\right\}-\frac{e^2}{4mc^2}\{3(ra)^2-(r\sigma)^2\}_{nn}. \quad (23)$$

The first term is the one which is usually given alone. For $\nu=0$ it goes over into the corresponding value for the dielectric constant.[13] We see therefore, as is well known, that the dispersion of the dielectric constant is determined by the position and strength of the absorption lines that correspond to electrical dipole transitions. Similarly, the second term goes, for the statical case, over into the paramagnetic part[13] of $(\mu-1)/4\pi N$. This formula apparently has to be amended if M has diagonal terms. This is the case for the single particle whenever orientation effects occur, i.e., in all paramagnetic atoms and most molecules. However, a method due to Waller[14] shows that formula (23) is valid even then. Waller considers a paramagnetic crystal, in particular one in which the paramagnetism is due entirely to the spin. The spins of the different atoms have an interaction energy. If one quantizes now the whole crystal, each state n which would be present for the free particles is split into a large (2^N) number of states n' with energy $E_{n'}$. Waller shows that $M_{n'n'}{}^{\alpha,\sigma}=0$ where M is the magnetic moment of the whole system, so that in the correctly quantized system no diagonal terms of the perturbation energy occur. This can be understood because in the unperturbed system opposite directions of the total spin are equally probable and there are therefore continuous transitions from one to the other, just as in the familiar case of the NH_3 pyramid the nitrogen atom oscillates between the two possible positions.

Waller investigates the behavior of this system in an alternating field and finds exactly the paramagnetic part of (23), he is, however, not sure up to what frequencies this applies. The application of the Dirac dispersion theory, however, as made here, can be made just as well to the new system, showing that the general formula for the paramagnetic part is

$$\sum_{n'}\sum_{l'}\frac{\nu_{n'l'}}{h}\frac{|M_{n'l'}|^2}{\nu_{n'l'}^2-\nu^2}\frac{N_{n'}-N_{l'}}{N}. \quad (24)$$

Here n', l' applies to *all* the states including the new ones into which the old levels, n, l have been split by the interaction energy.[15] The negative terms come from the "negative" dispersion due to forced emission.

If we take into account the smallness of $E_{n'}-E_{l'}$, we find

$$N_{n'}-N_{l'}=+(h\nu_{n'l'}/kT)N_{l'},$$

and

$$\frac{1}{NkT}\sum_{n'}\sum_{l'}\frac{\nu^2{}_{n'l'}}{\nu^2{}_{n'l'}-\nu^2}|M_{n'l'}|^2N_{n'}.$$

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[13] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, 1932).

[14] I. Waller, Zeits. f. Physik **79**, 370 (1932).

[15] The factor 2 has been left out because in 24 every term occurs twice.

For $\nu=0$ that goes over into[13]

$$\frac{1}{NkT}\sum_{n'} N_{n'} \sum_{l'} |M_{n'l'}|^2 = \frac{1}{NkT}\sum_{n'} N_{n'} M^2_{n'n'} = \frac{M_n{}^2}{kT},$$

the usual diagonal term of the unperturbed state.

One has always to take only the component of M in the direction of the external magnetic field.

Waller estimates the $\nu_{n'n''}$ at about 1 cm^{-1}.

It is true that Waller has developed this idea only for a crystal, but it can probably be applied similarly to a gas.

The next two sums have a different variation with the frequency than the two preceding ones. Because of the factor ν^2 in front, they give no contribution to ϵ or μ in statics. The order of magnitude of the third and fourth sum is the same, but they correspond to different absorption lines, the third to those caused by electric quadrupole transitions, the fourth to electric dipole lines, which are always also permitted in tetraeder transitions. (The factor i is multiplied by another i coming from $\dot{r}$.)

Finally the last term corresponds to diamagnetism. It has not quite the usual static form, which it takes only if we average over all orientations of the molecule, when

$$\overline{(ra)}^2 = \overline{(r\sigma)}^2$$

and therefore

$$3\overline{(ra)}^2 - \overline{(r\sigma)}^2 = \overline{(ra)}^2 + \overline{(r\sigma)}^2.$$

We see that diamagnetism is independent of the frequencies up to x-rays, when we can not neglect any more the form factor, i.e., the phase differences of the light wave within the atom.

It is interesting to note that for atoms the ratio of the dielectric to the diamagnetic term at vanishing frequency is

$$(2e^2/h\nu_{kn})(ar)_{nk}{}^2/(e^2/2mc^2)(ra)^2{}_{nn} \quad \text{or} \quad \sim 4mc^2/h\nu_{kn}.$$

The previous results are partly contained in Blaton's[16] investigation of dispersion in the neighborhood of quadrupole lines; the diamagnetic term is present there also, although its meaning is not mentioned; the paramagnetic terms are left out because in the absence of spin the transition probabilities are zero.

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[16] J. Blaton, Zeits. f. Physik **74**, 418 (1932).