PHYSICAL REVIEW B VOLUME 13, NUMBER 12 15 JUNE 1976

Superconvergence and sum rules for the optical constants: Natural and magneto-optical activity*

D. Y. Smith
Argonne National Laboratory, Argonne, Illinois 60439

(Received 22 December 1975)

Superconvergence techniques are systematically applied to dispersion relations for the index of refraction in optically active systems to find sum rules applicable to the optical constants for circularly polarized electromagnetic waves. New results include the theorems that (i) the zeroth moment of the circular dichroism and (ii) the first moment of the circular birefringence are zero. The latter theorem yields the simple rule that the rotation of the plane of polarization of linear light caused by an optically active medium averages to zero when integrated over all energies. Generalizations of the *f* and inertial sum rules to circularly polarized modes are given, as well as a new rule relating the second moment of the circular dichroism to the cyclotron frequency in magneto-optics or to the rotatory strengths in natural optical activity.

I. INTRODUCTION

Recently, new sum rules for the optical constants of isotropic media have been reported.[1,2] These rules explicitly involve the dispersive part of the optical constants as opposed to the well-known *f* sum rule applicable to absorption. For instance, the real part of the refractive index $n(\omega)$ of an isotropic medium has been found to obey[1]

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

a rule resulting[2] primarily from the requirement that the dielectric response obey both causality and the law of inertia.

The proof of these new rules is based on the validity of dispersion relations of the Kramers-Kronig form for the optical constants that hold for the linearly polarized normal electromagnetic modes appropriate to isotropic systems. However, in optically active media, electromagnetic modes are generally elliptically polarized and the dispersion relations and sum rules for the optical constants are more complex.[3] Indeed, in certain cases of spatial dispersion simple dispersion relations and sum rules do not appear to hold at all.[4]

In the present paper this situation is considered for the simple but important case of circularly polarized normal modes encountered in optically active systems. Here the left and right circularly polarized modes do not satisfy the Kramers-Kronig relations individually.[5-11] Rather, the dispersion relations and sum rules couple left- and right-hand modes. For example, the indices of refraction obey the sum rules

$$\int_0^\infty \left(\frac{n_r(\omega) + n_l(\omega)}{2} - 1\right) d\omega = 0 \tag{2}$$

and

$$\int_0^\infty \omega\,[n_r(\omega) - n_l(\omega)]\, d\omega = 0\,. \tag{3}$$

The first of these relations has the form of Eq. (1), but with the average index $\frac{1}{2}[n_r(\omega) + n_l(\omega)]$ in the role of the isotropic index $n(\omega)$. The second rule, Eq. (3), is new and involves the first moment of the circular birefringence $n_r(\omega) - n_l(\omega)$.

The existence of dispersion relations and, hence, sum rules involving the difference in optical constants for right- and left-hand modes is of practical importance since many experiments measure these differences directly. Thus, The Faraday rotation $\phi_F(\omega)$ is proportional to the difference in refractive indices for right- and left-hand light and Eq. (3) yields

$$\int_0^\infty \phi_F(\omega)\, d\omega = 0\,, \tag{4}$$

a useful consistency check on both experiment and theory.

In Sec. II dispersion relations for circularly polarized modes are reviewed and in Sec. III the most straightforward of the sum rules are systematically derived by superconvergence techniques. In Sec. IV these are discussed and applied to various experimental situations.

II. DISPERSION RELATIONS

Both the inverse dielectric tensor $\epsilon_{ij}(\omega)^{-1}$ and, in all known systems, the dielectric tensor itself $\epsilon_{ij}(\omega)$ obey the Kramers-Kronig relations.[12] Similar relations hold for the magnetic permeability. This is a direct consequence of the causal response of matter. On the other hand, most optical applications require dispersion relations for the complex refractive index $N(\omega)$. $N(\omega)$, however, is generally a complicated function of the various $\epsilon_{ij}(\omega)$'s and causality arguments are not directly applicable. Consequently the Kramers-Kronig relations only hold for $N(\omega)$ in special cases such as linear modes in an isotropic medium.[13-15]

In the case of circularly polarized modes encountered in magneto-optics and natural optical activity, the real and imaginary parts of the index of refraction do not separately obey dispersion relations of the Kramers-Kronig form.[5-11] The basic reason is that the analytic functions describing the propagation of circular and elliptic modes involve one handedness for positive frequencies but the opposite handedness for negative frequencies.[11] The crossing relations for the optical constants are consequently asymmetric leading in turn to asymmetric dispersion relations.

For the present purposes it is convenient to write these dispersion relations in terms of the sum and difference of the optical constants. Denoting the complex index of refraction by

$$N_\pm(\omega) = n_\pm(\omega) + i\kappa_\pm(\omega)\,,$$

where $n_\pm(\omega)$ and $\kappa_\pm(\omega)$ are the real and imaginary parts, respectively, and where the "+" and "−" signs denote left- and right-hand polarization, the dispersion relations for an insulating medium are[11]

$$\frac{n_+(\omega)+n_-(\omega)}{2} - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega'}{\omega'^2-\omega^2}\left(\frac{\kappa_+(\omega')+\kappa_-(\omega')}{2}\right) d\omega'\,, \tag{5}$$

$$\frac{\kappa_+(\omega)+\kappa_-(\omega)}{2} = -\frac{2}{\pi}\,\omega P \int_0^\infty \frac{1}{\omega'^2-\omega^2}\left(\frac{n_+(\omega')+n_-(\omega')}{2} - 1\right) d\omega'\,, \tag{6}$$

$$n_+(\omega) - n_-(\omega) = \frac{2}{\pi}\,\omega P \int_0^\infty \frac{1}{\omega'^2-\omega^2}\,[\kappa_+(\omega') - \kappa_-(\omega')]\, d\omega'\,, \tag{7}$$

and

$$\kappa_+(\omega) - \kappa_-(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\omega'}{\omega'^2-\omega^2}\,[n_+(\omega') - n_-(\omega')]\, d\omega'\,. \tag{8}$$

The first two of the circular-mode dispersion relations have the same form as the Kramers-Kronig relations but with the optical constants replaced by the average index $\frac{1}{2}(n_+ + n_-)$, and the average extinction coefficient $\frac{1}{2}(\kappa_+ + \kappa_-)$. These reduce to the Kramers-Kronig result in the limit of no circular dichroism. The second two relations are significantly different in that ω and ω' change roles in the numerator of the integrand compared with the Kramers-Kronig relations.

In the case of conductors $N_\pm(\omega)$ has a $\omega^{-1/2}$ behavior near $\omega = 0$ corresponding to the pole at $\omega = 0$ in the conductivity term in the dielectric tensor. It is then necessary to write dispersion relations for the function $\omega[N_\pm(\omega) - 1]$ which is square integrable.[11] This yields four relations similar to Eqs. (5)–(8) but with additional factors of ω and ω'. The equations for $\frac{1}{2}[n_+(\omega) + n_-(\omega)] - 1$ and $\kappa_+(\omega) - \kappa_-(\omega)$ are simply Eqs. (5) and (8) multiplied on both sides by ω and so are identical to the insulating results when $\omega \neq 0$. The relations for $\kappa_+(\omega) + \kappa_-(\omega)$ and $n_+(\omega) - n_-(\omega)$ are new[11]:

$$\frac{\omega[\kappa_+(\omega)+\kappa_-(\omega)]}{2} = -\frac{2}{\pi} P \int_0^\infty \frac{\omega'^2}{\omega'^2-\omega^2}\left(\frac{n_+(\omega')+n_-(\omega')}{2} - 1\right) d\omega'\,, \tag{9}$$

$$\omega\,[n_+(\omega) - n_-(\omega)] = \frac{2}{\pi} P \int_0^\infty \frac{\omega'^2}{\omega'^2-\omega^2}\,[\kappa_+(\omega') - \kappa_-(\omega')]\, d\omega'\,. \tag{10}$$

In Sec. III A these will be shown to reduce to Eqs. (6) and (7), respectively, when $\omega \neq 0$ by making use of the low-frequency limit of $\omega N_\pm(\omega)$.

The difference relations are of particular interest in discussing optical rotation and its relation to circular dichroism either natural or induced by an external magnetic field. The angle by which the plane of polarization of linear polarized light is rotated in passing through an optically active sample, is given by[16]

$$\phi(\omega) = (\omega/2c)\,(n_l - n_r) = (\pi/\lambda)\,(n_+ - n_-) \tag{11}$$

per unit thickness of crystal. Here c is the velocity of light in vacuum. The difference in extinction coefficients for right- and left-hand light, $\Delta\kappa(\omega)$, as measured in a circular dichroism experiment is therefore related to $\phi(\omega)$ by

$$\Delta\kappa(\omega) = \frac{4c}{\pi} P \int_0^\infty \frac{\phi(\omega')}{\omega'^2-\omega^2}\, d\omega'\,, \tag{12}$$

with the inverse transformation

$$\phi(\omega) = \frac{-\omega^2}{c\pi} \int_0^\infty \frac{\Delta\kappa(\omega')}{\omega'^2-\omega^2}\, d\omega'\,, \tag{13}$$

where

$$\Delta\kappa(\omega) = \kappa_-(\omega) - \kappa_+(\omega) = \kappa_r(\omega) - \kappa_l(\omega).$$

III. SUM RULES

Sum rules for the optical constants may be obtained directly by considering the limiting values of the dispersion relations for high and low frequencies and then equating these to values known from physical considerations.

A. Low-frequency limits

The simplest case is the $\omega = 0$ limit for insulators. In the static limit the dispersion relation for the birefringence Eq. (7) yields

$$n_+(0) = n_-(0) \equiv n(0) \quad \text{(insulators)}. \tag{14}$$

This is consistent with the physical argument that if the modes are to remain circular to arbitrarily low frequencies, the medium must be isotropic in the plane perpendicular to the direction of propagation in the limit of $\omega \to 0$. Combining the $\omega = 0$ limit of Eq. (5) for $n_+(\omega) + n_-(\omega)$ with Eq. (14) yields

$$n(0) - 1 = \frac{1}{\pi} P \int_0^\infty \frac{1}{\omega} [\kappa_+(\omega) + \kappa_-(\omega)]\, d\omega \qquad \text{(insulators)}. \tag{15}$$

This is a generalization of the formula[17] for the static index (or static dielectric constant) of isotropic media in terms of the inverse first moment of the extinction coefficient (or the imaginary part of the dielectric function).

In the static limit there is no dissipation in insulators so that

$$\kappa_+(0) = \kappa_-(0) = 0 \quad \text{(insulators)}. \tag{16}$$

The $\omega = 0$ limit of Eq. (8) for $\kappa_+(\omega) - \kappa_-(\omega)$ may be combined with this requirement to yield a second rule

$$\int_0^\infty \left(\frac{n_+(\omega) - n_-(\omega)}{\omega} \right) d\omega = 0 \quad \text{(insulators)}. \tag{17}$$

This result is potentially quite useful as a check on experiment since rotatory dispersion measurements given the difference $[n_+(\omega) - n_-(\omega)]$ directly.

Note that both the rules Eqs. (15) and (17) hold only for insulators since the $\omega = 0$ limits of Eqs. (5) and (8) do not apply to metals. In metals $\kappa_+(\omega)$, $\kappa_-(\omega)$ and $n_+(\omega)$, $n_-(\omega)$ and their differences have $\omega^{-1/2}$ singularities so that the integrals involved in these rules diverge.

Two additional low-frequency-limit sum rules applicable to both metals and insulators may be derived from dispersion relations for $\omega N(\omega)$. Using the fact that near $\omega = 0$, $\kappa_+(\omega)$ and $\kappa_-(\omega)$ behave as $\omega^{-1/2}$ for metals or approach zero for insulators, the left-hand side of Eq. (9) for $\omega[\kappa_+(\omega) + \kappa_-(\omega)]$ is zero in the static limit yielding

$$\int_0^\infty \left(\frac{n_+(\omega) + n_-(\omega)}{2} - 1 \right) d\omega = 0. \tag{18}$$

This is a generalization of the inertial sum rule, Eq. (1), to the case of optically active media. Similarly, the $\omega = 0$ limit of Eq. (10) for $\omega[n_+(\omega) - n_-(\omega)]$ yields

$$\int_0^\infty [\kappa_+(\omega) - \kappa_-(\omega)]\, d\omega = 0. \tag{19}$$

This sum rule is closely related to one for "rotational strengths" published by Kuhn[18] in 1929 on the basis of a mechanical model of natural optical activity. A proof for a quantum model was given by Rosenfeld in 1928.[19,20] The present proof shows that the rule is independent of the details of the models used and applies to both natural and magneto-optical activity.

The two sum rules just found are sufficient to prove that Eqs. (9) and (10) which hold for metals reduce to Eqs. (6) and (7) originally derived for insulators provided $\omega \neq 0$. Both Eq. (9) and (10) involve $\omega'^2/(\omega'^2 - \omega^2)$ which may be written

$$\omega'^2/(\omega'^2 - \omega^2) = 1 + \omega^2/(\omega'^2 - \omega^2). \tag{20}$$

Substituting this into Eq. (9) yields

$$\omega[\kappa_+(\omega) + \kappa_-(\omega)] = -\frac{2}{\pi} \int_0^\infty [n_+(\omega') + n_-(\omega') - 2]\, d\omega' - \frac{2}{\pi} \omega^2 P \int_0^\infty \frac{n_+(\omega') + n_-(\omega') - 2}{\omega'^2 - \omega^2}\, d\omega', \tag{21}$$

but by the generalized inertial sum rule, Eq. (18), the first integral on the right-hand side is zero so that for $\omega \neq 0$,

$$\kappa_+(\omega) + \kappa_-(\omega) = -\frac{2}{\pi} \omega P \int_0^\infty \frac{n_+(\omega') + n_-(\omega') - 2}{\omega'^2 - \omega^2}\, d\omega', \tag{6'}$$

which is the same as Eq. (6). Similar considerations hold for Eq. (10) with the difference that the "Kuhn" sum rule, Eq. (19), is used to eliminate the first integral leaving the equivalent of Eq. (7). Since it has been shown previously that Eqs. (5) and (8) hold for metals, we conclude that the generalized dispersion relations Eqs. (5)-(8) hold for both insulators and metals provided $\omega \neq 0$ and that Eqs. (9) and (10) involving $\omega[\kappa_+(\omega) + \kappa_-(\omega)]$ and $\omega[n_+(\omega) - n_-(\omega)]$ are redundant.

B. High-frequency limits

In the limit of high frequencies, photon energies are much greater than electronic binding energies, Zeeman splittings, etc., and to a first approximation the electrons in a medium respond as though they were free. Thus, the leading terms in the refractive indices for right- and left-hand modes in a medium with $\mathfrak{N}$ electrons per unit volume is

$$\lim_{\omega\to\infty}[N_\pm(\omega)-1]=-2\pi\mathfrak{N}e^2/m\omega^2=-\tfrac{1}{2}\omega_p^2/\omega^2\,, \tag{22}$$

where e and m are the electronic charge and mass, respectively. That is, $n_\pm(\omega)-1$ falls off like $-\frac{1}{2}\omega_p^2/\omega^2$, while $\kappa(\omega)$ falls off faster than ω^{-2}. In a simple Lorentz model,[11,21] $\kappa_\pm(\omega)$ falls off like ω^{-3}, but it is sufficient to assume the less stringent behavior[22]

$$\kappa_\pm(\omega)=O(\omega^{-2}\ln^{-\alpha}\omega),\quad \alpha>1,\quad \omega\to\infty\,. \tag{23}$$

Applying the superconvergence theorem [in the form of Eq. (A11) of Ref. 1] to the dispersion relation for $n_-(\omega)+n_-(\omega)$, Eq. (5), one has

$$\lim_{\omega\to\infty}[n_+(\omega)+n_-(\omega)-2]=-\frac{2}{\pi\omega^2}\int_0^\infty\omega'[\kappa_+(\omega')+\kappa_-(\omega')]\,d\omega'+O(\omega^{-2}\ln^{1-\alpha}\omega)\,. \tag{24}$$

Equating the asymptotic behavior of Eqs. (22) and (24) yields the generalized Thomas-Reike-Kuhn f sum rule[1,23]

$$\int_0^\infty\omega\frac{\kappa_+(\omega)+\kappa_-(\omega)}{2}\,d\omega=\tfrac{1}{4}\pi\omega_p^2\,. \tag{25}$$

Here the average extinction coefficient $\frac{1}{2}[\kappa_+(\omega)+\kappa_-(\omega)]$ plays the role of the isotropic extinction coefficient in the usual statement of the f sum rule for linear light.

Comparison of the generalized f sum rule [Eq. (25)] and the Kuhn sum rule [Eq. (19)] shows that, in general, $\kappa_+(\omega)$ and $\kappa_-(\omega)$ do not obey the f sum rule separately. This will be discussed from the point of view of transition probabilities in Sec. IV C.

The inertial sum rule for circularly polarized modes may also be derived by applying the superconvergence theorem to the dispersion relations for $\kappa_+(\omega)+\kappa_-(\omega)$, Eq. (6). Applying the superconvergence theorem (with $\beta=\frac{3}{2}$) to Eq. (6) after a change in variables yields

$$\lim_{\omega\to\infty}\frac{\kappa_+(\omega)+\kappa_-(\omega)}{2}=\frac{2}{\pi\omega}\int_0^\infty\left(\frac{n_+(\omega')+n_-(\omega')}{2}-1\right)d\omega'+O(\omega^{-2})\,. \tag{26}$$

But the left-hand side falls off faster than ω^{-1} so

$$\int_0^\infty\left(\frac{n_+(\omega)+n_-(\omega)}{2}-1\right)d\omega=0\,. \tag{27}$$

Since this derivation assumes Eq. (6), it applies only to insulators. However, we have already shown the inertial sum rule holds for metals by taking the $\omega=0$ limit of Eq. (10).

Asymptotic expressions for the difference in $N_\pm(\omega)$ are required for deriving sum rules from the difference dispersion relations, Eq. (7) and (8). From Eq. (22) the difference in indices must decrease faster than ω^{-2}, but the exact form may be calculated in any convenient model since only the asymptotic behavior is needed. In the magneto-optic case a classical[11,21] or quantum[24] calculation shows that if spin polarization is neglected

$$\lim_{\omega\to\infty}N_+(\omega)-N_-(\omega)=\omega_p^2\,\omega_c/\omega^3\,, \tag{28}$$

where ω_c is the cyclotron frequency eH/mc. If the spin system is polarized, i.e., $\langle S_z\rangle\neq0$, ω_c is augmented by a term proportional to the spin-orbit interaction but the asymptotic behavior remains $O(\omega^{-3})$. This is discussed in Sec. IV D. Similarly in a naturally optically active system[9,20,25]

$$\lim_{\omega\to\infty}N_+(\omega)-N_-(\omega)=\frac{-16\pi\mathfrak{N}_0}{3\hbar}\sum_b\frac{\omega_{ba}^2R_{ba}}{\omega^3}\,, \tag{29}$$

where R_{ba} is the rotational strength,

$$R_{ba}=-R_{ab}=\mathrm{Im}(\langle a|\,\vec{\mu}\,|b\rangle\cdot\langle b|\,\vec{\mathrm{m}}\,|a\rangle) \tag{30}$$

for the transition from state a to state b with transition energy $\hbar\omega_{ba}=E_b-E_a$. The electric and magnetic dipole moments have been abbreviated as

$$\vec{\mu}=e\sum_i\vec{\mathrm{r}}_i\quad\text{and}\quad\vec{\mathrm{m}}=\mu_B\sum_i\vec{\mathrm{L}}_i$$

and $\mathfrak{N}_0$ is the number of optically-active species per unit volume.

In both cases of optical activity[22]

$$n_+(\omega)-n_-(\omega)=O(\omega^{-3}),\quad \omega\to\infty\,, \tag{31}$$

while $\kappa_+(\omega)-\kappa_-(\omega)$ falls off faster than ω^{-3},

$$\kappa_+(\omega)-\kappa_-(\omega)=o(\omega^{-3}),\quad \omega\to\infty\,. \tag{32}$$

For present purposes it is sufficient to assume that[22]

$$\kappa_+(\omega)-\kappa_-(\omega)=O(\omega^{-3}\ln^{-\alpha}\omega),\quad \alpha>1,\quad \omega\to\infty\,,$$

since in an actual physical system $\kappa_+(\omega)-\kappa_-(\omega)$ is expected to decrease even faster than this. For example, in the Lorentz model[11,21] the magneto-circular dichroism $\kappa_+(\omega)-\kappa_-(\omega)$ falls off like ω^{-4}.

Sum rules may now be derived from the first difference dispersion relation for $n_+(\omega)-n_-(\omega)$, Eq. (7), by employing the identity equation (20) to expand $1/(\omega'^2-\omega^2)$. This yields

$$n_+(\omega)-n_-(\omega) = \frac{2}{\pi}\left(-\frac{1}{\omega}\int_0^\infty [\kappa_+(\omega')-\kappa_-(\omega')]\,d\omega' + \frac{1}{\omega}P\int_0^\infty \frac{\omega'^2}{\omega'^2-\omega^2}[\kappa_+(\omega')-\kappa_-(\omega')]\,d\omega'\right). \tag{33}$$

The superconvergence theorem [in the form of Eq. (A11) of Ref. 1] may be applied to the second integral and comparison with the asymptotic behavior, Eq. (28), yields two rules

$$\int_0^\infty [\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega=0 \tag{34}$$

and

$$\int_0^\infty \omega^2[\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega = \begin{cases} -\frac{1}{2}\pi\,\omega_p^2\omega_c\,, & \langle S_z\rangle=0 \quad \text{(mag. opt.)}, \\ \dfrac{8\pi^2\mathfrak{N}_0}{3\hbar}\sum_b \omega_{ba}^2 R_{ba} & \text{(nat. opt.)} \end{cases} \tag{35}$$

for the magneto- and natural-optically active cases, respectively. The first is the "Kuhn" sum rule already familiar from taking the $\omega=0$ limit of Eq. (10). The second is new and gives the splitting of the levels absorbing right- and left-hand light. Equation (35) can alternatively be derived by applying the superconvergence theorem to Eq. (10) for $\omega[n_+(\omega)-n_-(\omega)]$.

The second difference dispersion relation, Eq. (8), yields a second sum rule for $n_+(\omega)-n_-(\omega)$ that is valid for both metals and insulators. Applying the superconvergence theorem yields the limit

$$\lim_{\omega\to\infty}[\kappa_+(\omega)-\kappa_-(\omega)] = -\frac{2}{\pi}\frac{1}{\omega^2}\int_0^\infty \omega'[n_+(\omega')-n_-(\omega')]\,d\omega' + O(\omega^{-3})]. \tag{36}$$

However, from Eq. (32) the left-hand side falls off faster than ω^{-2} so that equating powers of $1/\omega^2$ gives the rule

$$\int_0^\infty \omega[n_+(\omega)-n_-(\omega)]\,d\omega=0\,. \tag{37}$$

This result should be compared with the earlier sum rule, Eq. (17), obtained from the static limit which holds for insulators only,

$$\int_0^\infty \frac{n_+(\omega)-n_-(\omega)}{\omega}\,d\omega=0 \quad \text{(insulators)}. \tag{17}$$

It should be noted that the ω^{-3} asymptotic high-frequency behavior of $n_+(\omega)-n_-(\omega)$ given by Eq. (31) is actually more restrictive than is needed to derive Eqs. (34) and (37). The fact that $N_+(\omega)-N_-(\omega)=o(\omega^{-2})$, as $\omega\to\infty$ [which may be inferred from Eq. (22)] guarantees both of these rules. However, to obtain Eq. (35) it is necessary that $\kappa_+(\omega)-\kappa_-(\omega)$ fall of faster than ω^{-3}.

C. Higher-order sum rules

An infinite number of sum rules may be derived for the optical constants by considering analytic functions formed by taking various powers of the optical constants and their products with powers of ω.[2,26] While only a few of the results appear to be of practical importance, some straightforward relations based on the products $N_+^2(\omega)$, $N_-^2(\omega)$, $N_+(\omega)N_-(\omega)$, and their linear combinations may be derived. For further details the interested reader is referred to treatment of the case for linear light in Refs. 2 and 26 which may be extended to the circular case without difficulty.

By considering the function $[N_+(\omega)-N_-(\omega)]^2$, or equivalently taking linear combinations of sum rules for $N_+^2(\omega)$, $N_-^2(\omega)$, and $N_+(\omega)N_-(\omega)$ sum rules for the product of circular dichroism and rotatory dispersion are obtained. For both metals and dielectrics

$$\int_0^\infty \omega[n_+(\omega)-n_-(\omega)][\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega=0 \tag{38}$$

holds. In addition for insulators a second rule obtains

$$\int_0^\infty \frac{[n_+(\omega)-n_-(\omega)][\kappa_+(\omega)-\kappa_-(\omega)]}{\omega}\,d\omega=0 \quad \text{(insulators)}. \tag{39}$$

These should be compared with the rotatory dispersion rules Eqs. (37) and (17) which have an identical form, but with the factor $\kappa_+(\omega)-\kappa_-(\omega)$ replaced by unity. Not only does the rotatory dispersion obey a first- and inverse first-moment rule, but it obeys the same rules when weighted by the circular dichroism.

A further result is that the norms of the circular dichroism and the rotatory dispersion obey

$$\int_0^\infty [n_+(\omega)-n_-(\omega)]^2\,d\omega - \int_0^\infty [\kappa_+(\omega)-\kappa(\omega)]^2\,d\omega = -4\pi^2\{\sigma_{xx}(0)-[\sigma_{xx}^2(0)+\sigma_{xy}^2(0)]^{1/2}\}, \tag{40}$$

where $\sigma_{ij}(0)$ are the elements of the *dc* conductivity tensor. This is a generalization of the theorem that the norm of a function is preserved in Hilbert transforms [cf. Altarelli and Smith, Ref. (2), Eq.

(55′)]. A generalization of the weighted average-index sum rule is also found,

$$\int_0^\infty \omega\{[n_+(\omega)-1]\kappa_+(\omega)+[n_-(\omega)-1]\kappa_-(\omega)\}\,d\omega=0. \tag{41}$$

This is to be compared with the generalized inertial sum rule Eq. (18) which is similar in form but does not contain the weighting factors $\omega\kappa_\pm(\omega)$.

D. Summary of results

To summarize the results of this section the principal sum rules obtained are listed below. For metals and insulators one has (a) generalized Thomas-Reike-Kuhn f sum rule

$$\int_0^\infty \omega\,\frac{\kappa_+(\omega)+\kappa_-(\omega)}{2}\,d\omega=\frac{\pi}{4}\,\omega_p^2\,; \tag{42}$$

(b) generalized inertial sum rule

$$\int_0^\infty \left(\frac{n_+(\omega)+n_-(\omega)}{2}-1\right)d\omega=0; \tag{43}$$

(c) first-moment circular-birefringence rule

$$\int_0^\infty \omega[n_+(\omega)-n_-(\omega)]\,d\omega=0; \tag{44}$$

(d) Kuhn's zeroth-moment circular-dichroism rule

$$\int_0^\infty [\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega=0; \tag{45}$$

(e) second-moment circular-dichroism rule

$$\int_0^\infty \omega^2[\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega = \begin{cases} -\tfrac{1}{2}\pi\omega_p^2\,\omega_c, & \langle S_z\rangle=0 \quad \text{(mag. opt.)} \\[4pt] \dfrac{8\pi^2\mathfrak{N}_0}{3\hbar}\displaystyle\sum_b \omega_{ba}^2 R_{ba} & \text{(nat. opt.)} \end{cases} \tag{46}$$

for magnetic and natural optical activity, respectively; in addition, for insulators one also has the following relations:

(f) static index sum rule

$$n_+(0)=n_-(0)$$
$$=1+\frac{2}{\pi}\int_0^\infty \frac{\kappa_+(\omega)+\kappa_-(\omega)}{2\omega}\,d\omega \quad \text{(insulators)}; \tag{47}$$

(g) inverse first-moment circular-birefringence sum rule

$$\int_0^\infty \frac{n_+(\omega)-n_-(\omega)}{\omega}\,d\omega=0 \quad \text{(insulators)}. \tag{48}$$

Sum rules involving higher powers of the optical constants have also been proved. Most appear to be of limited value in the analysis of data, but a useful result for checking inversions of circular-dichroism–circular-birefringence (CD–CB) data in metals and insulators is

(h) the first-moment CD–CB rule

$$\int_0^\infty \omega[n_+(\omega)-n_-(\omega)][\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega=0. \tag{49}$$

In addition for insulators on has (i) the inverse first-moment CD–CB rule

$$\int_0^\infty \frac{[n_+(\omega)-n_-(\omega)][\kappa_+(\omega)-\kappa_-(\omega)]}{\omega}\,d\omega=0 \quad \text{(insulators)}; \tag{50}$$

(j) the CD–CB norm rule

$$\int_0^\infty [n_+(\omega)-n_-(\omega)]^2\,d\omega=\int_0^\infty [\kappa_+(\omega)-\kappa_-(\omega)]^2\,d\omega \quad \text{(insulators)}. \tag{51}$$

IV. DISCUSSION

In the present section the dispersion theory results are compared with well-known predictions of detailed models and the physical basis of the sum rules is explored quantum mechanically. Sections IV A and IV B deal with the Drude-Rosenfeld formula used widely in analysis of rotatory dispersion and with the use of sum rules to separate solute from solvent rotations. In Sec. IV C the Kuhn sum rule and the generalized f sum rule are derived by considering transition matrix elements. In Sec. IV D the classical second-moment circular dichroism rule for ω_c is investigated similarly. The derivation is extended to include spin-orbit contributions and the results compared with the moments results of Bennett and Stern[27] and Henry, Schnatterly, and Slichter.[28]

A. Rotational strengths, the Drude-Rosenfeld formula, and asymptotic behavior

A quantum-mechanical description of natural rotatory dispersion was first formulated by Rosenfeld[19] who showed that the rotation, $\phi(\omega)$, of a plane polarized beam of light by a optically active medium is given by

$$\phi(\omega)=\frac{8\pi\mathfrak{N}_0}{3\hbar c}\,\omega^2\sum_b \frac{R_{ba}}{\omega_{ba}^2-\omega^2}\,. \tag{52}$$

Here $\mathfrak{N}_0$ is the number of optically active molecules per unit volume and R_{ba} is the rotational strength. A similar result was derived earlier by Drude[29] from a classical model. Comparison of the Drude-Rosenfeld formula with the dispersion theory result, Eq. (13),

$$\phi(\omega)=\frac{-\omega^2}{c\pi}\int_0^\infty \frac{\kappa_r(\omega')-\kappa_l(\omega')}{\omega'^2-\omega^2}\,d\omega' \qquad (13)$$

shows that both the Drude and Rosenfeld models correspond to a circular dichroism consisting of δ functions with strength proportional to R_{ba},

$$\kappa_r(\omega)-\kappa_l(\omega)=-\frac{8\pi^2\mathfrak{N}_0}{3\hbar}\sum_b R_{ba}\delta(\omega-\omega_{ba})\,. \qquad (53)$$

Alternatively, one can view $\kappa_r(\omega)-\kappa_l(\omega)$ as giving the spectral density of rotational strength in a generalized Drude-Rosenfeld theory in which the summation in Eq. (52) is replaced by an integration.

Substitution of Eq. (53) into the sum rule for the zeroth moment of $[\kappa_+(\omega)-\kappa_-(\omega)]$, Eq. (45) yields

$$\sum_b R_{ba}=0\,. \qquad (54)$$

This is the rotational strength sum rule[20,25] as originally stated by Kuhn.[18]

The low-frequency behavior of $\phi(\omega)$ for both natural and magneto-optic systems may be inferred directly from Eq. (13). At energies much lower than any significant circular dichroism the integral becomes a constant and

$$\phi(\omega)=A\omega^2 \text{ (low frequencies)}\,, \qquad (55)$$

where

$$A=-(c\pi)^{-1}\int_0^\infty \omega'^{-2}[\kappa_r(\omega')-\kappa_l(\omega')]\,d\omega'\,. \qquad (56)$$

Similarly, at frequencies higher than any significant circular dichroism expansion of the factor $1/(\omega'^2-\omega^2)$ in Eq. (13) and use of the Kuhn sum rule, Eq. (45), yields

$$\phi(\omega)\sim\omega^{-2}B\,, \qquad (57)$$

where by Eq. (46),

$$B=\frac{1}{c\pi}\int_0^\infty \omega'^2[\kappa_r(\omega')-\kappa_l(\omega')]\,d\omega'$$

$$=\frac{\omega_p^2\omega_c}{2c} \text{ (mag. opt.)}\,,$$

or (58)

$$B=-\frac{8\pi\mathfrak{N}_0}{3\hbar c}\sum_b \omega_{ba}^2 R_{ba} \text{ (nat. opt.)}\,.$$

This, of course, is precisely the behavior built into the theory from the known high-frequency form of $n_+(\omega)-n_-(\omega)$.

B. Rotatory dispersion and Faraday rotation

The sum rules for differences in refractive index are directly applicable to experimentally observed rotations of the plane of polarization of light as it passes through an optically active substance. Comparison of Eq. (11) for the rotation with the first-moment birefringence rule, Eq. (44) shows that for both conductors or insulators

$$\int_0^\infty \phi(\omega)\,d\omega=0 \qquad (59a)$$

or equivalently

$$\int_0^\infty \lambda^{-2}\phi(\lambda)\,d\lambda=0\,. \qquad (59b)$$

In addition for insulators the inverse first-moment birefringence rule, Eq. (48) yields the restriction

$$\int_0^\infty \omega^{-2}\phi(\omega)\,d\omega=0 \text{ (insulators)} \qquad (60a)$$

or equivalently

$$\int_0^\infty \phi(\lambda)\,d\lambda=0 \text{ (insulators)}\,. \qquad (60b)$$

Note that for insulators one has the curious reciprocal requirement that both the zeroth and inverse second moment of the rotation are zero using either frequency or wavelength as integration variable.

These relations provide self-consistency checks on experiments and on the subtraction of background rotations when dealing with the rotation of dilute impurities in an optically active solvent. Studies of color centers in insulating crystals are on example of the latter. At low temperatures paramagnetic color centers display strong magneto-optic activity but this is superimposed on a background rotation arising from the host crystal or other centers.[30] Since the absorptions responsible for the host crystal rotation are usually well removed from the absorptions of the color centers, the background rotation produced by the solvent is varying slowly and can be approximated by a simple analytic form such as a three-parameter Drude-Rosenfeld fit

$$\phi_{\text{background}}=a/\lambda^2+b/(\lambda^2-Q^2)\,. \qquad (61)$$

By applying rules Eqs. (59) and (60) to the solute rotations the consistency of the background subtraction can be checked and, where appropriate, the parameters varied to achieve consistency.

C. Kuhn circular dichroism and the *f* sum rules

The quantum mechanical origin of sum rules involving extinction coefficients may be demonstrated by expressing them in terms of matrix elements of the electromagnetic field interaction. In the semiclassical approximation this interaction has the form[24,27]

$$-(e/mc)\vec{\Pi}\cdot\vec{A}_L\,,$$

where $\vec{A}_L$ is the vector potential of the light and $\vec{\Pi}$ is the canonical momentum operator including spin-orbit effects

$$\vec{\Pi}(\vec{r}_i) = -i\hbar\vec{\nabla}_i - (e/c)\vec{A}_m(\vec{r}_i) + (1/2mc^2)\vec{S}\times\vec{\nabla}_i V(\vec{r}_i). \tag{62}$$

Here $\vec{A}_m(\vec{r})$ is the vector potential for the external magnetic field, $\frac{1}{2}\vec{H}\times\vec{r}$, e is the electronic charge (a negative number) and $V(\vec{r})$ is the one-electron potential assumed in reducing the Dirac equation.

An approximate expression[31] for $\kappa(\omega)$ in terms of matrix elements of $\vec{\Pi}$ may be obtained[32] by equating the decrease in intensity of the propagating wave as measured by $2\omega\kappa/c$ to the energy absorbed by transitions induced by the radiation. Ignoring the details of band shapes, this yields in the dipole approximation

$$\kappa(\omega) = \frac{2\pi^2 e^2}{\omega^2 m^2 \hbar} \sum_{f\neq i} \left| \langle \phi_f | \sum_s \vec{I}\cdot\vec{\Pi}_s | \phi_i \rangle \right|^2 \delta(\omega_{fi} - \omega). \tag{63}$$

Here $\vec{I}$ is the unit polarization vector; for circularly polarized modes it is $(\hat{x} \pm i\hat{y})/\sqrt{2}$. The initial- and final-state wave functions are denoted by ϕ_i and ϕ_f respectively and the sum over s runs over all electrons. The circular frequency for the transition $i \to f$ is denoted by ω_{fi}. This expression may be transformed into the more familiar dipole form by using the dipole-momentum identity

$$(E_k - E_j)\langle k|\vec{r}_i|j\rangle = -(i\hbar/m)\langle k|\vec{\Pi}_i|j\rangle, \tag{64}$$

which follows directly from the commutator of $\vec{r}$ with the Hamiltonian. Combining Eqs. (63) and (64) yields

$$\kappa(\omega) = \frac{2\pi^2 e^2}{\hbar} \sum_{f\neq i} |\langle \phi_f | \vec{I}\cdot\vec{R} | \phi_i \rangle|^2 \delta(\omega_{fi} - \omega). \tag{65}$$

Here $\vec{R}$ is the dipole operator for the $\mathcal{N}$ electrons in the system $\sum_{s=1}^{\mathcal{N}} \vec{r}_s$. For the present purpose of illustrating the quantum mechanical basis of the sum rules, Eqs. (63) and (65) will be used interchangably. However, it should be noted from Eq. (64) that it is possible to have $\langle k|\vec{\Pi}|j\rangle = 0$ but $\langle k|\vec{r}|j\rangle \neq 0$ if $\omega_{kj} = 0$. Examples of this occur for intraband transitions in metals.[33]

1. Kuhn sum rule

In the form given by Eq. (45) this rule states that the average circular dichroism expressed as the difference in extinction coefficients in zero. Since the extinction coefficient is proportional to the rate of photon absorption, an alternative statement is that the net transition rates for right- and left-hand light are equal. The direct quantum-mechanical proof proceeds by substituting Eq. (65) into Eq. (45) and using closure

$$\begin{aligned}\int_0^\infty [\kappa_r(\omega) - \kappa_l(\omega)]\,d\omega \\ &\propto \sum_{f\neq i} |\langle \phi | (X - iY) | \phi_i \rangle|^2 - |\langle \phi_f | (X + iY) | \phi_i \rangle|^2 \\ &\propto \langle \phi_i | |X - iY|^2 | \phi_i \rangle - \langle \phi_i | |X + iY|^2 | \phi_i \rangle \\ &\equiv 0,\end{aligned} \tag{66}$$

where X and Y are the x and y components of the dipole operator $\vec{R}$. The sum over f in the second line originally excludes ϕ_i, but may be extended to include this state since $|\langle \phi_i | X + iY | \phi_i \rangle|^2 = |\langle \phi_i | X - iY | \phi_i \rangle|^2$.

2. f sum rule

While the total transition rates for right- and left-hand light are equal, the oscillator strengths (which are proportional to energies times transition probabilities) are not equal and the f sum rule does not apply to either mode separately.[34]

The physical origin of this may be seen from the conventional quantum mechanical proof of the f sum rule. By evaluating the position-momentum commutator, it is easily shown that the oscillator strength for each orthogonal component of *linearly* polarized light equals the electron density $\mathcal{N}$ of the system.[23,35] That is,

$$\mathcal{N} = \sum_\beta f_{\alpha\beta} = \frac{2m}{\hbar^2} \sum_\beta (E_\beta - E_\alpha) |\langle \phi_\beta | R_i | \phi_\alpha \rangle|^2. \tag{67}$$

Here $f_{\alpha\beta}$ is the oscillator strength of the transition from state α to state β and R_i is either X, Y, or Z, the dipole operators for linear light. The sum over β runs over all possible final states of the system. On the other hand, the sum of the oscillator strengths associated with dipole transitions of *circularly polarized* light is

$$\begin{aligned}\sum_\beta f_{\pm\alpha\beta} &= \frac{2m}{\hbar^2} \sum_{\beta\neq\alpha} (E_\beta - E_\alpha) \left| \langle \phi_\beta | \frac{X \pm iY}{\sqrt{2}} | \phi_\alpha \rangle \right|^2 \\ &= \mathcal{N} \mp \frac{2m}{\hbar^2} \sum_\beta (E_\beta - E_\alpha) \\ &\quad \times \operatorname{Im}\langle \phi_\alpha | X | \phi_\beta \rangle \langle \phi_\beta | Y | \phi_\alpha \rangle.\end{aligned} \tag{68}$$

Here Eq. (67) has been used to replace the summation over the direct terms involving matrix elements of X or Y by $\mathcal{N}$. The cross term involving dipole matrix elements of X times dipole matrix elements of Y is in general nonzero so that the f sums for right- and left-handed light are greater or less than $\mathcal{N}$ by the magnitude of the cross term's contribution. However, if the

f sums for right- and left-hand light are added, the cross terms cancel yielding

$$\sum_{\beta} \frac{f_{+\alpha\beta}+f_{-\alpha\beta}}{2} = \mathfrak{N} . \tag{69}$$

That is, the average oscillator strength is just $\mathfrak{N}$ in agreement with Eq. (42).

A particularly simple form for the cross term may be obtained by using the dipole-momentum identity Eq. (64) and the property of closure to perform the sum over β. Equation (68) then becomes

$$\sum_{\beta} f_{\pm\alpha\beta} = \mathfrak{N} \pm \frac{1}{\hbar}\bigg(\langle\alpha|L_z|\alpha\rangle - \frac{eH}{2c}\langle\alpha|X^2+Y^2|\alpha\rangle + \frac{1}{2mc^2}\langle\alpha|S_z(X\nabla_x V + Y\nabla_y V)|\alpha\rangle\bigg) , \tag{70}$$

where L_z is the z component of the angular momentum operator. This result, with the exception of the spin-orbit term, has been given previously by Hasagawa and Howard.[34]

D. Second-moment circular-dichroism (CD) sum rule

The second-moment CD rule for magneto-optics given by Eq. (46) has been derived ignoring the possibility of spin polarization. Considerably deeper insight may be obtained by a more detailed quantum calculation including spin-orbit effects. In the present section we show that in the dipole approximation nonzero contributions to the second moment of the circular dichroism arise only from velocity-dependent terms in the Hamiltonian (such as the magnetic and spin-orbit interactions). This is the source of magneto-optical phenomena. Natural optical activity enters the theory as a consequence of the spatial variation of the electromagnetic wave over the system and will be discussed elsewhere.

1. Exact evaluation of the second moment and the classical limit

An exact result for the second moment of the circular dichroism in the magneto-optic case may be obtained from the kinetic momentum expression for κ. From Eq. (63) the second moment is

$$\begin{aligned}\int_0^\infty \omega^2[\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega &= \frac{2\pi^2e^2}{m^2\hbar}\sum_{f\neq i}\bigg|\langle\phi_f|\sum_s \vec{\mathrm{I}}_+\cdot\vec{\Pi}(\vec{\mathrm{r}}_s)|\phi_i\rangle\bigg|^2 - \bigg|\langle\phi_f|\sum_s \vec{\mathrm{I}}_-\cdot\Pi(\vec{\mathrm{r}}_s)|\phi_i\rangle\bigg|^2 \\ &= i\,\frac{2\pi^2e^2}{m^2\hbar}\langle\phi_i|\sum_{s,t}[\Pi_x(\vec{\mathrm{r}}_s),\Pi_y(\vec{\mathrm{r}}_s)]|\phi_i\rangle .\end{aligned} \tag{71}$$

Here the sum over f has been extended to include ϕ_i because the ϕ_i term is identically zero and closure has been used to obtain the second line. Explicit evaluation of the commutator yields

$$[\Pi_x(\vec{\mathrm{r}}_s),\Pi_y(\vec{\mathrm{r}}_t)] = -i\hbar\bigg\{-\frac{e}{c}H_z + \frac{1}{2mc^2}\bigg[S_z\bigg(\frac{\partial^2V}{\partial x^2}+\frac{\partial^2V}{\partial y^2}\bigg) - S_x\frac{\partial^2V}{\partial x\partial z} - S_y\frac{\partial^2V}{\partial y\partial z}\bigg]\bigg\}\delta_{s,t} . \tag{72}$$

The first term arises from the magnetic field which is the z direction; the second from the spin-orbit interaction. The latter is important in magnetic materials and at low temperature where spin polarization is possible.

In the classical limit the expectation value of spin is zero and the second moment becomes

$$\int_0^\infty \omega^2[\kappa_+(\omega)-\kappa_-(\omega)]\,d\omega = -\tfrac{1}{2}\pi\,\omega_p^2\omega_c , \tag{73}$$

in accord with Eq. (46).

This result is closely related to a magnetoconductivity sum rule discovered by Bennett and Stern[27,36] for the imaginary part of the conductivity

$$\int_0^\infty \omega\,\mathrm{Im}\sigma_{xy}(\omega)\,d\omega = \frac{\pi e^3\mathfrak{N}}{2m^2c}H . \tag{74}$$

The relationship may be seen by observing that according to the argument of Ref. 31, Eq. (73) implies a sum rule for the corresponding dielectric functions $\epsilon_\pm(\omega) = N_\pm^2(\omega)$,

$$\int_0^\infty \omega^2\,\mathrm{Im}[N_+^2(\omega) - N_-^2(\omega)] = 2\int_0^\infty \omega^2\,\mathrm{Re}\epsilon_{xy}(\omega) = -\pi\omega_p^2\,\omega_c = -\frac{4\pi^2e^3\mathfrak{N}}{m^2c}H , \tag{75}$$

where the second form for the integral follows from $N_\pm^2 = \epsilon_{xx} \pm i\epsilon_{xy}$. However, the conductivity is given by

$$\epsilon_{ij}(\omega) = \delta_{ij} + 4\pi i\sigma_{ij}(\omega)/\omega , \tag{76}$$

and combining this with Eq. (75) completes the proof of the conductivity sum rule, Eq. (74). The point of importance here is that the physical basis of all these rules is identical, viz., the asymptotic behavior of the off-diagonal response of the system

$$\lim_{\omega\to\infty} \epsilon_{xy}(\omega) = -\frac{i\omega_p^2\omega_c}{\omega^3} , \tag{77a}$$

which implies

$$\lim_{\omega\to\infty} (N_+ - N_-) = \frac{\omega_p^2\omega_c}{\omega^3} \tag{77b}$$

and

$$\lim_{\omega\to\infty}\sigma_{xy}(\omega)=-\frac{\omega_p^2\omega_c}{4\pi\omega^2}\,. \tag{77c}$$

2. Role of velocity-dependent potentials and approximate formulations

The importance of velocity-dependent potentials and the connection between the exact second-moment sum rule and previous approximate treatments[28] may be brought out by expressing the sum rule in terms of position matrix elements. Using Eq. (65) the second moment becomes

$$\begin{aligned}\int_0^\infty &\omega^2[\kappa_+(\omega)-\kappa_-(\omega)]d\omega\\ &=\frac{\pi^2e^2}{\hbar}\sum_{f\neq i}\omega_{fi}^2(|\langle\phi_f|X+iY|\phi_i\rangle|^2-|\langle\phi_f|X-iY|\phi_i\rangle|^2)\\ &=\frac{\pi^2e^2}{\hbar^3}\langle\phi_i|[[[(X-iY),H],H],(X+iY)]|\phi_i\rangle.\end{aligned} \tag{78}$$

The last line is obtained by adding the term $f=i$ to the sum and using completeness. To evaluate the triple commutator it is convenient to use a model Hamiltonian which explicitly separates velocity-dependent and velocity-independent potentials. Let

$$H=H_0+h\,, \tag{79}$$

where H_0 contains the kinetic energy, and the velocity-independent potentials including the crystal potential and the spin-Zeeman interaction;

$$H_0=\sum_s\frac{p_s^2}{2m}+V_s(\vec{\mathrm{r}})+g\mu_B\vec{\mathrm{H}}\cdot\vec{\mathrm{S}}_s\,. \tag{80}$$

The velocity-dependent part h is then the sum of orbit-Zeeman and spin-orbit terms

$$h=\sum_s\vec{\eta}(\vec{\mathrm{r}})\cdot\vec{\mathrm{L}}_s=\sum_s\mu_B\vec{\mathrm{L}}_s\cdot\vec{\mathrm{H}}+\zeta(\vec{\mathrm{r}})\vec{\mathrm{L}}_s\cdot\vec{\mathrm{S}}_s. \tag{81}$$

It is easily shown that

$$[[[r_i,H_0],H_0],r_j]\equiv0 \tag{82}$$

for r_i and r_j any combination of position vectors. Thus from Eqs. (78) and (82): *If the Hamiltonian contains no velocity dependent-potentials the second moment of the circular dichroism is zero in the dipole approximation*

$$\int_0^\infty\omega^2[\kappa_+(\omega)-\kappa_-(\omega)]d\omega=0. \tag{83}$$

Furthermore, it is easily shown that

$$[[[r_i,h],h],r_j]=0. \tag{84}$$

That is, there is no contribution to the second-moment quadratic in velocity-dependent potentials in the dipole approximation. Nonzero contributions arise only from commutators with cross terms in h and H. In evaluating these H may be replaced by H_0 if desired because of Eq. (84). Explicit evaluation then yields

$$\begin{aligned}\int_0^\infty\omega^2[\kappa_+(\omega)-\kappa_-(\omega)]d\omega&=\frac{\pi^2e^2}{\hbar^3}\langle\phi_i|[[[(X-iY),h],H],(X+iY)]+[[[(X-iY),H],h],(X+iY)]|\phi_i\rangle\\ &=\frac{\pi^2e^2}{\hbar^3}\sum_{f,f'}\{(E_f+E_{f'}-2E_i)(\langle\phi_i|X-iY|\phi_f\rangle\langle\phi_f|h|\phi_{f'}\rangle\langle\phi_{f'}|X+iY|\phi_i\rangle\\ &\qquad-\langle\phi_i|X+iY|\phi_{f'}\rangle\langle\phi_{f'}|h|\phi_f\rangle\langle\phi_f|X-iY|\phi_i\rangle)\\ &\qquad+(E_f+E_i-2E_{f'})(\langle\phi_i|h|\phi_f\rangle\langle\phi_f|X-iY|\phi_{f'}\rangle\langle\phi_{f'}|X+iY|\phi_i\rangle\\ &\qquad-\langle\phi_i|X+iY|\phi_{f'}\rangle\langle\phi_{f'}|X-iY|\phi_f\rangle\langle\phi_f|h|\phi_i\rangle)\}\,.\end{aligned} \tag{85}$$

The right-hand side of the last expression is of the form of a generalized oscillator strength (energy times the product of dipole matrix elements) times the matrix element of the velocity-dependent potentials in the Hamiltonian. The energies E_l in Eq. (85) may be either those of H_0 or H as indicated above.

A particularly simple example[37] occurs when the initial state ϕ_i is a singlet and the only excited states to which there are significant optical transitions from a triplet transforming like x, y, and z which is unsplit by velocity-independent potentials in the Hamiltonian such as the crystal field. Taking advantage of the freedom of choice in energies, the excited-state energies will be taken as the (degenerate) eigenvalues of H_0, E_l^0. One then finds

$$\begin{aligned}\int_0^\infty&\omega^2[\kappa_+(\omega)-\kappa_-(\omega)]d\omega\\ &=-\frac{2}{\hbar}\left(\frac{4\pi^2e^2}{\hbar^2}(E_l^0-E_i^0)\langle\phi_i|Y|\phi_y^l\rangle\langle\phi_x^l|X|\phi_i\rangle\right)\\ &\quad\times i\langle\phi_y^l|\eta_zL_z|\phi_x^l\rangle\,,\end{aligned} \tag{86}$$

where the excited states in the lth triplet transforming like x is denoted by ϕ_x^l, etc. Since the triplet states transform like x, y, and z,

$$\langle\phi_i|Y|\phi_y^l\rangle=\langle\phi_i|X|\phi_x^l\rangle, \quad \text{etc.},$$

the term in large parentheses in Eq. (86) may be shown to be proportional to the sum of oscillator strengths for transitions of "+" and "−" light to the lth triplet, $\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega$. Equation (86) then becomes

$$\frac{\int_0^\infty \omega^2[\kappa_+^l(\omega)-\kappa_-^l(\omega)]d\omega}{\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega}=-i\frac{2}{\hbar}\langle\phi_y^l|\eta_z L_z|\phi^l\rangle$$

$$=\frac{1}{\hbar}(2g_{\text{orb}}^l\mu_B H+\tfrac{2}{3}\Delta^l\langle S_z\rangle). \tag{87}$$

The last line follows by substituting for η_z from Eq. (81) and using the definition[28]

$$g_{\text{orb}}^l=-i\langle\phi_y^l|L_z|\phi_x^l\rangle \tag{88}$$

for the orbital g factor and

$$\Delta^l=-\tfrac{3}{2}i\langle\phi_y^l|\zeta(r)L_z|\phi_x^l\rangle \tag{89}$$

for the spin-orbit splitting of the lth triplet. The ground-state expectation value of the z component of spin is devoted by $\langle S_z\rangle$.

Taken at face value Eq. (87) appears to be contradictory to the exact result for the second moment, Eq. (73). For example, with $\langle S_z\rangle=0$ the approximate result involves g_{orb}^l, a parameter depending on the excited state, whereas the exact result involves only the fundamental constants via ω_p and ω_c. The reason for this apparent contradiction is the assumption that all but the most prominent absorption can be neglected. This leads to the replacement of $(\frac{1}{2}\pi)\omega_p^2$ in Eq. (73) with the quantity $g_{\text{orb}}^l\times\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega$, where l labels the band in question. Indeed it is clear that g_{orb}^l can be measured only if it is possible to separate the circular dichroism of an individual band from that of other bands, otherwise one just measures ω_c corresponding to the classical case of $g_{\text{orb}}=1$.

To resolve the conflict it is necessary to include all final states in discussing Eq. (87). In the case of a system with well separated absorptions for which there is negligible magnetic mixing between excited states, an orbital moment g_{orb}^l may be defined for each group of sublevels. Then from the f sum rule, Eq. (42),

$$\tfrac{1}{2}\pi\omega_p^2=\int_0^\infty \omega[\kappa_+(\omega)+\kappa_-(\omega)]d\omega$$

$$=\sum_l\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega. \tag{90}$$

Moreover, by summing Eq. (87) over all groups of states and using the exact result, Eq. (73), one has (still assuming $\langle S_z\rangle=0$ for simplicity)

$$\int_0^\infty \omega^2[\kappa_+(\omega)-\kappa_-(\omega)]d\omega$$

$$=-\tfrac{1}{2}\pi\omega_p^2\omega_c$$

$$=-\omega_c\sum_l g_{\text{orb}}^l\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega, \tag{91}$$

where the fact that $(2/\hbar)\mu_B H=-\omega_c$ has been used. Substituting for ω_p^2 from Eq. (90) then yields

$$\sum_l g_{\text{orb}}^l\left(\frac{f_l}{f}\right)=1, \tag{92}$$

where f_l is the oscillator strength for absorptions to the lth groups of states

$$\frac{m}{2\pi^2e^2}\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega,$$

and f is the total oscillator strength for absorption to all levels $\sum_l f^l$. That is, *the average of the orbital moment as weighted by the relative oscillator strengths is just unity, the classical value.*

3. First-moment formula of Henry, Schnatterly, and Slichter (HSS)

The approximate result obtained in Sec. IV D 2 is reminescent of the widely used result of Henry *et al.*[28] for the change in first moment of an isolated absorption band caused by a magnetic perturbation. The "first-moment" result may be obtained from Eq. (87) by rewriting and making several minor approximations.

The integral in the denominator of Eq. (87) may be expressed in terms of the first moment of the absorptions ω_0 via the definition

$$\int_0^\infty \omega[\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega\equiv\omega_0\int_0^\infty [\kappa_+^l(\omega)+\kappa_-^l(\omega)]d\omega. \tag{93}$$

In terms of ω_0 the numerator becomes

$$\int_0^\infty \omega^2[\kappa_+^l(\omega)-\kappa_-^l(\omega)]d\omega$$

$$=2\omega_0\int_0^\infty(\omega-\omega_0)[\kappa_+^l(\omega)-\kappa_-^l(\omega)]d\omega$$

$$+\int_0^\infty(\omega-\omega_0)^2[\kappa_+^l(\omega)-\kappa_-^l(\omega)]d\omega \tag{94}$$

on applying Kuhn's sum rule, Eq. (45), to eliminate ω_0^2 terms. By virtue of the choice of ω_0 as the center of gravity of the composite band $\kappa_+^l(\omega)+\kappa_-^l(\omega)$, one expects large cancellations in the second integral Eq. (94). More precisely, if, with Henry *et al.*[28] one assumes no mixing of the states responsible for the absorptions, the Kuhn sum rule holds for the individual absorption bands that is, the areas under $\kappa_+^l(\omega)$ and $\kappa_-^l(\omega)$ are equal. Further for a bell-shaped band the circular dichroism $\kappa_+^l(\omega) - \kappa_-^l(\omega)$ will be approximately an odd function about the center of the band[38] ω_0, so that the second integral in Eq. (94) will be small relative to the first.

Combining Eqs. (87), (93), and (94) and approximating $\frac{1}{2}\int_0^\infty [\kappa_+^l(\omega) + \kappa_-^l(\omega)]\,d\omega$ by the zeroth moment of $\kappa(\omega)$ before application of the field, $\int_0^\infty \kappa_0^l(\omega)\,d\omega$, yields

$$\int_0^\infty (\omega - \omega_0)[\kappa_+^l(\omega) - \kappa_-^l(\omega)]\,d\omega \bigg/ \int_0^\infty \kappa_0^l(\omega)\,d\omega \approx \frac{1}{\hbar}(2g_{\mathrm{orb}}^l \mu_B H + \tfrac{2}{3}\Delta^l \langle S_z \rangle). \quad (95)$$

This is the celebrated HSS first-moment formula in the present notation. Note that because of the Kuhn sum rule, the ω_0 in the numerator of Eq. (95) is unnecessary. Indeed, the first moment may be taken about any convenient origin.

E. Summary

In this section the predictions of dispersion theory have been compared with earlier model calculations and the circular-dichroism sum rules have been investigated quantum mechanically.

It has been shown that the Kuhn sum rule,

$$\int_0^\infty [\kappa_+(\omega) - \kappa_-(\omega)]\,d\omega = 0,$$

is equivalent to the statement that the net transition probabilities for right- and left-hand light are equal. Since the oscillator strength is proportional to the transition probability times the transition energy, it follows that the oscillator strengths for right- and left-hand circularly polarized light are unequal if the spectra are dichroic. However, the average of the oscillator strengths for right- and left-hand light is just equal to the electron density in analogy with the f sum rule for linear light.

In the dipole approximation the second moment of the circular dichroism may be related to the ground-state expectation value of the commutator of the x and y components of the canonical momentum. Nonzero contributions to this arise only from velocity-dependent terms in the Hamiltonian such as the orbit-Zeeman and spin-orbit interactions. If the complete magneto-circular-dichroism spectrum is considered, the second moment is proportional to the total oscillator strength times the cyclotron frequency in the absence of spin polarization. On the other hand, the second moment of the magneto-circular dichroism of individual absorption bands arising from orbital singlet-triplet transitions is in addition proportional to the orbital g factor of the final states. This leads to the rule that the average orbital g factor when weighted by the absorption strength is just unity. By making a number of approximations the second-moment circular-dichroism sum rule has been shown to be equivalent to the well-known Henry-Schnatterly-Slichter first-moment relation for the orbital g factor and the spin-orbit splitting of a color-center absorption band.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor H. M. Nussenzveig and Professor M. Altarelli for extremely valuable discussions and for critical readings of an early version of this manuscript. The aid of Dr. P. von Cziffra in obtaining a copy of Ref. 29 is greatly appreciated.

---

*Based on work performed under the auspices of the U. S. Energy Research and Development Administration.

[1] M Altarelli, D. L. Dexter, H. M. Nussenzveig, and D. Y. Smith, Phys. Rev. B 6, 4502 (1972).

[2] M. Altarelli and D. Y. Smith, Phys. Rev. B 9, 1290 (1974).

[3] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience, London, 1966).

[4] V. L. Ginzburg and N. N. Meiman, Zh. Eksp. Teor. Fiz. 46, 243 (1964) [Sov. Phys.-JETP 19, 169 (1964)].

[5] W. Moffitt and A. Moscowitz, J. Chem. Phys. 30, 648 (1959).

[6] F. C. Brown and G. Laramore, Appl. Opt. 6, 669 (1967).

[7] C. A. Emeis, L. J. Oosterhoff and Gonda de Vries, Proc. R. Soc. Lond. A 297, 54 (1967).

[8] D. Y. Smith, Proc. Inter. Symposium on Color Centers in Alkali Halides, Rome, 1968 (unpublished) p. 252.

[9] D. J. Caldwell and H. Eyring, *The Theory of Optical Activity* (Interscience, New York, 1971).

[10] W. P. Healy and E. A. Power, Am. J. Phys. 42, 1070 (1974).

[11] D. Y. Smith, J. Opt. Soc. Am. (to be published).

[12] P. C. Martin, Phys. Rev. 161, 143 (1967).

[13] J. S. Toll, thesis (Princeton University, 1952) (unpublished); and Phys. Rev. 104, 1760 (1956).

[14] F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15.

[15] H. M. Nussenzveig, *Casuality and Dispersion Relations* (Academic, New York, 1972).

[16] The conventional definition for positive rotation of the plane of polarization as seen by an observer looking toward the source is employed here. In magneto-optics the sense of rotation and in some, but not all, cases the handedness of the light are generally referred to the magnetic field direction. This may lead to a difference in sign in the definition of ϕ. See S. D. Smith, *Handbuch der Physik*, Vol. XXV/2a (Springer,

Heidelberg, 1967) and Ref. 30, Eq. (1).

[17] See, for example, H. Fröhlich, *Theory of Dielectrics* (Oxford U. P., London, 1958), Chap. 2.

[18] W. Kuhn, Z. Phys. Chem. B 4, 14 (1929); Trans. Faraday Soc. 26, 293 (1930).

[19] L. Rosenfeld, Z. Phys. 52, 161 (1928).

[20] E. U. Condon, Rev. Mod. Phys. 9, 432 (1937).

[21] A. Sommerfeld, *Optics* (Academic, New York, 1954), Sec. 20.

[22] The notation $\phi = O(\psi)$ as $x \rightarrow \infty$ means that $\phi/\psi \rightarrow 0$ as $x \rightarrow \infty$; and $\phi = O(\psi(x))$ as $x \rightarrow \infty$ means that there exist positive constants A and x_0 such that $|\phi(x)| < A|\psi(x)|$, $x \geq x_0$.

[23] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), Secs. 59, 61, and 62.

[24] I. M. Boswarva, R. E. Howard, and A. B. Lidiard, Proc. R. Soc. Lond. A 269, 125 (1962).

[25] A. Moscowitz, in *Advances in Chemical Physics*, edited by I. Prigogine (Interscience, New York, 1962), Vol. IV.

[26] A. Villani and A. H. Zimmerman, Phys. Lett. A 44, 295 (1973); Phys. Rev. B 8, 3914 (1973).

[27] H. S. Bennett and E. A. Stern, Phys. Rev. 137, A448 (1965).

[28] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[29] P. Drude, Gottingen Nachrichten (1892) p. 400; *Lehrbuch der Optik* 2nd ed. (Verlag, Leipzig, 1906) [*Theory of Optics* (Longmans, Green, New York, 1920)].

[30] See, for example, J. Mort, F. Luty, and F. C. Brown, Phys. Rev. 137, A566 (1965), especially Fig. 1.

[31] This approach is approximate since the decrease in intensity involves both absorption and coherent scattering i.e., reflection not absorption alone. The correct approach is to set the heat generated,

$$q(\omega) = \frac{\omega}{4\pi} \operatorname{Im}[N_\pm^2(\omega)] E_0 E_0^*,$$

(see Ref. 11) equal to the energy absorbed to obtain an expression for $\operatorname{Im}(N_\pm^2)$,

$$\operatorname{Im}(N_\pm^2) = \frac{4\pi^2 e^2}{\omega^2 m^2 \hbar} \sum_{f \neq i} \left| \langle \phi_f | \sum_s \vec{\mathrm{I}}_\pm \cdot \vec{\Pi}_s | \phi_i \rangle \right|^2 \delta(\omega_{fi} - \omega).$$

Since $2n_\pm \kappa_\pm = \operatorname{Im}(N_\pm^2)$, this expression reduces to Eq (63) for $n \approx 1$. However, the approximation actually leads to exact results when used in deriving sum rules. The reason is that, as shown in Sec. III B., the second moment sum rule for N depend on the high-frequency behavior of $N - 1$. Similarly, there are sum rules for $\tilde{\epsilon}_\pm(\omega) = N_\pm(\omega)^2$ that depend on the high-frequency behavior of $\tilde{\epsilon}_\pm(\omega) - 1$. Quantum mechanically the latter are more readily obtained because of the above expression. However, from the relation $N = \tilde{\epsilon}^{1/2}$ it follows that the asymptotic forms of $N - 1$ and $\tilde{\epsilon} - 1$ differ by only a factor of 2 so that the sum rules for κ and $\operatorname{Im} N^2 = \operatorname{Im} \tilde{\epsilon}$ are, except for the factor of 2, of the same form. Thus, the sum rules resulting from the exact expression for $\operatorname{Im} N_\pm^2$ imply sum rules for $\kappa_\pm$. Moreover, these are identical to those resulting from the approximate expression of Eq. (63) which is smaller by the required factor of 2.

[32] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 6.

[33] See, for example, A. Sommerfeld and H. Bethe, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Springer, Berlin, 1928), Vol. 24/2, p. 376.

[34] H. Hasegawa and R. E. Howard, J. Phys. Chem. Solids 21, 179 (1961).

[35] D. Y. Smith and D. L. Dexter, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1972) Vol. X, Secs. 3 and 4.

[36] Note that there is a confusion in the sign of e in Ref. 27. In the discussion of the classical model e is the charge of the electron. In the quantum mechanical discussion e is taken as the absolute value of the charge, but this is compensated for by an inadvertant sign change in evaluating $[\Pi_x, \Pi_y]$. Thus e is the conductivity sum rule given by Eq. (66) of Ref. 27 has the sign of the actual charge. This is the same convention as used throughout the present paper.

[37] D. Y. Smith, Phys. Rev. B 8, 3939 (1973).

[38] See for example, Ref. 6, Fig. 3.