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DISPERSION RELATIONS AND SUM RULES FOR NATURAL OPTICAL ACTIVITY

by

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ABSTRACT

Dispersion relations and sum rules are derived for the complex rotatory power of an arbitrary linear (nonmagnetic) isotropic medium showing natural optical activity. Both previously known dispersion relations and sum rules as well as new ones are obtained. It is shown that the Rosenfeld-Condon dispersion formula is inconsistent with the expected asymptotic behavior at high frequencies. A new dispersion formula based on quantum electrodynamics removes this inconsistency; however, it still requires modification in the low-frequency limit.

I - INTRODUCTION

A systematic procedure for the derivation of sum rules for the optical constants of material media has been recently formulated and applied to the dielectric tensor and refractive index of various types of media [1,2]. The basic ingredients are causality, expressed through dispersion relations, and the requirement that, at sufficiently high frequencies, the medium must respond like a free-electron plasma. Previously known results, such as the f-sum rules, together with a variety of new ones, follow from these conditions.

This procedure has also been applied to obtain sum rules for the optical constants associated with natural and magneto-optical activity [3]. For natural optical activity, however, several aspects in the derivation of both dispersion relations and sum rules need additional consideration.

Natural optical activity is the simplest manifestation of spatial dispersion, requiring one to go beyond the electric dipole approximation in treating the interaction of light with matter. The need to take into account retardation over molecular dimensions requires a careful discussion of the high-frequency behavior of the optical constants, taking into account the delicate interplay between microscopic and macroscopic descriptions.

Here we adopt the macroscopic, phenomenological viewpoint, based on constitutive relations. As has been emphasized by Condon [4], these relations are the touchstone of a successful theory of optical activity. We deal with an arbitrary linear (nonmagnetic) isotropic medium.

In Sect. II, we derive dispersion relations for the complex rotatory power from the constitutive relations and primitive causality, together with bounds on the high-frequency behavior. It is also shown that the average dielectric tensor and the average complex refractive index verify the same dispersion relations that hold for an optically inactive medium.

In Sect. III, sum rules involving the complex rotatory power are derived by applying superconvergence techniques [1]. We recover previously known sum rules [3] and obtain some new ones. The sum rules concern the averages of optical constants over the whole frequency spectrum, taken with various weight functions. Both for the rotatory power and for the ellipticity (which is a measure of the circular dichroism), these averages are zero; the latter rule expresses the equality of the average net transition rates for opposite circular polarizations. Similar results are found for the product of the two optical constants, and their mean squares turn out to be equal. The sum rules may be useful to check the consistency of experimental data, and also as constraints on theories of natural optical activity. They also enable us to interrelate various forms of dispersion relations by "undoing subtractions".

All the dispersion relations and sum rules obtained are collected together in Sect. IV. We also examine the compatibility between quantum dispersion formulas for the complex rotatory power and the sum rules. For the widely employed Rosenfeld-Condon dispersion formula [4], the well-known Kuhn sum rule holds. However, we find that this dispersion formula, where the effects of damping were not derived, but merely included by analogy with the Kramers-Heisenberg formula, is inconsistent with the requirement of free-electron response at high frequencies. A modified dispersion formula based on recent quantum-electrodynamic treatments is obtained. This formula differs very little from the Rosenfeld-Condon one within each optically active absorption band, but it is consistent with the expected high-frequency behavior. On the other hand, it still appears to require modification in the low-frequency limit.

The relationships between the present treatment and previous ones are discussed at the end of Sect. IV.

II - DISPERSION RELATIONS

We consider only linear nonmagnetic isotropic media that show natural optical activity. We assume to begin with that the medium is an insulator. The effect of conductivity is discussed in Sect. IIE.

A - Constitutive Relations

As shown by Condon [4], the constitutive relations for a medium with the above properties take the form[1]

$$\underset{\sim}{D} = \varepsilon \underset{\sim}{E} - g\, \partial \underset{\sim}{H}/\partial t, \qquad (1)$$

$$\underset{\sim}{B} = \underset{\sim}{H} + g\, \partial \underset{\sim}{E}/\partial t, \qquad (2)$$

where, on account of dispersion, it is understood, as usual, that the relations are strictly applicable only to monochromatic fields. Thus, if ω denotes the circular frequency, $\varepsilon = \varepsilon(\omega)$ is the complex dielectric constant. The presence of optical activity is characterized by the material constant $g(\omega)$, which is a pseudoscalar, so that a medium with inversion symmetry cannot have $g \neq 0$.

For a monochromatic plane wave travelling in the medium, we have, taking the z axis along the direction of propagation,

$$\underset{\sim}{E} = \mathrm{Re}\,\{\underset{\sim}{E}_0\ \exp[i(Nk_0 z-\omega t)]\} \qquad (3)$$

and a similar expression for $\underset{\sim}{H}$, where $k_0=\omega/c$ is the vacuum wave number and $N(\omega)$ is the complex refractive index. Substituting these expressions in Maxwell's equations, we find that the normal modes of propagation in a medium characterized by (1) and (2) are circularly polarized waves

$$\underset{\sim}{E}{}_0^{\pm} = E_0^{\pm}\ (\hat{\underset{\sim}{x}} \pm i\hat{\underset{\sim}{y}}) \qquad (4)$$

associated with left and right circular polarization, respectively. The corresponding complex refractive indices are

$$N_{\pm} = \sqrt{\varepsilon} \pm \omega g\ . \qquad (5)$$

Setting

$$N_{\pm}(\omega) = n_{\pm}(\omega) + i\kappa_{\pm}(\omega)\ , \qquad (6)$$

we see that the medium exhibits circular birefringence: it rotates the plane of polarization of linearly polarized light. The angle of rotation per unit propagation length defines the rotatory power

$$\phi(\omega)= \omega[n_+(\omega)-n_-(\omega)]/2c\ . \qquad (7)$$

The medium also shows circular dichroism, converting linearly polarized light into elliptically polarized light. The ellipticity per unit length is given by[2]

$$\theta(\omega) = \omega[\kappa_+(\omega) - \kappa_-(\omega)]/2c\ . \qquad (8)$$

We can combine (7) and (8) by defining the complex rotatory power of the medium,

$$\Phi(\omega) = \phi(\omega) + i\theta(\omega) = \omega[N_+(\omega) - N_-(\omega)]/2c\ . \qquad (9)$$

According to (5),

$$\omega g(\omega) = \frac{1}{2}[N_+(\omega) - N_-(\omega)], \qquad (10)$$

so that

$$\Phi(\omega) = \omega^2 g(\omega)/c\ . \qquad (11)$$

On the other hand, the average complex refractive index of the medium is given by

$$N_{av}(\omega) = \frac{1}{2}[N_+(\omega) + N_-(\omega)] = \sqrt{\varepsilon(\omega)}. \qquad (12)$$

B - Crossing Relations

A general wave train propagating in the z direction can be represented as a superposition of normal modes:

$$\underset{\sim}{E}(z,t) = \int_{-\infty}^{\infty} \{E_0^+(\omega)\,(\hat{\underset{\sim}{x}} + i\hat{\underset{\sim}{y}})\exp[i\omega N_+(\omega)z/c]$$

$$+ E_0^-(\omega)\,(\hat{\underset{\sim}{x}} - i\hat{\underset{\sim}{y}})\exp[i\omega N_-(\omega)z/c]\}\exp(-i\omega t)\,d\omega\ . \qquad (13)$$

Since $\underset{\sim}{E}$ must be real, we find the crossing relations

(for real ω)

$$E_0^+(-\omega) = [E_0^-(\omega)]^* , \tag{14}$$

$$N_+(-\omega) = [N_-(\omega)]^* . \tag{15}$$

It follows from (10) - (12) and (15) that

$$\varepsilon(-\omega) = \varepsilon^*(\omega) , \tag{16}$$

$$g(-\omega) = g^*(\omega) , \tag{17}$$

$$\Phi(-\omega) = \Phi^*(\omega) . \tag{18}$$

According to (14), we always need both terms in (13) in order to represent a real field. Thus, the complex refractive index associated with, e.g., left circular polarization is $N_+(\omega)$ for $\omega>0$ and $N_-(\omega)$ for $\omega<0$ (cf. (15)); this is connected with the fact that the sense of rotation changes with the sign of ω. As a consequence of this, the dispersion relations derived below involve a mixture of the two helicities; one cannot derive a dispersion relation for a single helicity - e.g., for left-handed light [5,6].

C - High-Frequency Behavior

The constitutive relations (1) and (2) lead to the following form for the frequency-and wave-vector-dependent dielectric tensor:

$$\varepsilon_{ij}(\omega,\underset{\sim}{k}) = [\varepsilon(\omega) - \omega^2 g^2(\omega)]\delta_{ij} + icg(\omega)\, \epsilon_{i\ell j} k_\ell \tag{19}$$

where $\epsilon_{i\ell j}$ is the Levi-Civita pseudotensor. Here, ω and $\underset{\sim}{k}$ may be regarded as independent variables for problems involving external sources; however, for wave propagation in the absence of external sources in the medium, spatial dispersion is reduced to frequency dispersion [7] through the relation

$$\underset{\sim}{k} = (\omega/c) N\, \underset{\sim}{\hat{s}}, \tag{20}$$

where $\underset{\sim}{\hat{s}}$ is a unit vector in the direction of propagation. Since N is double-valued, the same holds for ε_{ij}, so that we have different dielectric tensors for the two different normal modes, respectively

$$\varepsilon_{ij}^{\pm} = \varepsilon_{ij}(\omega, \underset{\sim}{k} = \frac{\omega}{c} N_\pm(\omega)\underset{\sim}{\hat{s}}) , \tag{21}$$

where $N_\pm(\omega)$ is given by (5).

At sufficiently high frequencies, we expect the medium to behave as if all its electrons were free. Thus, asymptotically,

$$\varepsilon_{ij} \approx (1 - \omega_p^2/\omega^2)\delta_{ij} , \qquad \omega \to \infty , \tag{22}$$

where

$$\omega_p{}^2 = 4\pi\, Ne^2/m \tag{23}$$

is the square of the plasma frequency, N being the number of electrons per unit volume.

Indeed, according to linear response theory, we have [8]

$$\varepsilon_{ij}(\omega,\underset{\sim}{k}) = (1 - \omega_p{}^2/\omega^2)\delta_{ij} - 4\pi(e^2/\hbar\omega^2)\chi_{ij} , \tag{24}$$

where

$$\chi_{ij}(\omega,\underset{\sim}{k}) = \sum_n \left[\frac{(J_{\underset{\sim}{k}i})_{on}(J^+_{\underset{\sim}{k}j})_{no}}{\omega - \omega_{no}+i0} - \frac{(J^+_{\underset{\sim}{k}j})_{on}(J_{\underset{\sim}{k}i})_{no}}{\omega + \omega_{no}+i0} \right] \tag{25}$$

is the transverse current-current response tensor. In this expression, ω_{no} are the unperturbed transition frequencies from the ground state to the various excited states n, and

$$\underset{\sim}{J}_{\underset{\sim}{k}} = \frac{1}{2m} \sum_j \left[\underset{\sim}{p}_j \exp(-i\underset{\sim}{k}.\underset{\sim}{r}_j) + \exp(-i\underset{\sim}{k}.\underset{\sim}{r}_j)\underset{\sim}{p}_j\right] \tag{26}$$

is the current operator. In (26), the sum extends over all particles and $\underset{\sim}{p}$ is the momentum operator.

From (24) and (25), we are led to (22); also, we see that "at sufficiently high frequencies" corresponds to $\omega \gg \omega_{no}$ for all n. According to (19), (21) and (22) we must have[3]

$$\varepsilon(\omega) - 1 = -\omega_p{}^2/\omega^2 + \mathcal{O}(\omega^{-2}), \quad \omega \gg \omega_{no}, \tag{27}$$

$$\omega g(\omega) = c\Phi(\omega)/\omega = \mathcal{O}(\omega^{-2}), \qquad \omega \gg \omega_{no}, \tag{28}$$

where we have also employed (11). Finally, combining (5), (27) and (28), we get

$$N_\pm(\omega) - 1 = -\omega_p{}^2/2\omega^2 + \mathcal{O}(\omega^{-2}), \qquad \omega \gg \omega_{no} . \tag{29}$$

D - Causality and Dispersion Relations

We assume that $\omega g(\omega)$ is a square integrable function, i.e.,

$$\int_{-\infty}^{\infty} \omega^2 \; |g(\omega)|^2 d\,\omega < \infty \;, \tag{30}$$

where $g(\omega)$ is defined by (17) for $\omega < 0$. This assumption is consistent with (28); in addition, it excludes nonintegrable singularities of the integrand at finite frequencies, e.g., at $\omega = 0$.

As has already been emphasized, the constitutive relation (2) applies only to monochromatic components, so that it should be written in the form

$$\underset{\sim}{B}_\omega - \underset{\sim}{H}_\omega = 4\pi\underset{\sim}{M}_\omega = -i\omega g(\omega)\underset{\sim}{E}_\omega, \tag{31}$$

where the index ω denotes a Fourier component of circular frequency ω and $\underset{\sim}{M}$ is the magnetization. All vectors are taken at a given point $\underset{\sim}{r}$ in the medium (the dependence on $\underset{\sim}{r}$ is omitted).

We define

$$\mathcal{G}(t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \omega g(\omega) \exp(-i\omega t)d\omega , \tag{32}$$

which is real, by (17). Assuming, as usual, that $\underset{\sim}{E}(t)$ is square integrable, (31) is equivalent to

$$4\pi\underset{\sim}{M}(t) = \int_{-\infty}^{\infty} \mathcal{G}(t-t')\underset{\sim}{E}(t')dt'. \tag{33}$$

Thus, $\mathcal{G}(t)$ is a local response function, connecting a time-varying electric field with the magnetization that it induces in an optically active medium. The primitive causality condition [9] implies

$$\mathcal{G}(\tau) = 0, \quad \tau < 0 . \tag{34}$$

It follows from (30), (32) and (34), by Titchmarsh's theorem [9], that $\mathrm{Re}(\omega g)$ and $\mathrm{Im}(\omega g)$ satisfy dispersion relations.

In view of (9) and (10), these relations may be written as

$$\frac{\phi(\omega)}{\omega} = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\theta(\omega')}{\omega'(\omega'-\omega)}\, d\omega', \tag{35}$$

$$\frac{\theta(\omega)}{\omega} = -\frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\phi(\omega')}{\omega'(\omega'-\omega)}\, d\omega', \tag{36}$$

where P denotes the Cauchy principal value. Taking into account the crossing relation (18), these results become

$$\phi(\omega) = \frac{2}{\pi}\, \omega^2\, P\int_0^{\infty} \frac{\theta(\omega')}{\omega'(\omega'^2-\omega^2)}\, d\omega', \tag{37}$$

$$\theta(\omega) = -\frac{2}{\pi}\, \omega P\int_0^{\infty} \frac{\phi(\omega')}{\omega'^2-\omega^2}\, d\omega'. \tag{38}$$

Similarly, from the constitutive relation (1), we obtain

$$\underset{\sim}{D}_\omega - \underset{\sim}{E}_\omega = 4\pi \underset{\sim}{P}_\omega = [\varepsilon(\omega) - 1]\underset{\sim}{E}_\omega + i\omega g(\omega)\underset{\sim}{H}_\omega, \tag{39}$$

where $\underset{\sim}{P}$ is the polarization. By analogy with (33), we get

$$4\pi\underset{\sim}{P}(t) = \int_{-\infty}^{\infty} \mathcal{K}(t-t')\underset{\sim}{E}(t')\,dt' - \int_{-\infty}^{t} \mathcal{G}(t-t')\underset{\sim}{H}(t')\,dt', \tag{40}$$

where

$$\mathcal{K}(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} [\varepsilon(\omega)-1]\, \exp(-i\omega t)\, d\omega \tag{41}$$

and we have made use of (32) and (34). As stated at the beginning of Sect. II, we are still assuming the medium to be an insulator, so that $\varepsilon(\omega) - 1$ is bounded and may be taken as square integrable

(cf. (27)). Primitive causality now implies

$$\mathcal{K}(\tau) = 0, \qquad \tau < 0, \tag{42}$$

and it follows that $\varepsilon(\omega)-1$ satisfies the usual Kramers-Kronig relations, which are therefore not affected by the presence of optical activity.

We also learn from Titchmarsh's theorem that $\varepsilon(\omega)-1$ and $\omega g(\omega)$, besides being regular in the upper half of the ω plane, are also square integrable along any parallel to the real axis in this half-plane.

It does not necessarily follow from the regularity of ε and ωg in $\mathrm{Im}\,\omega > 0$ that the same is true for $N_\pm(\omega)$, because (5) would allow the existence of branch points at zeros of $\varepsilon(\omega)$. However, the regularity of $N_\pm(\omega)$ in the upper half-plane follows from the relativistic version of causality applied to the propagation of a wave train through a thin slab [9, 10] of thickness δ. By (13), this leads to the regularity of the functions $\exp[i(\omega\delta/c)N_+(\omega)] \pm \exp[i(\omega\delta/c)N_-(\omega)]$, which can only be true for all (sufficiently small) δ if $N_+(\omega)$ and $N_-(\omega)$ have the same property. On the other hand, the square integrability of $\varepsilon-1$ and ωg along any parallel to the real axis in $\mathrm{Im}\,\omega>0$ entails the same property for $N_\pm(\omega)-1$ (cf.(5)).

The conditions of Titchmarsh's theorem are therefore verified by the function (see (12))

$$N_{av}(\omega) - 1 = \tfrac{1}{2}\left[N_+(\omega)+N_-(\omega)\right]-1, \tag{43}$$

so that this quantity fulfils the usual Kramers-Kronig relations (note that $N_{av}(-\omega)=N_{av}(\omega)^*$ by (15)). Finally, as a consequence of the above results, together with (19) and (21), the average dielectric tensor

$$\varepsilon_{ij,av} = \frac{1}{2}\,(\varepsilon^{+}_{ij} + \varepsilon^{-}_{ij}) \qquad (44)$$

also verifies the usual dispersion relations.

Thus, besides deriving the dispersion relations (37) and (38) for the complex rotatory power, we have shown that $\varepsilon(\omega)$, $N_{av}(\omega)$ and $\varepsilon_{ij,av}(\omega)$, which reduce to the ordinary material constants when natural optical activity is absent, satisfy the usual dispersion relations for these constants.

E - Effect of DC Conductivity

So far we have assumed that the medium is an insulator. The presence of a dc conductivity $\sigma(0)\neq 0$ can be taken into account by the well-known replacement

$$\varepsilon(\omega) \to \varepsilon(\omega) + 4\pi i\sigma(0)/\omega\ , \qquad (45)$$

which introduces a pole at $\omega=0$. This pole leads to an $\omega^{-1/2}$ singularity at the origin in the refractive index, but it does not affect [1,9] the causality arguments, which refer to the quantities $(\omega/c)N_{\pm}(\omega)$. Since the complex rotatory power (9) depends only on the difference $N_{+} - N_{-}$, it follows from (45) and (5) that $\Phi(\omega)$ is unaffected by the presence of a dc conductivity. In particular, the dispersion relations (37) and (38) remain unchanged. As discussed above, the effect on the average optical constants is the same as for optically inactive media [1].

III - SUM RULES

Sum rules for optical constants may be derived [1] from "superconvergence", i.e., from the knowledge that such a constant has a faster fall-off at high frequencies than warranted just by square integrability. We now apply this technique to the complex rotatory power.

A - Sum Rules For ϕ

According to (28), the function ωg falls off faster than ω^{-2} as $\omega\to\infty$. Physically, this is related [1,2] with the short-time behavior of the response function (32), corresponding to the conditions (cf. (55) below)

$$\mathcal{G}(0) = \dot{\mathcal{G}}(0) = 0, \qquad (46)$$

implying that the overall dielectric response function is dominated, at short times, by the free-electron inertial behavior (cf.(22)).

In order to apply the superconvergence theorem^{4}, we make a minimal assumption, consistent with (28), that allows us to sharpen the estimates of asymptotic fall-off, namely^{5},

$$\omega \mathrm{Re} g(\omega) = c\phi(\omega)/\omega = \mathcal{O}(\omega^{-2}\ell n^{-\alpha}\omega), \qquad \alpha>1,\ \omega\to\infty\ . \qquad (47)$$

We stress that this is the <u>only</u> assumption that will be made about the high-frequency behavior of material constants in optical activity; all other asymptotic estimates will be derived from it. From (19), (24) and (25), we actually expect a stronger bound than (47) to hold (cf. Sect. IV), namely, that $\omega \mathrm{Re} g(\omega) = \mathcal{O}(\omega^{-3})$ as $\omega\to\infty$.

From (11), (47) and the superconvergence theorem^{5}

applied to (38), we find

$$\theta(\omega) = \frac{2}{\pi\omega} \int_0^\infty \phi(\omega')d\omega' + \mathcal{O}(\omega^{-1}\ell n^{1-\alpha}\omega), \qquad \omega\to\infty . \tag{48}$$

In order for this to be consistent with (28), $\phi(\omega)$ must obey the sum rule

$$\int_0^\infty \phi(\omega)d\omega = 0, \tag{49}$$

and this also enables us to conclude from (48) that

$$c\theta(\omega)/\omega = \omega \mathrm{Im} g(\omega) = \mathcal{O}(\omega^{-2}\ell n^{1-\alpha}\omega), \qquad \alpha>1,\ \omega\to\infty . \tag{50}$$

The weaker estimate (which follows a fortiori from (28))

$$\theta(\omega)/\omega = \mathcal{O}(\omega^{-2}),\ \omega\to\infty,$$

together with (37) and the superconvergence theorem, suffices to imply

$$\frac{\phi(\omega)}{\omega^2} = -\frac{2}{\pi\omega^2}\int_0^\infty \frac{\theta(\omega')}{\omega'}d\omega' + \mathcal{O}(\omega^{-3}), \qquad \omega\to\infty , \tag{51}$$

and therefore, by (28),

$$\int_0^\infty \frac{\theta(\omega)}{\omega}d\omega = 0 . \tag{52}$$

This result enables one to rewrite the dispersion relation (37) in a different form, by applying the technique known in dispersion theory as "undoing subtractions". We employ the identity

$$\frac{1}{\omega'^2-\omega^2} = -\frac{1}{\omega^2} + \frac{\omega'^2}{\omega^2(\omega'^2-\omega^2)} \tag{53}$$

to rewrite (37) as

$$\phi(\omega) = -\frac{2}{\pi}\int_0^\infty \frac{\theta(\omega')}{\omega'}d\omega' + \frac{2}{\pi}P\int_0^\infty \frac{\omega'\theta(\omega')}{\omega'^2-\omega^2}d\omega',$$

where the integrals are separately convergent on account of (50). In view of (52), we get

$$\phi(\omega) = \frac{2}{\pi}P\int_0^\infty \frac{\omega'\theta(\omega')}{\omega'^2-\omega^2}d\omega' . \tag{54}$$

Taking into account (18), we see that (38) and (54) form a pair of dispersion relations connecting ϕ and θ, rather than ϕ/ω and θ/ω, as was the case for (35) and (36). Since $\Phi(\omega)$ is square integrable according to (47) and (50), we conclude that it is a causal transform [9], even though it has no immediate interpretation as a linear response function.

By combining (11), (17) and (32), we find the following expression for the response function $\mathcal{G}(t)$:

$$(\pi/c)\,\mathcal{G}(t) = \int_0^\infty \cos(\omega t)\theta(\omega)/\omega\, d\omega - \int_0^\infty \sin(\omega t)\phi(\omega)/\omega\, d\omega . \tag{55}$$

When differentiation under the integral sign is allowed, we see immediately from (55) that the sum rules (52) and (49) are respectively equivalent to the two conditions in (46).

B - Sum Rules For Φ^2

Let us now assume, besides (30), that $\omega^2 g^2$ is also square integrable, which is again consistent with (28). It then follows from (32) and from the convolution theorem that $-\omega^2 g^2$ is the Fourier transform of the function

$$\mathcal{F}(t) = \mathcal{G} * \mathcal{G} = H(t) \int_0^t \mathcal{G}(t-\tau)\mathcal{G}(\tau)d\tau, \tag{56}$$

where $*$ denotes the convolution product, $H(t)$ is the Heaviside step function, and we have employed (34). Therefore, by Titchmarsh's theorem, $\mathrm{Re}(\omega^2 g^2)$ and $\mathrm{Im}(\omega^2 g^2)$ are connected by dispersion relations. Taking into account (11) and (18), these relations take the form

$$\phi^2(\omega) - \theta^2(\omega) = \frac{4}{\pi}\omega^2 \, P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'(\omega'^2-\omega^2)} d\omega', \tag{57}$$

$$\frac{\phi(\omega)\theta(\omega)}{\omega} = -\frac{\omega^2}{\pi} \, P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'^2(\omega'^2-\omega^2)} d\omega'. \tag{58}$$

From (47) and (50), we have

$$\phi(\omega)\theta(\omega) = \mathcal{O}(\omega^{-2} \ell n^{-\beta}\omega), \qquad \beta = 2\alpha - 1 > 1, \tag{59}$$

$$\phi^2(\omega) - \theta^2(\omega) = \mathcal{O}(\omega^{-2} \ell n^{-\gamma}\omega), \qquad \gamma = 2(\alpha-1) > 0. \tag{60}$$

Therefore, we can employ (53) to rewrite (57) and (58) as

$$\phi^2(\omega) - \theta^2(\omega) = -\frac{4}{\pi}\int_0^\infty \phi(\omega')\theta(\omega')\frac{d\omega'}{\omega'} + \frac{4}{\pi} P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'^2-\omega^2}\omega' d\omega', \tag{61}$$

$$\frac{\phi(\omega)\theta(\omega)}{\omega} = \frac{1}{\pi}\int_0^\infty [\phi^2(\omega')-\theta^2(\omega')]\frac{d\omega'}{\omega'^2} - \frac{1}{\pi} P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'^2-\omega^2} d\omega'. \tag{62}$$

The estimates (59) and (60) allow us to apply the superconvergence theorem to the last integrals appearing in (61) and (62), leading to

$$P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'^2-\omega^2}\omega' d\omega' = -\frac{1}{\omega^2}\int_0^\infty \phi(\omega')\theta(\omega')\omega' d\omega' + \mathcal{O}(\omega^{-2}\ell n^{1-\beta}\omega), \qquad \beta > 1, \qquad \omega\to\infty, \tag{63}$$

$$P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'^2-\omega^2} d\omega' = -\frac{1}{\omega^2}\int_0^\infty [\phi^2(\omega')-\theta^2(\omega')]d\omega' + \mathcal{O}(\omega^{-3}), \qquad \omega\to\infty. \tag{64}$$

Inserting these estimates in (61) and (62) and comparing the results with (59) and (60), we obtain the sum rules

$$\int_0^\infty \phi(\omega)\,\theta(\omega)\frac{d\omega}{\omega} = \int_0^\infty \phi(\omega)\,\theta(\omega)\omega\, d\omega = 0, \tag{65}$$

$$\int_0^\infty \frac{\phi^2(\omega)}{\omega^2} d\omega = \int_0^\infty \frac{\theta^2(\omega)}{\omega^2} d\omega, \tag{66}$$

$$\int_0^\infty \phi^2(\omega)d\omega = \int_0^\infty \theta^2(\omega)d\omega. \tag{67}$$

By the same token, (61) and (62) become

$$\phi^2(\omega) - \theta^2(\omega) = \frac{4}{\pi} P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'^2-\omega^2}\omega' d\omega', \tag{68}$$

$$\frac{\phi(\omega)\theta(\omega)}{\omega} = -\frac{1}{\pi} P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'^2-\omega^2} d\omega', \tag{69}$$

which are equivalent to dispersion relations connecting $\mathrm{Re}(\Phi^2)$ and

$\mathrm{Im}(\phi^2)$.

As we have seen, both $\Phi(\omega)$ and $\Phi(\omega)/\omega$ are causal transforms, so that their real and imaginary parts are connected by Hilbert transform [9] relations. The sum rules (66) and (67) also follow from the norm-preserving character of the Hilbert transform [11].

C - Other Sum Rules

We obtain additional sum rules by considering the behavior of $\omega g(\omega)$ as $\omega \to 0$. For an insulating medium, we have (cf. (6))

$$n_+(0) = n_-(0) = n(0),$$

$$\kappa_+(0) = \kappa_-(0) = 0 \quad \text{(insulator)}, \tag{70}$$

so that (cf.(10))

$$\lim_{\omega\to 0} [\omega g(\omega)] = \frac{1}{2} \lim_{\omega\to 0} [N_+(\omega) - N_-(\omega)] = 0. \tag{71}$$

We expect this result still to remain true for an isotropic conductor, in spite of the $\omega^{-1/2}$ singularity in $N_\pm(\omega)$ as $\omega \to 0$ (Sect. IIE). Indeed, such a medium, in the static limit, cannot distinguish between right and left circular polarization, so that the difference between the associated complex refractive indices should vanish.

Substituting (71) in (38), we obtain the sum rule

$$\int_0^\infty \frac{\phi(\omega)}{\omega^2}\, d\omega = 0 . \tag{72}$$

Similarly, substituting it in (57), we get

$$\int_0^\infty \frac{\phi(\omega)\,\theta(\omega)}{\omega^3}\, d\omega = 0 . \tag{73}$$

Substitution in other dispersion relations leads to already derived sum rules.

Under the above conditions, we can rewrite (38) as

$$\theta(\omega) = -\frac{2}{\pi}\, \omega \int_0^\infty \frac{\phi(\omega')}{\omega'^2} d\omega' - \frac{2}{\pi}\, \omega^3\, P\!\int_0^\infty \frac{\phi(\omega')}{\omega'^2(\omega'^2-\omega^2)}\, d\omega'$$

and (72) implies

$$\theta(\omega) = -\frac{2}{\pi}\, \omega^3\, P\!\int_0^\infty \frac{\phi(\omega')}{\omega'^2(\omega'^2-\omega^2)}\, d\omega' . \tag{74}$$

Together with (37), this forms a pair of dispersion relations connecting the real and imaginary parts of $\Phi(\omega)/\omega^2$ or, equivalently, of $g(\omega)$.

Sum rules for higher powers of Φ can be derived by iterating the procedure of Sect. IIIB, and a variety of other types of sum rules can also be considered [2,12].

Finally, as was shown in Sect. IID, the average optical constants such as N_{av} and $\varepsilon_{ij,av}$ verify the same dispersion relations that hold in the absence of optical activity - and their asymptotic high-frequency behavior obeys the same bounds. Thus, one can immediately write down sum rules for these quantities as direct extensions of those derived [1,2] for optically inactive media. Examples of such sum rules are

$$\int_0^\infty [n_{av}(\omega) - 1]\, d\omega = 0, \tag{75}$$

$$\int_0^\infty \omega\, \kappa_{av}(\omega)\, d\omega = \pi\omega_p^2/4, \tag{76}$$

which may be regarded as extensions of the "inertial" sum rule and of the f-sum rule, respectively, to media with natural optical activity.

IV - DISCUSSION

A - Summary of Dispersion Relations and Sum Rules

For convenience, we collect here all the dispersion relations and sum rules for natural optical activity derived in Sects. II and III. They apply to linear nonmagnetic isotropic media, including conductors.

(i) Dispersion relations for $\Phi(\omega)/\omega$:

$$\phi(\omega) = \frac{2}{\pi}\omega^2 P\int_0^\infty \frac{\theta(\omega')}{\omega'(\omega'^2-\omega^2)}\,d\omega', \tag{77}$$

$$\theta(\omega) = -\frac{2}{\pi}\omega P\int_0^\infty \frac{\phi(\omega')}{\omega'^2-\omega^2}\,d\omega'. \tag{78}$$

(ii) Dispersion relations for $\Phi(\omega)$:

$$\phi(\omega) = \frac{2}{\pi} P\int_0^\infty \frac{\omega'\theta(\omega')}{\omega'^2-\omega^2}\,d\omega', \tag{79}$$

the companion relation being equivalent to (78).

(iii) Dispersion relations for $\Phi(\omega)/\omega^2$:

$$\theta(\omega) = -\frac{2}{\pi}\omega^3 P\int_0^\infty \frac{\phi(\omega')}{\omega'^2(\omega'^2-\omega^2)}\,d\omega' \qquad \text{if } \Phi(\omega)/\omega \underset{\omega\to 0}{\to} 0\,, \tag{80}$$

which is the same as condition (71). The companion relation is equivalent to (77).

(iv) Dispersion relations for $\Phi^2(\omega)/\omega^2$:

$$\phi^2(\omega) - \theta^2(\omega) = \frac{4}{\pi}\omega^2 P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'(\omega'^2-\omega^2)}\,d\omega', \tag{81}$$

$$\frac{\phi(\omega)\theta(\omega)}{\omega} = -\frac{\omega^2}{\pi} P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'(\omega'^2-\omega^2)}\,d\omega'. \tag{82}$$

(v) Dispersion relations for $\Phi^2(\omega)$:

$$\phi^2(\omega)-\theta^2(\omega) = \frac{4}{\pi} P\int_0^\infty \frac{\phi(\omega')\theta(\omega')}{\omega'^2-\omega^2}\,\omega' d\omega', \tag{83}$$

$$\frac{\phi(\omega)\theta(\omega)}{\omega} = -\frac{1}{\pi} P\int_0^\infty \frac{[\phi^2(\omega')-\theta^2(\omega')]}{\omega'^2-\omega^2}\,d\omega'. \tag{84}$$

(vi) Sum rules for $\phi(\omega)$:

$$\int_0^\infty \phi(\omega)\,d\omega = 0, \tag{85}$$

$$\int_0^\infty \frac{\phi(\omega)}{\omega^2}\,d\omega = 0 \qquad \text{if } \Phi(\omega)/\omega \underset{\omega\to 0}{\to} 0. \tag{86}$$

(vii) Sum rules for $\theta(\omega)$:

$$\int_0^\infty \frac{\theta(\omega)}{\omega}\,d\omega = 0. \tag{87}$$

(viii) Sum rules for $\phi(\omega)\theta(\omega)$:

$$\int_0^\infty \omega\phi(\omega)\theta(\omega)\,d\omega = 0, \tag{88}$$

$$\int_0^\infty \frac{\phi(\omega)\theta(\omega)}{\omega}\,d\omega = 0, \tag{89}$$

$$\int_0^\infty \frac{\phi(\omega)\theta(\omega)}{\omega^3}\,d\omega = 0 \qquad \text{if } \Phi(\omega)/\omega \underset{\omega\to 0}{\to} 0\,. \tag{90}$$

(ix) Norm sum rules:

$$\int_0^\infty \phi^2(\omega)d\omega = \int_0^\infty \theta^2(\omega)d\omega, \tag{91}$$

$$\int_0^\infty \frac{\phi^2(\omega)}{\omega^2}\, d\omega = \int_0^\infty \frac{\theta^2(\omega)}{\omega^2}\, d\omega . \tag{92}$$

B - The Rosenfeld-Condon Dispersion Formula

In the microscopic theory of optical activity, the basic constitutive relation (2) follows from the expression for the induced magnetic moment $\underset{\sim}{\mu}$ associated with each individual molecule [4],

$$\underset{\sim}{\mu} = (\beta/c)\ \partial\underset{\sim}{E}'/\partial t, \tag{93}$$

where $\underset{\sim}{E}'$ is the effective local field acting on the molecule. For dense media, it is usually assumed that $\underset{\sim}{E}'$ differs from $\underset{\sim}{E}$ by the Lorentz correction

$$\underset{\sim}{E}' = \underset{\sim}{E} + (4\pi/3)\ \underset{\sim}{P}. \tag{94}$$

This leads to the following expression [4] for the material constant g:

$$\begin{aligned} g(\omega) &= 4\pi\ \mathcal{N}[\varepsilon(\omega) + 2]\,\beta(\omega)/3c \\ &= 4\pi\,\mathcal{N}[N_{av}^2(\omega) + 2]\,\beta(\omega)/3c, \end{aligned} \tag{95}$$

where $\mathcal{N}$ is the number of molecules per unit volume and N_{av} is given by (12).

To obtain a dispersion formula for $\Phi(\omega)$, it suffices therefore to derive such a formula for the molecular parameter $\beta(\omega)$. In the quantum theory, this was first done by Rosenfeld [13], who found the expression

$$\beta(\omega) = \frac{2c}{3\hbar} \sum_n \frac{R_{no}}{\omega_{no}^2 - \omega^2}, \tag{96}$$

assuming that the molecules are initially in the ground state, from which they make transitions to the excited states n, with transition energy $\hbar\omega_{no} = E_n - E_o$. The associated rotational strength R_{no} is given by

$$R_{no} = \mathrm{Im}(\langle 0|\underset{\sim}{d}|n\rangle\ .\langle n|\underset{\sim}{m}|0\rangle) = -R_{on}, \tag{97}$$

where $\underset{\sim}{d}$ and $\underset{\sim}{m}$ are respectively the electric dipole and magnetic dipole moment operators.

The Rosenfeld dispersion formula (96) is at best an approximation valid in regions of transparency, since it gives no circular dichroism[6] and it cannot be employed when $\omega \to \omega_{no}$. At the time Condon wrote his review article [4], a generalization to include circular dichroism had not been worked out. Condon found it "probable", by analogy with the Kramers-Heisenberg dispersion formula, that (96) would have to be replaced by

$$\beta(\omega) = \frac{2c}{3\hbar} \sum_n \frac{R_{no}}{\omega_{no}^2 - \omega^2 - i\omega\gamma_{no}}, \tag{98}$$

where γ_{no} is the linewidth associated with the $n \to 0$ transition. Substituting (98) in (95) and (11), one obtains the Rosenfeld-Condon dispersion formula, which we write down, for simplicity, without the local field correction (94) (note that this does not affect the high-frequency behavior, because $[N^2_{av}(\omega)+2]/3\to 1$ as $\omega\to\infty$):

$$\Phi(\omega) = \frac{8\pi N}{3\hbar c} \sum_n \frac{\omega^2 R_{no}}{\omega^2_{no} - \omega^2 - i\omega\gamma_{no}} . \tag{99}$$

Separating real and imaginary parts, we find

$$\phi(\omega) = \frac{8\pi N}{3\hbar c} \omega^2 \sum_n \frac{(\omega^2_{no}-\omega^2) R_{no}}{(\omega^2_{no}-\omega^2)^2 + \omega^2 \gamma^2_{no}} , \tag{100}$$

$$\theta(\omega) = \frac{8\pi N}{3\hbar c} \omega^3 \sum_n \frac{\gamma_{no} R_{no}}{(\omega^2_{no}-\omega^2)^2 + \omega^2\gamma^2_{no}} . \tag{101}$$

The expression (99) is regular for $\text{Im}\,\omega>0$; it has poles in the lower half-plane close to $\pm\omega_{no} - i\gamma_{no}/2$, since $\gamma_{no} \ll \omega_{no}$. Furthermore, $\Phi(\omega)/\omega = \mathcal{O}(\omega)$ as $\omega\to 0$, so that (71) is satisfied. On the other hand, (100) yields

$$\frac{\phi(\omega)}{\omega} = -\frac{8\pi N}{3\hbar c\omega} \sum_n R_{no} + \mathcal{O}(\omega^{-3}), \quad \omega \gg \text{Max}\ \omega_{no},$$

which is consistent with (28) if

$$\sum_n R_{no} = 0. \tag{102}$$

This is the Kuhn sum rule [4], which is indeed verified by (97):

$$\sum_n R_{no} = \text{Im}(\langle 0|\underset{\sim}{d}\cdot\underset{\sim}{m}|0\rangle) = 0.$$

On the other hand, according to (101),

$$\frac{\theta(\omega)}{\omega} = \frac{8\pi N}{3\hbar c} \frac{1}{\omega^2} \sum_n \gamma_{no} R_{no} + \mathcal{O}(\omega^{-4}), \quad \omega \gg \text{Max}\ \omega_{no} . \tag{103}$$

In general, it is to be expected that

$$\sum_n \gamma_{no} R_{no} \neq 0, \tag{104}$$

so that (103) is not consistent with (28).

We conclude that the Rosenfeld-Condon dispersion formula violates the expected free-electron behavior at high frequencies.

C - Dispersion Formulas Based on Quantum Electrodynamics

Recent theories of optical activity are based on the application of quantum electrodynamics to evaluate the polarization of photons scattered by molecules. A calculation by Stephen [14], neglecting damping, yields for the rotation of the plane of polarization [15]

$$\phi_{33}(\omega) = -\frac{2\pi N e^2}{m^2\hbar c\omega} \text{Im} \sum_n \left[\frac{(p_y e^{-i\omega z/c})_{on} (p_x e^{i\omega z/c})_{no}}{\omega_{no} + \omega} + \frac{(p_x e^{i\omega z/c})_{on} (p_y e^{-i\omega z/c})_{no}}{\omega_{no} - \omega} \right] , \tag{105}$$

where ϕ_{33} is the rotation per unit length for light incident along the z direction on a system of N molecules per unit volume (local field corrections are neglected), z is an intramolecular coordinate and $\underset{\sim}{p}$ is the momentum operator. This expression should be compared with (24)-(26), taking (19) into account.

At optical frequencies, one has $|\omega z/c| \ll 1$ in the matrix elements of (105), so that one can apply the multipole expansion, stopping at the magnetic dipole term:

$$\exp(\pm i\omega z/c) \simeq 1 \pm i\omega z/c. \tag{106}$$

For freely rotating molecules, the rotation averaged over all orientations becomes

$$\phi(\omega) = \frac{1}{3}(\phi_{11} + \phi_{22} + \phi_{33}), \tag{107}$$

and one finds [15] that (105) yields, in this approximation, the Rosenfeld dispersion formula.

The effect of including damping has been discussed by Hameka [16] within the framework of Heitler's theory of damping [17], which represents an improved version of the Weisskopf-Wigner approximation. The result, when ω is close to a resonance frequency ω_{no}, is that the corresponding term in (105) should be modified as follows:

$$\frac{(p_x e^{i\omega z/c})_{on}(p_y e^{-i\omega z/c})_{no}}{\omega_{no} - \omega} \longrightarrow \frac{(p_x e^{i\omega z/c})_{on}(p_y e^{-i\omega z/c})_{no}}{\omega_{no} - \omega - i\gamma_{no}/2} \tag{108}$$

where γ_{no} is the associated linewidth.

A corresponding modification must be made in the antiresonant terms, namely,

$$\frac{(p_y e^{-i\omega z/c})_{on}(p_x e^{i\omega z/c})_{no}}{\omega_{no} + \omega} \longrightarrow \frac{(p_y e^{-i\omega z/c})_{on}(p_x e^{i\omega z/c})_{no}}{\omega_{no} + \omega + i\gamma_{no}/2}\,. \tag{109}$$

While antiresonant damping is negligible in the optical range, it has to be included for consistency with several requirements [18, 19], such as crossing symmetry and analyticity. Indeed, it is readily verified that the joint substitutions (108) and (109) in (105) are consistent with the symmetry relation (18); physically, the antiresonant terms arise from the "crossed diagrams" in which the time ordering between emission of the final photon and absorption of the initial one is interchanged [20]. Analytically, (109) has a pole at $\omega = -\omega_{no} - i\gamma_{no}/2$, symmetrical to the resonance pole in (108) with respect to the imaginary axis, in agreement with the physical interpretation [9] of such symmetrical poles in terms of time reversal and the consequent interchange of emission and absorption.

It might be thought, at first, that the violation of asymptotic free-electron behavior found in Sect. IVB for the Rosenfeld-Condon formula would be removed by the effects of retardation with the molecule, expressed by the exponential factors $\exp(\pm i\omega z/c)$ in the matrix elements of (108) and (109). By the Riemann-Lebesgue theorem, these matrix elements tend to zero as $\omega \to \infty$, and this introduces a rapidly decreasing convergence factor [21] that would indeed remove the discrepancy. However, this cannot be the correct explanation, because the effect is felt only at wavelengths much shorter than an atomic transition radius [21] of the order of the Bohr radius, and the entire macroscopic theory becomes meaningless at such high frequencies [22]. The much weaker condition $\omega \gg \omega_{no}$ should suffice for free-electron behavior of the corresponding resonance term.

Therefore, we may still employ the expansion (106). Substituting (108) and (109) in (105) and (107), we then find the following expression for the complex rotatory power:

$$\phi(\omega) = \frac{8\pi N}{3\hbar c} \sum_n \frac{\omega_{no}^2 R_{no}}{\omega_{no}^2 - (\omega + i\gamma_{no}/2)^2}. \tag{110}$$

Taking into account the Kuhn sum rule (102), this is equivalent to

$$\Phi(\omega) = \frac{8\pi N}{3\hbar c} \sum_n \frac{(\omega + i\gamma_{no}/2)^2 R_{no}}{\omega_{no}'^2 - \omega^2 - i\omega\gamma_{no}}, \tag{111}$$

where

$$\omega_{no}'^2 = \omega_{no}^2 + \gamma_{no}^2/4. \tag{112}$$

Note that, for $\gamma_{no} = 0$, this result reduces to the Rosenfeld dispersion formula.

Separating real and imaginary parts, we find

$$\phi(\omega) = \frac{8\pi N}{3\hbar c} \sum_n \frac{\left[\omega^2(\omega_{no}^2 - \omega^2 - \gamma_{no}^2/2) - \omega_{no}'^2 \gamma_{no}^2/4\right] R_{no}}{(\omega_{no}'^2 - \omega^2)^2 + \omega^2\gamma_{no}^2}, \tag{113}$$

$$\theta(\omega) = \frac{8\pi N}{3\hbar c}\, \omega \sum_n \frac{\gamma_{no}\, \omega_{no}^2\, R_{no}}{(\omega_{no}'^2 - \omega^2)^2 + \omega^2\gamma_{no}^2}. \tag{114}$$

For $\omega \gg \text{Max}\ \omega_{no}$, (113) yields, taking into account (102),

$$\frac{\phi(\omega)}{\omega} = -\frac{8\pi N}{3\hbar c} \frac{1}{\omega^3} \sum_n \omega_{no}^2\, R_{no} + \mathcal{O}(\omega^{-5}), \tag{115}$$

the same behavior predicted by the Rosenfeld formula, whereas (114) yields

$$\frac{\theta(\omega)}{\omega} = \frac{8\pi N}{3\hbar c} \frac{1}{\omega^4} \sum_n \omega_{no}^2 \gamma_{no} R_{no} + \mathcal{O}(\omega^{-6}), \tag{116}$$

which differs from (103) by a factor $(\omega_{no}/\omega)^2$ for each resonance term. This factor (cf. (114) and (101)), while making very little difference within the resonance region where $\theta(\omega)$ is appreciable, removes the inconsistency with free-electron asymptotic behavior found for the Rosenfeld-Condon formula.

On the other hand, if we accept the validity of (111) also at the low-frequency end of the spectrum, we see that (114) yields $\theta(\omega) = \mathcal{O}(\omega)$ as $\omega \to 0$, whereas (113) leads to

$$\phi(0) = -\frac{2\pi N}{3\hbar c} \sum_n \frac{\gamma_{no}^2 R_{no}}{\omega_{no}'^2}, \tag{117}$$

which, though small, is generally nonvanishing, contrary to our expectation. This would introduce a first-order pole at the origin in $\Phi(\omega)/\omega$, which would have to be subtracted out in order to derive dispersion relations for this quantity (similar to the dc conductivity for $\varepsilon(\omega)$), and (71) would also be violated.

There are several reasons, however, for doubting the validity of (111) as $\omega \to 0$. Already in the scattering by a single molecule, the Weisskopf-Wigner approximation, even in the improved version [17] employed in (108), is not expected to remain valid in the infrared limit [21].

Furthermore, at long wavelengths, screening and multiple scattering effects neglected in (111) have to be considered.

We conclude that a quantum dispersion formula for the complex rotatory power that conforms to expectations at both ends of the spectrum is not yet available. While (111), in contrast with the Rosenfeld-Condon formula, is consistent with the expected high-frequency behavior, it probably requires modification at low frequencies.

D - Relation to Prior Work and Conclusion

The idea of deriving dispersion relations for natural optical activity from primitive causality applied to the constitutive relations (1) and (2) goes back to Moscowitz [23], although a detailed discussion and derivation was not given at that time. The "cause" was chosen proportional to $\partial \underset{\sim}{E}/\partial t$, leading to the dispersion relations (77) and (80) for $\Phi(\omega)/\omega^2$. Here we have chosen $\underset{\sim}{E}(t)$ itself, which must be square integrable on physical grounds; this also has the advantage that assumption (71) is not required. The same comments apply to a similar discussion by Healy [24].

A different approach begins with the derivation of dispersion relations for $N_+(\omega)$ and $N_-(\omega)$ separately, leading to (77) and (78) through (10) and (11). Emeis et al [25] simply assumed the validity of dispersion relations for N_+ and N_-. Smith [6] proposed deriving these relations from those for the dielectric tensor, invoking thermodynamic arguments to eliminate the possibility of branch points in $\mathrm{Im}\,\omega>0$, as is usually done in the Russian literature [22]. However, this procedure cannot be applied here, because the frequency-dependent dielectric tensor itself depends on $N_\pm(\omega)$ (cf. (21)). Healy [10] applied relativistic causality to derive the analyticity of $N_\pm(\omega)$ in $\mathrm{Im}\,\omega>0$. This is not sufficient for proving dispersion relations; however, as we have shown in Sect. IID, the proof can be completed, so that the real and imaginary parts of $N_\pm(\omega)-1$ verify dispersion relations similar to (35) and (36). In view of the crossing relation (15), each of these relations involves both helicities, so that it is better to express them in terms of the physical quantities (10) and (12). Smith [3,6] also wrote down dispersion relations for $\omega[N_\pm(\omega)-1]$, corresponding to (79).

Finally, still another approach to the derivation of dispersion relations was taken by Healy and Power [5], who employed the formula

$$N_\pm(\omega) - 1 = 2\pi N \quad c^2 f_\pm(\omega)/\omega^2, \tag{118}$$

where $f_\pm(\omega)$ are forward scattering amplitudes from a single molecule, together with dispersion relations for such amplitudes. However, (118) is only an approximate result for a dilute medium, and the real part of this relationship is expected to break down at low frequencies [9], so that it cannot provide a suitable basis for deriving dispersion relations for optical constants.

The sum rule (87) was obtained by Emeis et al [25] from the assumption that the high-frequency behavior of $\Phi(\omega)$ justifies the validity of both (77) and (79), by subtracting one of these relations from the other one.

All other sum rules (85) to (92) were given by Smith [3], except for (88) and (91). These two sum rules, as well as the dispersion relations (83) and (84) for Φ^2, do not seem to have been previously reported.

The sum rules (vi) and (vii) express the vanishing of the average over the whole frequency spectrum both of the rotatory power and of the ellipticity, weighted with various powers of the frequency. These are examples of "inertial sum rules" [1,2] stating that, on the average over the whole spectrum, material media behave like the vacuum with respect to some optical properties [26]. Note that the ellipticity is a measure of circular dichroism, i.e., ultimately, of the difference between net transition rates for right and left circularly polarized light [3].

The sum rules (viii) imply the existence of correlations between the signs of ϕ and θ, such that their product, weighted with various powers of the frequency, has zero average over the whole spectrum. According to Natanson's rule [27], ϕ/θ changes sign as each optically active absorption band is crossed.

Finally, the sum rules (ix) relate the magnitudes of ϕ and θ, showing that they have the same "norm", with or without the weight function ω^{-2}.

These sum rules should provide useful consistency checks both for experimental data and for theories of natural optical activity. On the experimental side, it is useful to have sum rules with various weighting factors corresponding to positive and negative powers of the frequency, in order to emphasize or deemphasize low or high frequency contributions. The corresponding relationships for the refractive index and the dielectric constant have been experimentally verified for a variety of substances over a broad frequency range [2,28-29].

On the theoretical side, the sum rules express relatively strong constraints both on low and on high frequency behavior. The Rosenfeld-Condon dispersion formula does not satisfy these constraints at high frequencies. The dispersion formula (111), based on quantum electrodynamics, does not suffer from this defect, but it seems to require modification at low frequencies. The derivation of a satisfactory dispersion formula for the complex rotatory power over the whole spectrum remains an open problem.

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FOOTNOTES

[1] The quantum theory of dispersion actually leads to additional terms of the forms $f\underset{\sim}{H}$ and $f\underset{\sim}{E}$ on the right-hand sides of (1) and (2), respectively. However, as shown by Condon ([4], footnote 24), these extra terms do not contribute to optical activity.

[2] The result (8) is valid for a sufficiently small length of the medium; in practice, one usually has $\theta\ell \ll 1$.

[3] The notation $\phi = o(\psi)$ as $x\to\infty$ means that $\phi/\psi \to 0$ as $x\to\infty$.

[4] See reference 1, Appendix. In order to apply the theorem to a dispersion integral such as (38), it suffices to make the change of variable $\omega'^2=x$.

[5] The notation $\phi=O(\psi)$ as $x\to\infty$ means that $|\phi/\psi|$ remains bounded as $x\to\infty$.

[6] One can define an associated ellipticity given by a series of delta functions at the resonance frequencies ω_{no} [3] or, equivalently, consider this as limiting case when the absorption lines become infinitely narrow. Either description, however, corresponds to an unphysical model.