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Superconvergence and sum rules for the optical constants: Physical meaning, comparison with experiment, and generalization

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A physical interpretation of recently obtained sum rules for dielectric functions and for the index of refraction is provided in terms of the inertial properties of the linear dielectric response of material media. The superconvergent sum rules are then compared with experimental optical data for AgCl, Al, and Mo and shown to produce good agreement as well as a critical test of extrapolations and of the Kramers-Kronig relations. A straightforward extension to higher powers of the optical constants and their moments is briefly discussed.

I. INTRODUCTION

Investigation of optical properties is one of the most powerful experimental methods of probing the electronic structure and properties of matter.[1] However, since the range of frequencies over which an optical "constant" may be measured is necessarily limited, theoretical tools such as extrapolations, Kramers-Kronig inversions, and sum rules are needed for the analysis of optical experiments.

Recently, it was shown[2] that sum rules for the optical constants can be derived systematically and in a very general way from dispersion relations, by exploiting the rapid fall-off of the quantities of interest as ω approaches $\pm\infty$.[3] This high-frequency behavior is common to all electronic systems and may be inferred from the observation that, at frequencies much higher than any of its resonances, an electronic system responds to an electromagnetic perturbation in the same way as a system of an equal number of free electrons.

The purpose of the present paper is to investigate and further clarify the physical meaning of some of the results of Ref. 2, and to test them against experiment using materials for which data are available over a sufficiently wide frequency region. In particular, the connection between high-frequency behavior and short-time response will be emphasized, and the "inertial" character of the latter will be related to the physical meaning of the sum rules in Sec. II. In Sec. III a comparison with experiment is carried out for AgCl, Al, and Mo, and the usefulness of the sum rules as a test of extrapolations and of Kramers-Kronig inversions is demonstrated by a few examples. Section IV is devoted to a brief sketch of some extensions of the results of Ref. 2 to higher powers and moments of the optical constants, which may be of practical value because of the rapid convergence of the integrals involved.

II. PHYSICAL INTERPRETATION OF SUPERCONVERGENT SUM RULES

In the present section we discuss a number of the sum rules derived in Ref. 2 in terms of time-dependent (rather than frequency-dependent) linear response. It is found that the rules may be viewed as a consequence of the short-time behavior of the system following an excitation. In particular, the impossibility of an instantaneous response, i.e., inertia, leads to sum rules for components of the dielectric function tensor $\epsilon_{ij}(\omega)$ and its inverse, viz.,

$$\int_0^\infty [\mathrm{Re}\,\epsilon_{ij}(\omega) - \delta_{ij}]\, d\omega = -2\pi^2\sigma_{ij}(0) \tag{1}$$

and

$$\int_0^\infty [\mathrm{Re}\,\epsilon^{-1}_{ij}(\omega) - \delta_{ij}]\, d\omega = 0\ , \tag{2}$$

where $\sigma_{ij}(0)$ is the *ij*th component of the dc conductivity tensor, and to the sum rule for the real part of the refractive index $n(\omega)$ for a cubic or isotropic medium

$$\int_0^\infty [n(\omega) - 1]\, d\omega = 0\ . \tag{3}$$

For this reason these and similar rules in Sec. IV of the present paper might be classed as "inertial sum rules." Similar reasoning leads to the well-known result[4,5] that the *f* sum rules

$$\int_0^\infty \omega\, \mathrm{Im}\,\epsilon_{ij}(\omega)\, d\omega = \tfrac{1}{2}\pi\omega_p^2\delta_{ij}\ , \tag{4}$$

$$\int_0^\infty \omega\, \mathrm{Im}\,\epsilon^{-1}_{ij}(\omega)\, d\omega - \tfrac{1}{2}\pi\omega_p^2\delta_{ij}\ , \tag{5}$$

and

$$\int_0^\infty \omega\kappa(\omega)\, d\omega = \tfrac{1}{4}\pi\omega_p^2 \tag{6}$$

are a consequence of the dynamical equations of motion. For simplicity, in writing Eqs. (1), (2), (4), and (5) we have ignored spatial dispersion, which does not alter the arguments substantially.

The connection between the sum rules and the short-time response of the system may be related to the superconvergence theorem proof given in Ref. 2 by observing that in order to apply the theorem, certain conditions for the high-frequency behavior of $\epsilon(\omega)$, $n(\omega)$, etc., must be satisfied. In the time domain this corresponds to restrictions on the short-time response of the system. To see this in detail, consider the conventional classical discussion of the dielectric function in terms of volume polarization and the macroscopic electric field for an isotropic medium. The response of the medium may be characterized by the induced polarization

$$P(t)=(2\pi)^{-1/2}\int_{-\infty}^{+\infty} G(t-t')E(t')\,dt' , \tag{7}$$

where $E(t)$ is a component of the electric field, $P(t)$ is a component of the polarization, and $G(t-t')$ is the polarization kernel which gives the polarization at time t resulting from a unit-δ-function electric field pulse at time t'. Here, it is understood that $E(t)$ is square integrable, corresponding to a wave train of finite energy. Causality requires

$$G(t-t')=0 , \quad t<t' . \tag{8}$$

In the case of insulators, it is easily shown that[4]

$$G(\tau)=(2\pi)^{-1/2}\int_{-\infty}^{+\infty} \frac{\epsilon(\omega)-1}{4\pi}\, e^{-i\omega\tau}\,d\omega . \tag{9}$$

For metals, however, $\epsilon(\omega)$ has a simple pole at the origin since $\epsilon(\omega)=1+4\pi i\sigma(\omega)/\omega$, where $\sigma(\omega)$ is the complex conductivity, and Eq. (7) must be slightly modified to satisfy the theorems governing Fourier transforms. To this aim we follow the usual "adiabatic-switching" procedure,[5] and multiply $E(t')$ by a factor $e^{\eta t'}$, where η is positive and will be made to approach zero at the end of the calculation. Thus Eq. (7) takes the form

$$P(t)=(2\pi)^{-1/2}\int_{-\infty}^{+\infty} G(t-t')E(t')\,e^{\eta t'}\,dt' \tag{7$'$}$$

and Eq. (9) becomes

$$G(\tau)=(2\pi)^{-1/2}\int_{-\infty}^{+\infty} \frac{\epsilon(\omega+i\eta)-1}{4\pi} \times e^{-i(\omega+i\eta)\tau}\,d\omega . \tag{9$'$}$$

On closing the contour of integration in Eq. (9′) in the upper half-plane, it follows immediately from Cauchy's theorem that Eq. (8) is satisfied. Since the only singularity of ϵ lying on the real axis is at the origin, this procedure is equivalent to distorting the path of integration in Eq. (9) near the origin into the upper half-plane. Using the crossing relations for $\epsilon(\omega)$,

$$\epsilon(-\omega^*)=\epsilon^*(\omega) ; \tag{10}$$

and choosing a small semicircular distortion around the origin, we obtain

$$G(\tau)=(2\pi)^{-3/2}\left(\int_0^\infty [\mathrm{Re}\,\epsilon(\omega)-1]\cos(\omega\tau)\,d\omega + \int_0^\infty \mathrm{Im}\,\epsilon(\omega)\sin(\omega\tau)\,d\omega+2\pi^2\sigma(0)\right) . \tag{11}$$

Evaluating this expression for $\tau=0$, one obtains

$$G(\tau=0)=(2\pi)^{-3/2} \times\left(\int_0^\infty [\mathrm{Re}\,\epsilon(\omega)-1]\,d\omega+2\pi^2\sigma(0)\right) . \tag{12}$$

The sum-rule equation (1) for the real part of the dielectric tensor is therefore equivalent to the statement that

$$G(\tau=0)=0 . \tag{13}$$

In other words, there is no *instantaneous dielectric response,* because the inertia of the charges involved precludes an instantaneous polarization. The fact that the sum rule contains information about the inertial properties of the system should not be surprising, since its derivation[2] is based on the free-electron-like behavior of $\epsilon(\omega)$ at high frequencies, which in turn is a consequence of the dynamical equations.[6]

The f sum rule may also be related to the short-time behavior of the system, namely, to $dG/d\tau \equiv \dot{G}(\tau)$ at $\tau=0$. In order to show this, consider the inverse of Eq. (9′):

$$\frac{1}{4\pi}[\epsilon(\omega+i\eta)-1]=(2\pi)^{-1/2}\int_{-\infty}^{+\infty} G(\tau) \times e^{i(\omega+i\eta)\tau}\,d\tau=(2\pi)^{-1/2} \times \int_0^\infty G(\tau)\,e^{i(\omega+i\eta)\tau}\,d\tau , \tag{14}$$

where the causality requirement [Eq. (8)] was used. The validity of the inversion Eq. (14) is a consequence of the square integrability of ϵ along a straight line parallel to the real axis in the upper half-plane I_+. This, in turn, is a consequence of the square integrability of the conductivity $\sigma(\omega)$ on any such line.[7] Integrating Eq. (14) by parts twice and using Eq. (13), we obtain

$$\frac{1}{4\pi}[\epsilon(\omega+i\eta)-1]=-(2\pi)^{-1/2}\,\frac{1}{(\omega+i\eta)^2} \times\left(\dot{G}(0)+\int_0^\infty \ddot{G}(\tau)\,e^{i(\omega+i\eta)\tau}\,d\tau\right) . \tag{15}$$

Taking the limit of Eq. (15) as $\omega\to\infty$, the integral on the right-hand side vanishes (by the Riemann-Lebesgue lemma[8]), the left-hand side approaches the free-electron behavior

$$\epsilon(\omega)-1\sim-\omega_p^2/\omega^2 , \tag{16}$$

where ω_p is the plasma frequency, and therefore

$$\dot{G}(0^+)=\omega_p^2/2(2\pi)^{1/2} . \tag{17}$$

On the other hand, from Eq. (8),

$$\dot{G}(0^-) = 0 \ . \tag{18}$$

Therefore, the derivative of $G(\tau)$ has a discontinuity at $\tau = 0$.[9]

The f sum rule may be related to this short-time behavior by considering the derivative at $\tau = 0$ of the left-hand sides of the Fourier expansions Eq. (9′) or (11). Noting that this is a point of discontinuity for $\dot{G}(\tau)$, one obtains[10]

$$\int_0^\infty \omega \, \mathrm{Im}\epsilon(\omega)\, d\omega = (2\pi)^{3/2} \times \tfrac{1}{2}[\dot{G}(0^+) + \dot{G}(0^-)] = \tfrac{1}{2}\pi\omega_p^2 \ . \tag{19}$$

Summarizing, we have seen that $G(\tau)$, the response to an impulsive excitation at $\tau = 0$, remains identically zero for times up to and including $\tau = 0$. Then for small positive times $G(\tau)$ increases with a slope $\omega_p^2/2(2\pi)^{1/2}$. The continuity of $G(\tau)$ at $\tau = 0$, the moment of excitation, reflects the inertia of the system and is equivalent to the inertial sum rule [Eq. (1)]. The initial displacement, which is linear in τ, is the free-electron-like response expected for a system just following an impulsive excitation. That is, the response at times sufficiently short that displacements from equilibrium remain small and restoring and damping forces are negligible. This short-time response depends only on the charge and mass of the particles involved and not on the detailed interactions within the system. Physically, this is the content of the f sum rule [Eq. (4)].

It should be obvious at this point that a similar physical interpretation is possible for the sum rules equation (2) and (5) involving $\epsilon^{-1}(\omega)$. In this case P is related to the displacement D, and the argument is even simpler due to the absence of poles on the real axis. Actually, the use of the causality condition for the transform of ϵ^{-1} is justified on more fundamental grounds than its use for the transform of ϵ, a point that has been emphasized particularly by Martin.[11]

Let us now turn our attention to the sum rule equation (3) and (6), involving the complex index of refraction, $N(\omega)$. We shall consider the Fourier transform

$$R(\tau) = (2\pi)^{-1/2} \int_{-\infty}^{+\infty} [N(\omega) - 1]\, e^{-i\omega\tau}\, d\omega \ . \tag{20}$$

Despite the fact that R does not have a simple physical interpretation as a response function, its short-time behavior is determined by the dynamics of the system. The sum rules for the index can be given a physical interpretation very similar to that for the rules involving ϵ and ϵ^{-1}. To see this, let us first note that, in the case of metals, $N(\omega)$ has an integrable $\omega^{-1/2}$ singularity at the origin, and, its asymptotic behavior as $\omega \to \infty$ is

$$N(\omega) - 1 \sim -\tfrac{1}{2}\,\omega_p^2/\omega^2 \tag{21}$$

for either metals or nonmetals. From the analytic properties of $\epsilon(\omega) = N^2(\omega)$ and of N itself[2,7] it is easy to show that Eq. (20) can be written

$$R(\tau) = (2\pi)^{-1/2} \lim_{\eta \to 0^+} \int_{-\infty}^{+\infty} [N(\omega + i\eta) - 1] \times e^{-i(\omega + i\eta)\tau}\, d\omega \ . \tag{22}$$

Furthermore, application of the Phragmèn-Lindelöf theorem[12] to the function $\omega[N(\omega) - 1]$, which is bounded on the real axis and analytic in I_+,[13] allows one to conclude that the asymptotic behavior of Eq. (21) holds uniformly as $|\omega| \to \infty$ in I_+. Therefore, by closing the contour in Eq. (22) in the upper half-plane, one finds

$$R(\tau) = 0, \quad \tau < 0 \ . \tag{23}$$

In the special case of insulators, the same conclusion follows more simply from Titchmarsh's theorem.[7] From the relation between $N(\omega)$ and $\epsilon(\omega)$ it follows that

$$[\epsilon(\omega + i\eta) - 1] = 2[N(\omega + i\eta) - 1] + [N(\omega + i\eta) - 1]^2 \ . \tag{24}$$

Taking Fourier transforms, using the Faltung relations and Eqs. (22) and (23), we finally obtain

$$\begin{aligned} 4\pi G(\tau) &= 2R(\tau) + (2\pi)^{-1/2} \int_{-\infty}^{+\infty} R(s) R(\tau - s)\, ds \\ &= 2R(\tau) + (2\pi)^{-1/2} \int_0^\tau R(s) R(\tau - s)\, ds \ . \end{aligned} \tag{25}$$

Therefore, on evaluating Eq. (25) at $\tau = 0$ we have

$$R(\tau = 0) = 2\pi\, G(\tau = 0) \tag{26}$$

so that, using the symmetry properties of $N(\omega)$ in Eq. (22), we obtain

$$\int_0^\infty [n(\omega) - 1]\, d\omega = \tfrac{1}{2}(2\pi)^{3/2} G(\tau = 0) \ . \tag{27}$$

This relation, in analogy with Eq. (12), allows one to interpret the sum-rule equation (3) as a statement of the inertial properties of the dielectric response.

Differentiating Eq. (25) in the limit $\tau \to 0^+$, we obtain, using Eq. (17),

$$\dot{R}(0^+) = 2\pi \dot{G}(0^+) = (\tfrac{1}{2}\pi)^{1/2} \omega_p^2 \ , \tag{28}$$

and from Eq. (23)

$$\dot{R}(0^-) = 0 \ . \tag{29}$$

In analogy with Eq. (19), one then obtains from Eq. (22) the f sum rule

$$\int_0^\infty \omega \kappa(\omega)\, d\omega = \tfrac{1}{4}\pi\,\omega_p^2 \ ,$$

thus relating Eq. (6) with the short-time dynamics of the dielectric response. In summary, it has been shown that, despite the lack of a direct physical interpretation for $R(\tau)$, the dynamics of the system directly determine its short-time behavior and, in turn, the sum rules for the refractive index.

III. COMPARISON WITH EXPERIMENT

The optical properties of only a few materials have been investigated over a sufficiently wide energy range to be considered in light of the sum rules for n and $\mathrm{Re}\,\epsilon$. Here we discuss three examples: the insulator AgCl and two conductors, aluminum and molybdenum. Applications of the f sum rule to the first two of these have been discussed previously.[14,15] In general the published "experimental" optical constants have been obtained by Kramers-Kronig analysis of absorption and reflection measurements and represent self-consistent composites of experiments made over a number of different energy ranges.

To apply the sum rules, the published optical constants must be extrapolated outside the measured range to higher and lower frequencies. The low-frequency extrapolations for metals and insulators differ because of the low-frequency singularities in ϵ and N introduced by the conduction electrons. For insulators it was found that a satisfactory extrapolation of the electronic part of the dielectric function or index was obtained with a single-mode Lorentzian

$$\epsilon(\omega) \approx 1 + \omega_p^2/(\omega_0^2 - \omega^2) \quad \text{for } \omega \to 0 , \qquad (30)$$

where ω_0 and ω_p are obtained by fitting the optical constants at frequencies well below the fundamental absorption.

For metals the low-energy extrapolations were made in the free-electron model ($\omega_0 = 0$ limit) by fitting sufficiently low-energy data (usually well into the infrared) to the Drude expressions for $\mathrm{Re}\,\epsilon$ and $\mathrm{Im}\,\epsilon$

$$\mathrm{Re}\,\epsilon = n^2 - \kappa^2 = 1 - \omega_p^2/(\omega^2 + \tau^{-2}) , \qquad (31)$$

$$\mathrm{Im}\,\epsilon = 2n\kappa = \omega_p^2/\omega\tau(\omega^2 + \tau^{-2}) . \qquad (32)$$

Here the parameters required are the plasma frequency ω_p and the carrier relaxation time τ.

When comparing various "experimental" values of $\int_0^\infty [n(\omega) - 1]\,d\omega$ in light of the average-index sum rule, it is convenient to "normalize" the result to the integral of the absolute value by defining a "verification parameter"

$$\xi = \int_0^\infty [n(\omega) - 1]\,d\omega \Big/ \int_0^\infty |n(\omega) - 1|\,d\omega . \qquad (33)$$

According to the sum-rule equation (3), this should be zero. However, considering uncertainties in extrapolation and numerical methods, values of a few hundredths should be considered as good agreement with theory for the present discussion.

As an example of the average-index sum rule for an insulator we have considered Carrera and Brown's index-of-refraction data[14] for cubic AgCl. These data cover the range from 3.5 to 230 eV and were obtained from a Kramers-Kronig analysis of absorption and reflection measurements performed by Carrera and Brown[14] and by White and Straley.[16] The resulting refractive index together with extrapolations to lower and higher energies are shown in Fig. 1.

Over the range of energies treated by Carrera and Brown the index of refraction is essentially determined by electronic absorption. The more prominent features of this absorption include indirect band-to-band transitions forming the absorption edge at ~4 eV followed by strong direct exciton absorption at ~5 eV. Between 6 and 50 eV there are a variety of absorptions involving transitions from energy bands derived from Cl^--3s, Cl^--3p, and Ag^+-4d states. Between ~50 and 100 eV, the absorption is primarily from Ag^+-4p and -4s core states and just beyond 200 eV the $L_{\mathrm{II,III}}$ absorption of the Cl^--2p electrons occurs. The effect of all but the last of these can easily be seen as structure in the index curve of Fig. 1.

There are further absorptions at both higher and lower energies arising from excitation of ion-core x-ray levels and transverse-optical modes of the lattice. These, however, are well separated from the electronic absorption considered here and, to a good approximation, may be considered separately. That is, over the range in which these additional absorptions are important, the contribution to ϵ or N from the absorptions in the region from 3.5 to 230 eV is real and approximately a constant, say ϵ_0 or n_0. The x-ray and lattice absorptions may be regarded as due to oscillators in a medium characterized by constants ϵ_0 and n_0 rather than the

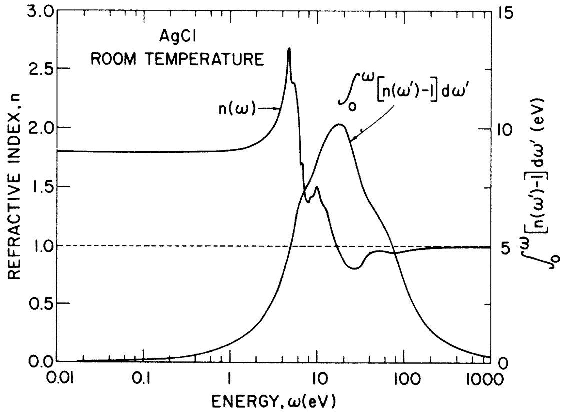

FIG. 1. Index of refraction of AgCl, after Carrera and Brown (Ref. 14), and the integral $\int_0^\omega [n(\omega') - 1]\,d\omega'$ as a function of energy.

vacuum values of unity. Thus, the contribution of these absorptions to Reϵ and n appear superimposed on the backgrounds ϵ_0 and n_0. By arguments similar to those used in proving the Reϵ and n sum rules, one expects the superimposed contributions to have equal areas above and below ϵ_0 and n_0 so that when integrated over frequency these additional contributions average to zero. The effect of these absorptions has therefore been neglected in the present study.

On evaluating the integral of $n(\omega) - 1$ for AgCl it was found that

$$\int_0^\infty [n(\omega') - 1]\, d\omega' = 0 \pm 0.03 \times \int_0^\infty |n(\omega') - 1|\, d\omega'$$

for all reasonable extrapolations. That is, the index-of-refraction data satisfy the inertial sum rule [Eq. (3)], with $|\zeta| < 0.03$. This is illustrated in Fig. 1 by means of the graph of the integral $\int_0^\omega [n(\omega') - 1]\, d\omega'$ as a function of ω. This function reaches a maximum at 17.5 eV, where n passes through unity and then decreases monotonically. For the particular extrapolation shown the integral approaches a limit of -0.06 eV [compared with $\int_0^\infty |n(\omega') - 1|\, d\omega' = 20.4$ eV], which may be considered to be zero to within the accuracy of the calculation.

In the case of metals the refractive index N has an $\omega^{-1/2}$ singularity at $\omega = 0$ arising from free-carrier absorption. This integrable singularity is particularly interesting because it weights the low-energy contributions to $\int_0^\infty [n(\omega') - 1]\, d\omega'$ heavily, making evaluation of this integral very sensitive to the optical constants in the far infrared.

As an example of a metal we consider aluminum which is cubic. The optical constants were first given over a wide energy range by Philipp and Ehrenreich[15] and subsequently revised by Sasaki and Inokuti[17] on the basis of more recent absorption studies. The latter index values cover the range from 0.02 to 10^4 eV and are shown up to 10^3 eV as the solid curve in Fig. 2. The prominent features of aluminum's optical properties in this energy range include intraband free-electron-like absorption at low frequencies, interband transitions involving conduction electrons leading to absorption peaks at ~0.5 and ~1.6 eV, and core excitations which yield the $L_{\mathrm{II,III}}$ edge at ~73 eV and K-shell excitations at ~1560 eV. In addition, most reflectance data show structure near 10 eV. This is attributed to surface plasmon excitations resulting from surface roughness.[18] Dispersion structures resulting from all except the 0.5 eV peak and the K edge are clearly seen in Fig. 2.

An alternative set of low-energy optical constants that are in agreement with measured reflectivities below ~0.155 eV has been proposed by Bennett and Bennett.[19] Their results for the index are shown in Fig. 2 by the dot-dash curve. The latter will be seen to join smoothly onto Sasaki and Inokuti's n values for higher energies, but there is considerable difference between the two below 0.1 eV. (Note the logarithmic scale.)

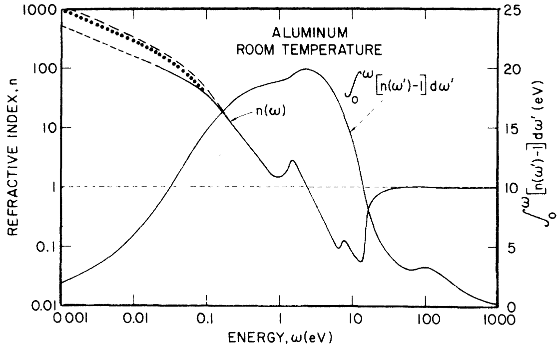

FIG. 2. Index of refraction of Al and the integral $\int_0^\omega [n(\omega') - 1]\, d\omega'$ as a function of energy. The index data of Sasaki and Inokuti (Ref. 17) are shown by the solid curve and that of Bennett and Bennett (Ref. 19) by the dot-dash curve. Low-energy extrapolations of the Sasaki-Inokuti data are shown by the dashed and dotted curves (see text). The integral shown corresponds to the extrapolation from 0.1 eV (dotted curve).

Interband absorption is negligible compared with free-electron absorption below ~0.4 eV.[20] The published index data were therefore extrapolated to low energies using the Drude-Lorentz expressions [Eqs. (31) and (32)] below this energy. A smooth extrapolation of Sasaki and Inokuti's data from 0.02 eV is shown by the dashed curve. Evaluation of $\int_0^\infty [n(\omega) - 1]\, d\omega$ for this extrapolation leads to $\zeta \sim 0.17$, a value well beyond acceptable bounds. This failure to verify the average index sum rule indicates an inconsistency between the data in the infrared and that at higher energies. Moreover, unacceptable values of ζ were found for all extrapolations from points below 0.1 eV. Similar large negative values of ζ were found using the index data of Philipp and Ehrenreich.

Use of Bennett and Bennett's low-energy index in place of that of Sasaki and Inokuti yields a value of $\zeta \sim +0.06$ which indicates approximate consistency. Even smaller values of ζ are obtained by ignoring the low-energy values of n in Sasaki and Inokuti's data and extrapolating to low energies from points above 0.1 eV. For all such extrapolations up to 0.6 eV—the point beyond which there is significant interference from band-to-band transitions—one finds values of ζ equal to less than 0.016 in magnitude, a very acceptable figure. One such low-energy extrapolation based on optical constants at 0.1 eV is shown as the dotted curve in Fig. 2.

These results prompted a reexamination of the calculations of Sasaki and Inokuti. It was found[21] that the difficulty lies in the assumption of a Hagen-Rubens asymptotic form below 0.1 eV—an assumption that does not hold for aluminum until much lower energies. This leads to a large underestimate of n below 0.1 eV, and hence large negative values for ζ. A revised set of optical constants is currently in preparation.[21]

This example of the use of the index sum rules is significant because it brings to light an inconsistency in analysis that normally would not have been detected. In particular, errors in the imaginary part of the index κ below 0.1 eV would not have led to significant deviations from the f sum rule. In that case the integrand involves $\omega\kappa(\omega)$ so that the integral is insensitive to $\kappa(\omega)$ at small ω. With the present technique the far infrared part of the spectrum is emphasized.

As an example of the Reϵ sum rule [Eq. (1)] we consider the measurements of Veal *et al.*[22] on bulk molybdenum at room temperature. Below about 0.2 eV the optical properties of this cubic metal are dominated by intraband electronic transitions which are well described in the Drude model.[23] Above this energy interband transitions become important and between 1 and 5.5 eV there are intense interband transitions involving large areas of the Brillouin zone.[23]

The dc conductivity $\sigma(0)$ may be estimated from the optical data in two different ways: (i) by fitting the low-energy part of Imϵ to the Drude model expression

$$\operatorname{Im}\epsilon(\omega) \approx 4\pi\sigma(0)/\omega \tag{34}$$

[For molybdenum this yields a value for $\sigma(0)$ of $103.8\hbar^{-1}$ eV]; (ii) by using the sum rule for Reϵ in the form

$$\sigma(0) = -\lim_{\omega\to\infty} \frac{1}{2\pi^2}\int_0^\omega [\operatorname{Re}\epsilon(\omega') - 1]\, d\omega' . \tag{35}$$

The value of this integral is plotted in Fig. 3 as a function of ω together with the value of $\sigma(0)$ obtained from the Drude model fit to Imϵ [Eq. (34)]. In accord with the sum rule the high-frequency limit of the integral and $\sigma(0)$ will be seen to agree to within the accuracy of the calculation.

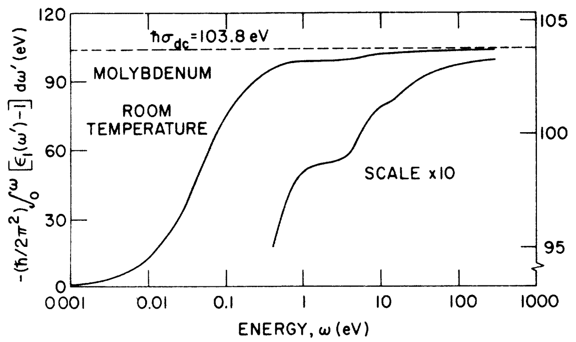

FIG. 3. Comparison of the dc conductivity of molybdenum as derived from Im ϵ via a fit to Drude theory and from $R\epsilon$ (abbreviated here as ϵ_1) via the sum-rule equation (1). The right-hand curve is drawn to an expanded scale to emphasize structure from interband transitions (after Veal, Ref. 22).

The effect of interband transitions on the integral above approximately 1 eV is shown on an expanded scale by the right-hand curve in Fig. 3. While it is only the conduction electrons which give a net contribution to Eq. (35), the interband transitions may cause the plateaulike structure shown and care must be taken to distinguish these plateaus from the high-frequency limit.

IV. SUM RULES INVOLVING POWERS OF THE OPTICAL CONSTANTS

We now discuss briefly the possibility of extending the sum rules for $N(\omega)$, $\epsilon(\omega)$, and $\epsilon^{-1}(\omega)$ to higher powers of these functions, i.e., to find sum rules for $[N(\omega)-1]^m$ or $\omega^n[N\omega)-1]^m$ and analogous expressions involving the dielectric tensor and its inverse. As pointed out independently by Villani and Zimerman,[24] the interesting feature of such sum rules is the rapid fall-off of the integrand as a function of ω as $\omega\to\infty$ and the consequent strong convergence of the integral.

Let us first consider the complex index of refraction $N(\omega)$ for a cubic or isotropic medium and separate the treatment of insulating media, for which $N(\omega)$ has no singularities on the real axis, from the case of metals, where both n and κ behave as $\sim\omega^{-1/2}$ in the vicinity of $\omega = 0$. In insulators, since $N(\omega) - 1$ is finite on the real axis, $[N(\omega) - 1]^m$, $(m = 1, \ldots)$ is square integrable; and if we define, in analogy with Eq. (20)

$$R_m(\tau) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty} [N(\omega) - 1]^m e^{-i\omega\tau}\, d\omega , \tag{36}$$

we obtain the recursion relation

$$R_m(\tau) = (2\pi)^{-1/2}\int_{-\infty}^{+\infty} R(s) R_{m-1}(\tau - s)\, ds \tag{37}$$

so that $R_m(\tau) = 0$ if $\tau < 0$ for all m. This together with square integrability implies, by Titchmarsh's theorem,[7] the existence of dispersion relations for $[N(\omega) - 1]^m$. Then from the first of these,

$$\operatorname{Im}\{[N(\omega) - 1]^m\} = -\frac{2\omega}{\pi}\, \mathcal{P}\int_0^\infty \frac{\operatorname{Re}\{[(N(\omega') - 1]^m\}\, d\omega'}{\omega'^2 - \omega^2} \tag{38}$$

the "superconvergence" theorem[2] yields

$$\int_0^\infty \operatorname{Re}\{[N(\omega') - 1]^m\}\, d\omega' = 0 \quad (m = 1, 2, 3, \ldots). \tag{39}$$

From the second,

$\operatorname{Re}\{[N(\omega) -]^m\}$

$$=\frac{2}{\pi}\mathcal{P}\int_0^\infty \frac{\omega'\,\mathrm{Im}\{[N(\omega')-1]^m\}}{\omega'^2-\omega^2}\,d\omega' \quad , \tag{40}$$

we obtain, in turn,

$$\int_0^\infty \omega'\,\mathrm{Im}\{[N(\omega')-1]^m\}d\omega' = \tfrac{1}{4}\pi\omega_p^2 \;\; (m=1)\,,$$
$$= 0 \qquad (m>1)\,. \tag{41}$$

In the case of conducting media we take $\omega[N(\omega)-1]$ as a starting point. This function is square integrable, is a casual transform[13] and therefore satisfies dispersion relations. Along the lines of the insulator case, it is then easy to show that $\omega^m[N(\omega)-1]^m$ satisfies dispersion relations as well. Attention must be paid to the fact that $\omega^m\,\mathrm{Re}\{[N(\omega)-1]^m\}$ is even (odd) if m is even (odd), whereas $\omega^m\,\mathrm{Im}\{[N(\omega)-1]^m\}$ is odd (even) if m is even (odd).

If m is odd, one dispersion relation reads

$$\omega^m\,\mathrm{Im}\{[N(\omega)-1]^m\}$$
$$=\frac{-2}{\pi}\mathcal{P}\int_0^\infty \frac{(\omega')^{m+1}\mathrm{Re}\{[N(\omega')-1]^m\}}{\omega'^2-\omega^2}\,d\omega'\,, \tag{42}$$

and taking the $\omega\to 0$ limit, we obtain

$$\int_0^\infty (\omega')^{m-1}\mathrm{Re}\{[N(\omega')-1]^m\}d\omega' = 0 \;\; (m=1,3,5,\ldots), \tag{43}$$

which is already a familiar result for $m=1$. The other dispersion relation is

$$\omega^m\,\mathrm{Re}\{[N(\omega)-1]^m\}$$
$$=\frac{2\omega}{\pi}\mathcal{P}\int_0^\infty \frac{(\omega')\,\mathrm{Im}\{[N(\omega')-1]^m\}}{\omega'^2-\omega^2}\,d\omega' \tag{44}$$

and, after dividing both sides by ω, the "superconvergence" theorem yields

$$\int_0^\infty (\omega')^m\,\mathrm{Im}\{[N(\omega')-1]^m\}d\omega'$$
$$=\begin{cases}\tfrac{1}{4}\pi\,\omega_p^2 & (m=1),\\ 0 & (m=3,5,7,..)\,.\end{cases} \tag{45}$$

Furthermore, for $m=3, 5, 7, \ldots$, we let $\omega\to 0$ after dividing Eq. (44) by ω and obtain

$$\int_0^\infty (\omega')^{m-2}\mathrm{Im}\{[N(\omega')-1]^m\}d\omega' = 0 \;\; (m=3,5,7,\ldots)\,. \tag{46}$$

Turning now to even m, one obtains by similar means from one dispersion relation the results

$$\int_0^\infty (\omega')^m\,\mathrm{Re}\{[N(\omega')-1]^m\}d\omega' = 0 \;\; (m=2,4,6,\ldots) \tag{47}$$

and

$$\int_0^\infty (\omega')^{m-2}\mathrm{Re}\{[N(\omega')-1]^m\}d\omega' = -\frac{\pi}{2}\lim_{\omega\to 0}\omega^{m-1}$$
$$\times\mathrm{Im}\{[N(\omega)-1]^m\} \;\; (m=2,4,6,\ldots)\,. \tag{48}$$

When $m=2$, Eq. (48) reduces to Eq. (1) and when $m=4, 6, 8,\ldots$ it becomes

$$\int_0^\infty (\omega')^{m-2}\mathrm{Re}\{[N(\omega')-1]^m\}d\omega' = 0 \;\; (m=4,6,8,\ldots)\,. \tag{49}$$

Furthermore, from the other dispersion relation, one has

$$\int_0^\infty (\omega')^{m-1}\mathrm{Im}\{[N(\omega')-1]^m\}d\omega' = 0 \tag{50}$$

and

$$\int_0^\infty (\omega')^{m+1}\mathrm{Im}\{[N(\omega')-1]^m\}d\omega'$$
$$=\begin{cases}-\tfrac{1}{8}\pi\omega_p^4 & (m=2),\\ 0 & (m=4,6,8,\ldots)\,.\end{cases} \tag{51}$$

Obviously, all the results obtained for metals, i.e., Eqs. (43) and (45)–(51) are valid for insulators as well, whereas the converse is not true for Eqs. (39) and (41).

Let us now consider the dielectric tensor $\epsilon_{ij}(\omega,\vec{k})$, and its inverse $\epsilon_{ij}^{-1}(\omega,\vec{k})$. The dielectric tensor for nonconducting media and the inverse dielectric tensor for all media are square integrable and have no singularities on the real axis. Therefore, we can follow the discussion outlined above for $N(\omega)-1$ in insulators and obtain a generalization of Eqs. (29), (30), (36), and (41)–(43) of Ref. 2, namely,

$$\int_0^\infty \mathrm{Im}\{[\epsilon_{ij}(\omega,\vec{k})-\delta_{ij}]^m\}d\omega$$
$$=\int_0^\infty \mathrm{Im}\{[\epsilon_{ij}(\omega,-\vec{k})-\delta_{ij}]^m\}d\omega \;(m=1,2,\ldots)\,, \tag{52}$$

$$\int_0^\infty \omega\,\mathrm{Im}\{[\epsilon_{ij}(\omega,\vec{k})-\delta_{ij}]^m+[\epsilon_{ij}(\omega,-\vec{k})-\delta_{ij}]^m\}d\omega$$
$$=\begin{cases}\pi\omega_p^2\delta_{ij} & (m=1)\,,\\ 0 & (m=2,3,\cdots)\,,\end{cases} \tag{53}$$

and

$$\int_0^\infty \mathrm{Re}\{[\epsilon_{ij}(\omega,\vec{k})-\delta_{ij}]^m+[\epsilon_{ij}(\omega,-\vec{k})-\delta_{ij}]^m\}d\omega = 0$$
$$(m=1,2,\ldots)\,. \tag{54}$$

The same results hold for ϵ^{-1}, the only difference being a change of sign in the right-hand side of Eq. (53) for $m=1$ [cf. Eqs. (30) and (42) of Ref.2]. As already emphasized, Eqs. (52)–(54) do not hold for metals, where the dielectric tensor has a simple pole at the origin. In that case, one may treat powers of $\omega[\epsilon_{ij}(\omega,\vec{k})-\delta_{ij}]$, i.e., of the conductivity tensor, or more generally expressions of the type $\omega^s[\epsilon_{ij}(\omega,\vec{k})-\delta_{ij}]^m$, as briefly discussed by Villani and Zimerman.[24]

As examples of the sum rules for various higher powers of $N(\omega)-1$, Eqs. (39) and (41) with $m=2$ and $m=3$ have been applied to Carrera and Brown's data for crystalline AgCl.[14] For these m values the explicit forms of Eq. (39) are

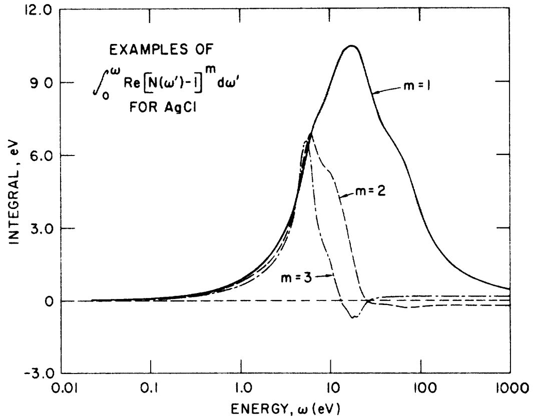

FIG. 4. Examples of sum-rule integrals involving $\mathrm{Re}[N(\omega)-1]^m$ for the room-temperature optical constants of AgCl reported by Carrera and Brown (Ref. 14).

$m=2$:

$$\int_0^\infty \{[n(\omega')-1]^2-\kappa^2(\omega')\}d\omega'=0\ , \tag{55}$$

$m=3$:

$$\int_0^\infty [n(\omega')-1]\{[n(\omega')-1]^2-3\kappa^2(\omega')\}d\omega'=0\ . \tag{56}$$

Similarly, Eq. (41) yields the rules

$m=2$:

$$\int_0^\infty \omega'\kappa(\omega')[n(\omega')-1]d\omega'=0\ , \tag{57}$$

$m=3$:

$$\int_0^\infty \omega'\kappa(\omega')\{3[n(\omega')-1]^2-\kappa^2(\omega')\}d\omega'=0\ . \tag{58}$$

In applying these rules, the integrals were studied as a function of their upper limits of integration as in the discussion of the $m=1$ case in Sec. III. The results are summarized in Figs. 4 and 5. For comparison the curves for $m=1$ are shown; with $m=1$, Eq. (39) reduces to the average-index sum-rule equation (3), while Eq. (41) yields the f sum rule for κ [Eq. (6)]. In general, it will be seen that the large the exponent m the faster the convergence of the integral.

The integrals for the sum rules involving $\mathrm{Re}[N(\omega)-1]^m$ [Eq. (39)] are shown in Fig. 4. Of these the $m=1$ integral does not approach its limiting value of approximately zero until well beyond 1000 eV, whereas the $m=2$ and $m=3$ integrals are reasonably well converged by 150 and 70 eV, respectively. The fact that the $m=2$ integral converges to a relatively small negative value and the $m=3$ integral converges to a small positive value rather than to zero indicates small errors in the function $N(\omega)$. That these errors are indeed small may be seen by noting that if "verification parameters" for $m=2$ and $m=3$ sum rules are defined in analogy with the $m=1$ case [Eq. (33)], values of only plus or minus several hundredth are found depending on how the data is extrapolated to lower and higher energies. This is taken to indicate satisfaction of the sum rules to within the accuracy of the data and the extrapolations used.

Similar results are found for the sum rules for $\mathrm{Im}[N(\omega)-1]^m$ [Eq. (41)]. These are indicated in Fig. 5. To interpret this figure it should be observed that Carrera and Brown's absorption data extends to 230 eV, which is just beyond the $\mathrm{Cl}^-\ L_{\mathrm{II,\,III}}$ edge. From the known excitation thresholds of the ion cores it is expected that for energies up to 200 eV—just below the $\mathrm{Cl}^-\ L_{\mathrm{II,\,III}}$ edge—26 electrons per Ag^+-Cl^- pair can contribute to real transitions. The corresponding value expected for the f sum integral ($m=1$ curve) is shown on the right-hand side of the figure by the mark denoted by $\frac{1}{4}\pi\omega_p^2$. When the experimental data is used in the $m=1$ integral, a value corresponding to transitions of between 23 and 24 electrons is found. This suggests either that there is further absorption lying beyond the $L_{\mathrm{II,III}}$ edge that is attributable to the most loosely bound 26 electrons per Ag^+-Cl^- pair or that the measured absorption is somewhat low. In any event, the f sum rule ($m=1$) curve shows the onset of a gentle plateauing below the $L_{\mathrm{II,III}}$ edge suggesting that the f sum rule for transitions below 200 eV is almost exhausted. On the other hand, the integrals for the $m=2$ and $m=3$ rules converge to relatively small values much faster apparently plateauing at approximately 200 and 110 eV, respectively. This suggests that the sum rules for higher powers are satisfied for practical

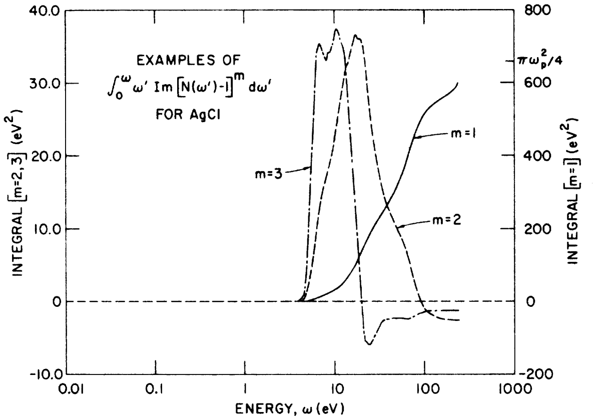

FIG. 5. Examples of sum-rule integrals involving $\mathrm{Im}[N(\omega)-1]^m$ for the room-temperature optical constants of AgCl reported by Carrera and Brown (Ref. 14). The right-hand scale refers to the $m=1$ case and the left-hand scale to the $m=2$ and $m=3$ cases. The value indicated by $\frac{1}{4}\pi\omega_p^2$ is the limiting value of the f sum-rule integral ($m=1$) for 26 electrons per AgCl pair that may be excited by energies below the $\mathrm{Cl}^-\ L_{\mathrm{II,III}}$ edge at approximately 200 eV.

purposes well before the f-sum rule has been exhausted. Here again the limiting values for the sum rules are considered small enough to indicate satisfaction of the rules to within the accuracy of the data.

It is perhaps worth remarking in connection with this example that Eq. (55) [the $m = 2$ case of Eq. (39)] may be rewritten in an easily remembered form, namely,

$$\int_0^\infty [n(\omega') - 1]^2 d\omega' = \int_0^\infty \kappa^2(\omega') d\omega' . \qquad (55')$$

This is a particular case of the general theorem that the norm of a function is preserved in Hilbert transforms.[25] While this fact does not seem to have been previously employed as a check on the inversion of optical data, it may prove useful in monitoring such calculations.

The sum rules given above and those in Ref. 24 are but a few examples of the immense number of such generalizations obtainable by the various techniques originally devised in high-energy physics.[26] It seems therefore that future developments should concentrate on identifying those sum rules which have direct physical interpretation, are relevant to other theoreticaly derivations, and are useful in the analysis of experiment, as in the example for aluminum treated in Sec. III.

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[1] See, for example, *Optical Properties of Solids*, edited by F. Abelès (North-Holland, Amsterdam, 1972).

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

[3] Some of the results are also found in W. N. Saslow, Phys. Lett. A 33, 157 (1970).

[4] See, for instance, F. Stern, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 15, p. 341.

[5] D. Pines and P. Nozières, *Theory of Quantum Liquids* (Benjamin, New York, 1966), Vol. 1, Sec. 2.3.

[6] See, e.g., H. Ehrenreich, in *The Optical Properties of Solids*, edited by J. Tauc (Academic, New York, 1966), p. 106, particularly Sec. 5.

[7] H. M. Nussenzveig, *Causality and Dispersion Relations* (Academic, New York, 1972), Theorem 1.6.1.

[8] E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford U. P., London, 1962).

[9] The discontinuity in $\dot{G}(\tau)$ at $\tau = 0$ is a result of the discontinuous nature of the (idealized) δ-function excitation. A feeling for the physical origin of this discontinuity can be obtained by treating the response of an oscillator to a δ-function pulse in the classical impulse approximation.

[10] Reference 8, Theorem (58).

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

[12] E. C. Titchmarsh, *The Theory of Functions* (Oxford U. P., London, 1968), Sec. 5.61; see also Ref. 7, Theorem 7.5.1.

[13] See Ref. 7, Sec. 1.4.

[14] N. J. Carrera and F. C. Brown, Phys. Rev. B 4, 3651 (1971).

[15] H. R. Philipps and H. Ehrenreich, J. Appl. Phys. 35, 1416 (1964).

[16] J. W. White and J. W Straley, J. Opt. Soc. Am. 58, 759 (1968).

[17] T. Sasaki and M. Inokuti, in *The Proceedings of the Third International Conference on Vacuum Ultra-Violet Radiation Physics* (The Physical Society of Japan, Tokyo, 1971).

[18] J. G. Endriz and W. E. Spicer, Phys. Rev. B 4, 4144 (1971); Phys. Rev. B 4, 4159 (1971).

[19] H. E. Bennett and J. M. Bennett, *Optical Properties and Electronic Structure of Metals and Alloys* edited by F. Abelès (North-Holland, Amsterdam 1966), p. 175.

[20] D. Brust, Phys. Rev. B 2, 818 (1970).

[21] M. Inokuti (private communication).

[22] B. Veal and A. P. Paulikas (unpublished).

[23] M. M. Kirillova, L. V. Nomerovannaya, and M. M. Noskov, Zh. Eksp. Teor. Fiz. 60, 2252 (1971) [Sov. Phys.-JETP 33, 1210 (1971)]; and D. D. Koelling, F. M. Mueller, and B. Veal (unpublished).

[24] A. Villani and A. H. Zimmerman, Phys. Rev. B 8, 3914 (1973); see also A. Villani and A. H. Zimerman, Phys. Lett. A 44, 295 (1973). We are indebted to the authors for communicating their results before publication.

[25] Reference 8, Theorems 90 and 91.

[26] For a comprehensive review, see C. Ferro Fontán, N. M. Queen, and G. Violini, Rivista del Nuovo Cimento 2, 357 (1972).