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Superconvergence and Sum Rules for the Optical Constants

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A systematic procedure is given for the derivation of sum rules for the optical constants of material media from dispersion relations, in analogy with superconvergence techniques of high-energy physics. In addition to the well-known f-sum rules, a number of new sum rules are obtained for the refractive index, the dielectric tensor, and its inverse. In particular, it is shown that the average value of the real refractive index over the whole frequency spectrum is equal to unity. The physical implications of the new results are discussed in connection with the dispersion of optical constants, with the effect of external perturbations, and with the theory of natural optical activity.

I. INTRODUCTION

It is well known that the optical "constants" of linear media verify various sum rules, of which the best known are the "f-sum rules." The latter rules follow[1] from the Kramers–Kronig relations, together with the physical requirement that in the high-frequency limit, i.e., at frequencies much higher than any resonant frequency of the medium, its electromagnetic response is essentially free-electron-like.

In the present work, we give a systematic derivation of sum rules, including, besides the known sum rules, some apparently new ones, which, in spite of their extremely simple and basic character, seem to have gone unnoticed hitherto. In particular, it will be shown that, if $N(\omega)=n(\omega)+i\kappa(\omega)$ denotes the complex refractive index of an isotropic or cubic medium at frequency ω, we have

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

The derivation of sum rules from dispersion relations is possible whenever the convergence of the dispersion integrals is sufficiently rapid. For this purpose, we employ a straightforward procedure, similar to that which leads to superconvergence relations[2] in high-energy physics.

The assumptions are the same as those that lead to the f-sum rule, so that the results should have equally general validity. Besides an isotropic medium, we also consider the more general case of an arbitrary (nonmagnetic) linear medium.

In Sec. II, we briefly recall some well-known sum rules, particularly various formulations of the "f-sum rule." In Sec. III, we derive sum rules for the refractive index of an isotropic medium. In Sec. IV, the results are extended to the frequency- and wave-number-dependent dielectric tensor and its inverse. Section V contains a summary of the results and a discussion of some of their consequences. The basic mathematical theorem on the asymptotic behavior of Hilbert transforms that is employed throughout the paper (henceforth referred to as the "superconvergence theorem") is discussed in the Appendix.

II. f-SUM RULES

There are various results that are generally termed "f-sum rules" in the literature. The original formulation is the Thomas–Reiche–Kuhn sum rule for dipole matrix elements of atomic transitions. Let j, j' be labels for two atomic states; the oscillator strength is defined by

$$f_{j'j} = (2m/\hbar)\,\omega_{j'j}\,|x_{j'j}|^2\ , \tag{2}$$

where $\omega_{j'j}=(E_{j'}-E_j)/\hbar$. The Thomas–Reiche–Kuhn rule[3] states that

$$\sum_{j'} f_{j'j} = Z\ , \tag{3}$$

where Z is the total number of electrons of the atomic system, and the summation over j' is understood to include the continuum states. Other sum rules for the oscillator strengths can be found in Ref. 3.

For a medium with $\mathfrak{N}$ electrons per unit volume, the oscillator strength density $f(\omega)$ at frequency ω is obtained by summing over all $f_{j'j}$ associated with this frequency, so that (3) becomes, when the system is in its ground state,

$$\int_0^\infty f(\omega)\,d\omega = \mathfrak{N}\ . \tag{4}$$

(If the system is not in its ground state, the integral is to be extended to negative frequencies as well.) The imaginary part of the dielectric constant is related to $f(\omega)$ by[1]

$$f(\omega) = \frac{m}{2\pi^2 e^2}\,\omega\,\mathrm{Im}\,\epsilon(\omega) \ , \tag{5}$$

so that (4) may be rewritten

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

where

$$\omega_p^2 = 4\pi\mathfrak{N}e^2/m \tag{7}$$

is the square of the plasma frequency. The relation (6) is usually referred to as the "*f*-sum rule."

There is, however, a different result that is also generally referred to as an "*f*-sum rule," namely,[4]

$$\int_0^\infty \omega\kappa(\omega)\,d\omega = \tfrac{1}{4}\pi\,\omega_p^2 \ , \tag{8}$$

where $\kappa(\omega)$ is the imaginary part of the refractive index, as defined before. Since

$$\mathrm{Im}\,\epsilon(\omega) = 2n(\omega)\kappa(\omega) \ , \tag{9}$$

it follows from (6) and (8) that

$$\int_0^\infty \omega\kappa(\omega)\,[n(\omega)-1]\,d\omega = 0 \ . \tag{10}$$

Another sum rule holds for $\mathrm{Im}\,\epsilon^{-1}(\omega)$, and it is sometimes also referred to as an "*f*-sum rule":

$$\int_0^\infty \omega\,\mathrm{Im}\,\epsilon^{-1}(\omega)\,d\omega = -\tfrac{1}{2}\pi\omega_p^2 \ . \tag{11}$$

All these familiar sum rules, among others, will be derived in the following sections.

III. REFRACTIVE INDEX

As a first example of the generation of sum rules by the superconvergence technique, let us consider the simple case of the complex refractive index for a nonconducting isotropic medium. According to the Kramers–Kronig relations,

$$n(\omega)-1 = \frac{2}{\pi}\,\mathcal{P}\int_0^\infty \frac{\omega'\kappa(\omega')}{\omega'^2-\omega^2}\,d\omega' \ , \tag{12}$$

$$\kappa(\omega) = -\frac{2\omega}{\pi}\,\mathcal{P}\int_0^\infty \frac{n(\omega')-1}{\omega'^2-\omega^2}\,d\omega' \ , \tag{13}$$

where $\mathcal{P}$ denotes the Cauchy principal value.

The basic assumption that the medium responds like a free-electron gas in the high-frequency limit (Sec. I) means that (recall that $N = n + i\kappa$)

$$N(\omega)-1 \approx -2\pi\mathfrak{N}e^2/m\omega^2 = -\tfrac{1}{2}\omega_p^2/\omega^2, \quad \omega\to\infty. \tag{14}$$

It is important to note that (14) makes two separate assertions: (i) that $n(\omega)-1$ behaves asymptotically like the right-hand side of (14) and (ii) that[5]

$$\kappa(\omega) = o(\omega^{-2}), \quad \omega\to\infty \ . \tag{15}$$

In order to apply the superconvergence theorem given in the Appendix, we employ a slightly more restrictive form of (15), by assuming that[5]

$$\kappa(\omega) = O(\omega^{-2}\ln^{-\alpha}\omega), \quad \alpha>1, \quad \omega\to\infty \ , \tag{16}$$

i.e., that $\kappa(\omega)$ decreases *at least* as fast as $\omega^{-2}\ln^{-\alpha}\omega$ as $\omega\to\infty$ [a similar assumption is made for $\omega\kappa'(\omega)$; cf. (A2)]. This is a very mild restriction, since we expect that $\kappa(\omega)$ will in fact decrease faster than (16) for any actual physical system.

With the change of variable $\omega'^2 = x$ in (12), we can then immediately apply the superconvergence theorem, in the form (A11), and conclude that

$$n(\omega)-1 = -\frac{2}{\pi\omega^2}\int_0^\infty \omega'\kappa(\omega')\,d\omega' + O(\omega^{-2}\ln^{1-\alpha}\omega), \quad \omega\to\infty \ . \tag{17}$$

Note that (16) already suffices to imply that $n(\omega) - 1 = O(\omega^{-2})$; by comparing (17) with (14), it follows that

$$\int_0^\infty \omega\kappa(\omega)\,d\omega = \tfrac{1}{4}\pi\,\omega_p^2 \ , \tag{18}$$

which is the *f*-sum rule in the form (8).

The physical assumption (14) or merely the result (17) now allows us to apply the superconvergence theorem to the other Kramers–Kronig relation (13). With the same change of variable $\omega'^2 = x$, we find that (17) corresponds to (A3), with $\beta = \frac{3}{2}$, so that (A12) yields

$$\kappa(\omega) = \frac{2}{\pi\omega}\int_0^\infty [n(\omega')-1]\,d\omega' + O(\omega^{-2}), \quad \omega\to\infty \ . \tag{19}$$

By comparing (19) with (16), we are led to the sum rule (1),

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

Although it was stated at the beginning of this section that the medium under consideration is nonconducting, all the results remain valid for an isotropic conducting medium, in spite of the singularity at $\omega = 0$ arising from the well-known low-frequency term $4\pi i\sigma(0)/\omega$ in the complex dielectric constant, where $\sigma(0)$ is the dc conductivity. This will be proved in Sec. IV.

We defer comments on the physical significance of the sum rule (1) to Sec. V.

IV. FREQUENCY- AND WAVE-VECTOR-DEPENDENT DIELECTRIC TENSOR

We now extend the results to the most general case of a linear nonmagnetic medium (i.e., a material for which the magnetic permeability can be set equal to unity at all frequencies). The electromagnetic response of the medium is then described by the frequency- and wave-vector-dependent dielectric tensor $\epsilon_{ij}(\omega, \vec{k})$, which is related to the complex conductivity tensor $\sigma_{ij}(\omega, \vec{k})$ by the well-known equation

$$\epsilon_{ij}(\omega, \vec{k}) = \delta_{ij} + 4\pi i\sigma_{ij}(\omega, \vec{k})/\omega \ . \tag{20}$$

Thus, if $\sigma_{ij}(0, \vec{k}) \neq 0$, then $\mathrm{Im}\,\epsilon_{ij}(\omega, \vec{k})$ has a pole at the origin in the ω plane. In analogy with (14), we now have

$$\epsilon_{ij}(\omega, \vec{k}) - \delta_{ij} \approx -(\omega_p^2/\omega^2)\delta_{ij}, \quad \omega \to \infty . \tag{21}$$

Since $\sigma_{ij}(\omega, \vec{k})$ is a causal transform,[6] it satisfies the Kramers–Kronig relations, which, by (20), can be written

$$\omega[\mathrm{Re}\,\epsilon_{ij}(\omega, \vec{k}) - \delta_{ij}] = \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\omega'\,\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k})}{\omega' - \omega}\,d\omega' , \tag{22}$$

$$\omega\,\mathrm{Im}\,\epsilon_{ij}(\omega, \vec{k}) = -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\omega'[\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) - \delta_{ij}]}{\omega' - \omega}\,d\omega' . \tag{23}$$

We can also write down dispersion relations with the help of subtraction techniques[6] by considering the function $[\sigma_{ij}(\omega, \vec{k}) - \sigma_{ij}(0, \vec{k})]/\omega$. The result, expressed in terms of ϵ_{ij}, is

$$\mathrm{Re}\,\epsilon_{ij}(\omega, \vec{k}) - \delta_{ij} = \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k})}{\omega' - \omega}\,d\omega' , \tag{24}$$

$$\mathrm{Im}\,\epsilon_{ij}(\omega, \vec{k}) - 4\pi\,\frac{\sigma_{ij}(0, \vec{k})}{\omega} = -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) - \delta_{ij}}{\omega' - \omega}\,d\omega' . \tag{25}$$

In a similar manner as Sec. III, we sharpen (21) by assuming for $\mathrm{Im}\,\epsilon_{ij}(\omega, \vec{k})$ an asymptotic behavior of the type (16) as $\omega \to \infty$. We also apply the identity

$$\frac{1}{\omega - \omega'} = \frac{1}{\omega} + \frac{\omega'}{\omega(\omega - \omega')} , \tag{26}$$

as well as the symmetry (crossing) relation (for real ω and $\vec{k}$)

$$\epsilon_{ij}(-\omega, -\vec{k}) = \epsilon_{ij}^*(\omega, \vec{k}) , \tag{27}$$

which follows from the reality condition for the fields. The relation (24) then becomes

$$\begin{aligned}\mathrm{Re}\,\epsilon_{ij}(\omega, \vec{k}) - \delta_{ij} &= -\frac{1}{\pi\omega}\int_0^{\infty} [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) - \mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})]\,d\omega' \\ &\quad - \frac{1}{\pi\omega}\,\mathcal{P}\int_0^{\infty} \left(\frac{\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k})}{\omega - \omega'} + \frac{\mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})}{\omega + \omega'}\right) \\ &\quad \times \omega'\,d\omega' .\end{aligned} \tag{28}$$

We can now apply the superconvergence theorem in the form (A11) to the last integral in (28). Comparing the result with (21), we get two sum rules,

$$\int_0^{\infty} [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) - \mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})]\,d\omega' = 0 , \tag{29}$$

$$\int_0^{\infty} [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) + \mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})]\,\omega'\,d\omega' = \pi\omega_p^2\delta_{ij} . \tag{30}$$

The sum rule (29) is nontrivial for gyrotropic media, which are characterized by

$$\epsilon_{ij}(\omega, \vec{k}) \neq \epsilon_{ij}(\omega, -\vec{k}) \tag{31}$$

and are therefore optically active. By means of the Onsager relation[7]

$$\epsilon_{ij}(\omega, \vec{k}) = \epsilon_{ji}(\omega, -\vec{k}) , \tag{32}$$

we can rewrite (29) in the alternative form

$$\int_0^{\infty} [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) - \mathrm{Im}\,\epsilon_{ji}(\omega', \vec{k})]\,d\omega' = 0 . \tag{33}$$

For nongyrotropic media, (30) becomes

$$\int_0^{\infty} \omega'\,\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k})\,d\omega' = \tfrac{1}{2}\pi\,\omega_p^2\delta_{ij} . \tag{34}$$

The results (30) and (34) are general formulations of the f-sum rule (6).

Let us now apply the same procedure to the other Kramers–Kronig relation (25). With the help of (27), this relation may be rewritten

$$\begin{aligned}\mathrm{Im}\,\epsilon_{ij}(\omega, \vec{k}) &= \frac{4\pi}{\omega}\,\sigma_{ij}(0, \vec{k}) \\ &\quad + \frac{1}{\pi}\,\mathcal{P}\int_0^{\infty} \frac{\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) - \delta_{ij}}{\omega - \omega'}\,d\omega' \\ &\quad + \frac{1}{\pi}\,\mathcal{P}\int_0^{\infty} \frac{\mathrm{Re}\,\epsilon_{ij}(\omega', -\vec{k}) - \delta_{ij}}{\omega + \omega'}\,d\omega' .\end{aligned} \tag{35}$$

By (21), we can now apply the superconvergence theorem in the form (A13), yielding the sum rule

$$\int_0^{\infty} [\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) + \mathrm{Re}\,\epsilon_{ij}(\omega', -\vec{k}) - 2\delta_{ij}]\,d\omega' = -4\pi^2\sigma_{ij}(0, \vec{k}) . \tag{36}$$

For nongyrotropic media, (36) becomes

$$\int_0^{\infty} [\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) - \delta_{ij}]\,d\omega' = -2\pi^2\sigma_{ij}(0, \vec{k}) . \tag{37}$$

Let us now consider the inverse dielectric tensor $\epsilon_{ij}^{-1}(\omega, \vec{k})$, which plays an important role in the discussion of electron energy-loss experiments. As a linear response function, it satisfies the dispersion relations[8]

$$\mathrm{Re}\,\epsilon_{ij}^{-1}(\omega, \vec{k}) - \delta_{ij} = \frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', \vec{k})}{\omega' - \omega}\,d\omega' , \tag{38}$$

$$\mathrm{Im}\,\epsilon_{ij}^{-1}(\omega, \vec{k}) = -\frac{1}{\pi}\,\mathcal{P}\int_{-\infty}^{+\infty} \frac{\mathrm{Re}\,\epsilon_{ij}^{-1}(\omega', \vec{k}) - \delta_{ij}}{\omega' - \omega}\,d\omega' . \tag{39}$$

On the other hand, it follows from (21) that

$$\epsilon_{ij}^{-1}(\omega, \vec{k}) - \delta_{ij} \approx (\omega_p^2/\omega^2)\delta_{ij}, \quad \omega \to \infty . \tag{40}$$

By comparison with (24) and (25), it is obvious that the superconvergence theorem, applied to (38) and (39), leads to the sum rules

$$\int_0^\infty \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', \vec{k})\,d\omega' = \int_0^\infty \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', -\vec{k})\,d\omega' = \int_0^\infty \mathrm{Im}\,\epsilon_{ji}^{-1}(\omega', \vec{k})\,d\omega' \,, \tag{41}$$

$$\int_0^\infty [\mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', \vec{k}) + \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', -\vec{k})]\,\omega'\,d\omega' = -\pi\omega_p^2\delta_{ij} \,, \tag{42}$$

$$\int_0^\infty [\mathrm{Re}\,\epsilon_{ij}^{-1}(\omega', \vec{k}) + \mathrm{Re}\,\epsilon_{ij}^{-1}(\omega', -\vec{k}) - 2\delta_{ij}]\,d\omega' = 0 \,. \tag{43}$$

For nongyrotropic media, (42) and (43) are simplified in an obvious way; (42) is the general formulation of the f-sum rule (11). Note that, in contrast to (29) and (33), the integrals in (41) are separately convergent at $\omega' = 0$ [cf. (20)].

Finally, let us go back to the discussion of the refractive index for an isotropic medium, and let us justify the statement made at the end of Sec. III that all the results of that section remain valid for a conducting medium, in spite of the fact that both $n(\omega)$ and $\kappa(\omega)$ behave like $\omega^{-1/2}$ as $\omega \to 0$. This follows from the fact that $\omega[N(\omega) - 1]$ is a causal transform,[9] so that it satisfies dispersion relations similar to (22) and (23). For $\omega \neq 0$, one can divide both sides of these dispersion relations by ω, and one recovers the Kramers–Kronig relations (12) and (13). The rest of the argument proceeds exactly as in Sec. III.

V. SUMMARY AND DISCUSSION

A. Summary of Results

We list here, for convenience, all the sum rules obtained above. For isotropic media, including the case of a conductor, we have

$$\int_0^\infty [n(\omega) - 1]\,d\omega = 0 \,, \tag{44}$$

$$\int_0^\infty \omega\kappa(\omega)\,d\omega = \tfrac{1}{4}\pi\,\omega_p^2 \,. \tag{45}$$

For any linear nonmagnetic medium, including the possibilities of anisotropy, spatial dispersion, and optical activity, we have

$$\int_0^\infty [\mathrm{Re}\,\epsilon_{ij}(\omega', \vec{k}) + \mathrm{Re}\,\epsilon_{ij}(\omega', -\vec{k}) - 2\delta_{ij}]\,d\omega' = -4\pi^2\sigma_{ij}(0, \vec{k}) \,, \tag{46}$$

$$\int_0^\infty [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) - \mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})]\,d\omega' = \int_0^\infty \mathrm{Im}[\epsilon_{ij}(\omega', \vec{k}) - \epsilon_{ji}(\omega', \vec{k})]\,d\omega' = 0 \,, \tag{47}$$

$$\int_0^\infty [\mathrm{Im}\,\epsilon_{ij}(\omega', \vec{k}) + \mathrm{Im}\,\epsilon_{ij}(\omega', -\vec{k})]\,\omega'\,d\omega' = \pi\omega_p^2\delta_{ij} \,, \tag{48}$$

$$\int_0^\infty [\mathrm{Re}\,\epsilon_{ij}^{-1}(\omega', \vec{k}) + \mathrm{Re}\,\epsilon_{ij}^{-1}(\omega', -\vec{k}) - 2\delta_{ij}]\,d\omega' = 0 \,, \tag{49}$$

$$\int_0^\infty \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', \vec{k})\,d\omega' = \int_0^\infty \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', -\vec{k})\,d\omega' = \int_0^\infty \mathrm{Im}\,\epsilon_{ji}^{-1}(\omega', \vec{k})\,d\omega' \,, \tag{50}$$

$$\int_0^\infty [\mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', \vec{k}) + \mathrm{Im}\,\epsilon_{ij}^{-1}(\omega', -\vec{k})]\,\omega'\,d\omega' = -\pi\omega_p^2\delta_{ij} \,. \tag{51}$$

For nongyrotropic media, $\epsilon_{ij}(\omega, \vec{k}) = \epsilon_{ij}(\omega, -\vec{k})$, so that these relations can be simplified [(47) and (50) become trivial in this case].

B. Alternative Derivations

The sum rules (46) and (47) also follow immediately from (22) and (23) by setting $\omega = 0$. The f-sum rule (48) can also be derived from (22), but still by applying the superconvergence theorem. Similarly, (44) follows from the dispersion relation for $\omega[N(\omega) - 1]$ by setting $\omega = 0$.

For isotropic nonconducting media, (44) can also be proved by extending the integral over the whole real axis [making use of the even character of $n(\omega)$] and by closing the contour at infinity in the upper half-plane. That the half-circle at infinity does not contribute, however, does not follow immediately from (14), which gives the asymptotic behavior along the real axis; nevertheless, this can be shown by a rather elaborate argument based on analytic function theory. Even greater caution is necessary in the case of a conductor, because of the singularity at the origin.

The above alternative derivations, although they may be simpler in some specific cases, are not uniformly applicable to obtain all of the sum rules. The superconvergence theorem seems to provide the most straightforward method to achieve this purpose.

C. Examples

Probably the simplest model that provides an illustration of the sum rules is the well-known Lorentz model. In this model

$$\epsilon(\omega) - 1 = 4\pi\frac{e^2}{m}\sum_j \frac{f_j}{(\omega_j^2 - \omega^2) - 2i\gamma_j\omega} \,, \tag{52}$$

which includes the possibility of a Drude-type conductivity term corresponding to $\omega_j = 0$. This is actually a fairly general type of dispersion formula.[10] The validity of the pertinent sum rules can readily be checked for this model by contour integration, using the fact that $\epsilon(\omega)$, as given by (52), has neither poles nor zeros in the upper half-plane.

As a second example, let us verify the longitudinal version of (49) for an electron gas, assuming zero temperature for simplicity. For an isotropic medium, the inverse dielectric tensor can be decomposed into a longitudinal and a transverse component, which satisfy separate dispersion relations,[10] so that one gets a separate sum rule,

$$\int_0^\infty [\mathrm{Re}\,\epsilon_L^{-1}(\omega', \vec{k}) - 1]\,d\omega' = 0 \,. \tag{53}$$

For the zero-temperature electron gas, $\epsilon_L^{-1}(\omega, \vec{k})$ is given by[11]

$$\epsilon_L^{-1}(\omega, \vec{k}) = 1 + (4\pi e^2/k^2) F^r(\omega, \vec{k}) \,, \qquad (54)$$

where $F^r(\omega, \vec{k})$ is the frequency Fourier transform of

$$F^r(\tau, \vec{k}) = -i\theta(\tau) \langle 0 | [\rho_{\vec{k}}(\tau), \rho_{-\vec{k}}(0)] | 0 \rangle \,, \qquad (55)$$

and $\theta(\tau)$ is the Heaviside step function. Here $\rho_{\vec{k}}(\tau)$ is the Fourier transform of the local density operator; note that $\rho_{\vec{k}}^{\dagger}(\tau) = \rho_{-\vec{k}}(\tau)$, since $\rho(\vec{r}, \tau)$ is Hermitian. We have[11]

$$\mathrm{Re} F^r(\omega, \vec{k}) = \sum_j |(\rho_{\vec{k}})_{j0}|^2 \, \frac{2\omega_{j0}}{\omega^2 - \omega_{j0}^2} \,, \qquad (56)$$

where j labels a complete set of eigenstates and the summation is to be understood as a principal value integral. We then have, since (56) is an even function of ω,

$$\int_0^\infty [\mathrm{Re}\,\epsilon_L^{-1}(\omega, \vec{k}) - 1] \, d\omega = \frac{2\pi e^2}{k^2} \int_{-\infty}^{+\infty} \mathrm{Re} F^r(\omega, \vec{k}) \, d\omega$$

$$= \frac{2\pi e^2}{k^2} \lim_{\tau \to +0} \mathrm{Re} F^r(\tau, \vec{k}) = 0 \,, \qquad (57)$$

in agreement with (53).

We see that this result is actually a property of $F^r(\omega, \vec{k})$, i.e., of the retarded density-density commutator (55). This quantity plays an important role not only for energy-loss experiments in charged systems, but also in the description of neutron scattering in condensed media. The neutron scattering cross section is proportional to the Van Hove structure function $S(\omega, \vec{k})$, which is related to (55) by

$$S(\omega, \vec{k}) = \mathrm{Im} F^r(\omega, \vec{k}) \,.$$

Thus, (53) can also be regarded as a sum rule for the Kramers–Kronig transform of the structure function.

D. Concluding Remarks

The sum rules that have been derived in this paper can be classified into roughly four different categories. The first one consists of the f-sum rules (45), (48), and (51), which are all well known and have been thoroughly discussed in the literature. All the other sum rules in Sec. V A seem to be new.

The second category relates to average values of $n(\omega) - 1$, and it includes (44) and (10). The existence of the latter sum rule had already been recognized by Stern.[4] The sum rules (46) and (49) for the real part of the dielectric tensor or its inverse define the third category. Finally, the fourth one refers to the relations (47) and (50), which have nontrivial content only for a gyrotropic medium.

Let us now discuss the sum rules (44) and (10). They assert that *the average value of the real refractive index over the whole frequency spectrum is equal to unity, whether or not the average is taken with the absorption coefficient* $\mu(\omega)$ [$= 2\omega\kappa(\omega)/c$] as a weighting factor. It seems rather remarkable that the very simple result (44), which stands on equal footing with the well-known f-sum rule (45), of which it is the Kramers–Kronig counterpart, has apparently been unnoticed heretofore.[12] A comparison between the two different versions of the result $n_{\mathrm{av}} = 1$ provides some insight into the qualitative behavior of the dispersion curve for $n(\omega) - 1$. The sum rule (44) states that the portions of this curve lying above and below the frequency axis must have the same total area. We know from (14) that the very-high-frequency contribution is negative. However, there must be additional negative contributions, because the result remains true with the weighting factor $\omega\kappa(\omega)$, which reduces the high-frequency contribution by a factor $o(\omega^{-1})$. This non-negative weighting factor emphasizes the contributions from high-absorption regions of the spectrum, so that one should expect $n(\omega) - 1$ to take negative values over part of these regions. For a conducting medium, there is a positive contribution from the integrable $\omega^{-1/2}$ singularity at the origin in (44), whereas in (10) the singularity disappears.

It is of interest to investigate the constraints on the possible perturbations of the optical constants of a medium by external agents (such as impurities in a solid or external fields) that follow from the above results. Let $N(\omega) = n(\omega) + i\kappa(\omega)$ and $N(\omega) + \Delta N(\omega) = N(\omega) + \Delta n(\omega) + i\Delta\kappa(\omega)$ be the refractive indices of the unperturbed and perturbed system, respectively. Owing to the linearity of the Kramers–Kronig relations, Eq. (17) still holds for the perturbed quantities, i.e.,

$$\Delta n(\omega) = -(c/\pi\omega^2) \int_0^\infty \Delta\mu(\omega) \, d\omega + o(\omega^{-2}), \quad \omega \to \infty \qquad (58)$$

where $\Delta\mu(\omega) = 2\omega\Delta\kappa(\omega)/c$ is the perturbation in the absorption coefficient $\mu(\omega)$.

It follows from (58) that, even for a variation $\Delta\mu(\omega)$ restricted to a narrow spectral interval, the corresponding real refractive index variation $\Delta n(\omega)$ has a long tail, with the same slow ω^{-2} decrease as a Lorentzian, far from the absorption region. This accounts for the large width of the Faraday rotation line shapes associated with Gaussian or other narrow impurity absorption structures.[13] An asymptotic decrease of Δn faster than ω^{-2} is only possible when the total area of the absorption coefficient variation $\Delta\mu(\omega)$ vanishes. This of course can only happen if absorption is reduced in some regions of the spectrum and enhanced in others; an interesting possibility might be provided by an antiresonance line shape.

Furthermore, in order to preserve the validity of (44) and (10) for the perturbed system, the following conditions must be satisfied:

$$\int_0^\infty \Delta n(\omega)\,d\omega = 0\,, \tag{59}$$

$$\int_0^\infty \omega\,\{\kappa(\omega)\Delta n(\omega) + [n(\omega) - 1]\,\Delta\kappa(\omega) + \Delta n(\omega)\Delta\kappa(\omega)\}\,d\omega = 0\,. \tag{60}$$

It is of course necessary, in addition, that the perturbed absorption coefficient $\mu + \Delta\mu$ remains positive.

Going over to the sum rules (46) and (49), we can readily extend some of the above remarks on the qualitative behavior of dispersion curves. In particular, we see from (46) that, for a conducting medium, there is an uncompensated negative contribution to the total area; for good conductors, this will usually arise from a large negative peak of $\mathrm{Re}\,\epsilon$ at $\omega = 0$.

The sum rules (46) and (49) also have implications on the behavior of the system in the time domain. They are related to the high-frequency response, which in turn corresponds to the short-time behavior. Thus, it can readily be shown, by employing these relations, that, even in the case of a sudden jump in the field, the buildup of the polarization is smooth, its response time being of the order of ω_p^{-1}. This reflects the inertia of the free-electron-like response at high frequencies.

Let us now discuss the remaining sum rules (47) and (50), which apply specifically to gyrotropic media and nondiagonal elements. As is obvious, e.g., from (47), these sum rules state that *the average value over the whole frequency spectrum of the imaginary part of the antisymmetric component of each of the tensors* ϵ_{ij} *and* ϵ_{ij}^{-1} *vanishes*. The physical interpretation of these quantities is that either one can be taken as characterizing the natural optical activity of the medium.[14] Thus, if we write, e.g., for ϵ_{ij}^{-1},

$$\epsilon^{-1}_{ij} = \mathrm{Re}\,\epsilon^{-1}_{ij,s} + i\,\mathrm{Im}\,\epsilon^{-1}_{ij,s} + \mathrm{Re}\,\epsilon^{-1}_{ij,a} + i\,\mathrm{Im}\,\epsilon^{-1}_{ij,a}\,, \tag{61}$$

where $\epsilon^{-1}_{ij,s} = \frac{1}{2}(\epsilon^{-1}_{ij} + \epsilon^{-1}_{ji})$ and $\epsilon^{-1}_{ij,a} = \frac{1}{2}(\epsilon^{-1}_{ij} - \epsilon^{-1}_{ji})$ are the symmetric and antisymmetric components of ϵ^{-1}_{ij}, respectively, then the optical activity tensor[14] is determined by $\mathrm{Im}\,\epsilon^{-1}_{ij,a}$.

When absorption is weak, the rotatory power $\rho(\omega)$ of an anisotropic medium, for propagation along an optical axis, taken as the z axis, is given by[15]

$$\mathrm{Im}\,\epsilon_{12,a} = 2cn(\omega)\rho(\omega)/\omega\,. \tag{62}$$

The same relation applies of course to isotropic media. There is an analogous relation[16] for $\mathrm{Im}\,\epsilon^{-1}_{ij,a}$.

Insofar as the absorption may be neglected, the sum rules (47) and (50) therefore imply that *the average value of the rotatory power, suitably weighted in terms of the real refractive index and the frequency, is equal to zero*. In practice, the assumption of weak absorption may well be verified in optically active fluids, and experimental evidence seems to be in qualitative agreement with the above result.[17] When strong absorption is present, the relation between the above sum rules and the rotatory power seems to be considerably more complicated.

Sum rules analogous to (47) and (50) can also be obtained for a medium that is rendered optically active by application of an external magnetic field.[18]

Finally, let us remark that the sum rules (44), (46) and (49) involve only the real part of the optical constants, for which the leading term in the asymptotic high-frequency behavior is explicitly known [cf. (14), (21), and (40)]. This allows one to reduce the domain of integration to a finite interval, by replacing the integrand by its asymptotic expression beyond a sufficiently large cutoff frequency ω_0 (this is analogous to the use of finite energy sum rules in high-energy physics[19]).

Let us illustrate this for the case of (44). Let ω_0 be large enough so that (14) holds for $\omega \geq \omega_0$; we may then rewrite (44) as

$$\int_0^{\omega_0}[n(\omega) - 1]\,d\omega = -\int_{\omega_0}^\infty [n(\omega) - 1]\,d\omega \approx \omega_p^2/2\omega_0\,. \tag{63}$$

The result (63) and the analogous ones for the dielectric tensors provide new consistency checks and saturation criteria which may supplement those provided by the f-sum rules. Note that an analogous cutoff procedure cannot be applied to the f-sum rules, since the precise form of the leading term in the asymptotic high-frequency behavior of the imaginary part of the optical constants is not generally known.

Experimentally, the most directly accessible quantity over a wide frequency range is the near-normal reflectivity $R = r^2$, where $re^{i\theta} = (N - 1)/(N + 1)$. The quantities $\ln R$ and θ are also connected by a dispersion relation,[20] which is usually employed to compute θ and thereby N; this procedure involves an extrapolation of $R(\omega)$ beyond the measured frequency range.[21] Unfortunately, the superconvergence theorem cannot be applied to this dispersion relation, because $\ln R = O(\ln\omega)$ as $\omega \to \infty$. We therefore do not get sum rules for this dispersion relation that would be helpful in performing the extrapolation.[22] The result (63) might provide a valuable cross check in this connection. With modern instrumentation covering a broad frequency spectrum, including synchrotron radiation, it would be possible to verify this relation for light elements.

APPENDIX: "SUPERCONVERGENCE" THEOREM

We want to derive the asymptotic behavior as $y \to \infty$ of the Hilbert transform

$$g(y) = \mathcal{P}\int_0^\infty \frac{f(x)}{y-x}\,dx \,, \tag{A1}$$

where $f(x)$ is a continuously differentiable function[23] that vanishes faster than x^{-1} at infinity. Specifically, we want to consider the following types of asymptotic behavior for $f(x)$ and its derivative:

$$f(x) = O\,(x^{-1}\ln^{-\alpha}x), \quad f'(x) = O\,(x^{-2}\ln^{-\alpha}x), \quad \alpha > 1 \tag{A2}$$

or

$$f(x) = O\,(x^{-\beta}), \quad f'(x) = O(x^{-\beta-1}), \quad 1 < \beta \leq 2 \tag{A3}$$

as $x \to \infty$.

We recall that $f(x) = O\,(\varphi(x))$ as $x \to \infty$ means that there exist positive constants A and x_0 such that

$$|f(x)| < A\,|\varphi(x)|, \quad x \geqslant x_0 \,. \tag{A4}$$

Let x_0 be chosen accordingly for (A2) or (A3). We split the integral in (A1) into integrals from 0 to x_0 and from x_0 to ∞, and define

$$R(y) = \mathcal{P}\int_{x_0}^\infty \frac{f(x)}{y-x}\,dx - \frac{1}{y}\int_{x_0}^{y} f(x)\,dx \,, \tag{A5}$$

where we have taken $y \gg x_0$.

It was shown by Frye and Warnock[24] that, in the case of (A2),

$$R(y) = O(y^{-1}\ln^{-\alpha}y) \,, \tag{A6}$$

whereas, if (A3) is valid,[25]

$$R(y) = O(y^{-\beta}), \quad 1 < \beta < 2$$

$$= O(y^{-2}\ln y), \quad \beta = 2, \quad y \to \infty \,. \tag{A7}$$

We also have

$$\int_0^{x_0} \frac{f(x)}{y-x}\,dx = \frac{1}{y}\int_0^{x_0} f(x)\,dx + O(y^{-2}), \quad y \to \infty \,. \tag{A8}$$

Furthermore, if (A2) is valid,

$$\int_y^\infty f(x)\,dx = O(\ln^{1-\alpha}y), \quad y \to \infty \tag{A9}$$

whereas, if (A3) holds,

$$\int_y^\infty f(x)\,dx = O(y^{1-\beta}) \,. \tag{A10}$$

Putting together all of the above results, we finally get the following theorem.

Theorem. Let $g(y)$ be defined by (A1), where $f(x)$ is continuously differentiable for sufficiently large x. Then, as $y \to \infty$,

$$g(y) = (1/y)\int_0^\infty f(x)\,dx + O(y^{-1}\ln^{1-\alpha}y) \tag{A11}$$

if (A2) holds, whereas, if (A3) holds,

$$g(y) = (1/y)\int_0^\infty f(x)\,dx + O(y^{-\beta}), \quad 1 < \beta < 2 \tag{A12}$$

$$g(y) = (1/y)\int_0^\infty f(x)\,dx + O(y^{-2}\ln y), \quad \beta = 2 \,. \tag{A13}$$

Finally, we note that, if the denominator $y - x$ is replaced by $y + x$ in (A1), the corresponding results remain true [it is not necessary to assume that $f(x)$ is continuously differentiable in this case].

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[1] Cf., e.g., L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, England, 1960), p. 261.

[2] V. de Alfaro, S. Fubini, G. Furlan, and C. Rossetti, Phys. Letters 21, 576 (1966).

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

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

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

[6] Cf. H. M. Nussenzveig, *Causality and Dispersion Relations* (Academic, New York, to be published), Chap. 1.

[7] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons* (Interscience, New York, 1966), p. 11.

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

[9] This can be shown by a slight extension of the proof given for $N(\omega) - 1$ for a nonconducting medium in Ref. 6, Sec. 1.9, by employing the causal transform character of the conductivity [cf. (22) and (23)].

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

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[16] See Ref. 7, p. 122.

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31, 775 (1960).

[22] An intuitive feeling on physical grounds for the absence of sum rules for the reflectivity can be arrived at by computing it in the case corresponding to a single Lorentz oscillator or to a collection of them, and noting the complicated dependence on the width, the strength, and the position of each oscillator.

[23] It is sufficient to assume that $f(x)$ is continuously differentiable for $x \geq x_0$, where x_0 may be arbitrarily large.

[24] G. Frye and R. L. Warnock, Phys. Rev. 130, 478 (1963), Appendix D.

[25] The result for $\beta = 2$ is not given in Frye and Warnock's paper, but it follows immediately by applying the same methods.

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Exact Korringa–Kohn–Rostoker Energy-Band Method with the Speed of Empirical-Pseudopotential Methods*

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A first-principles method of energy-band calculation is described which combines the arbitrary precision of the Korringa–Kohn–Rostoker or Green's-function method with the computational efficiency and intuitive appeal of the empirical-pseudopotential method and combined-d-plane-wave interpolation schemes. Although developed here in the context of energy-band theory, the method can be applied to any problem for which multiple scattering theory is appropriate. An illustrative application is described in which the occupied valence bands of copper are evaluated to millirydberg accuracy at the rate of 20 general $\vec{k}$'s per second (~ 8 msec per solution) on an IBM 360/91 computer.

I. INTRODUCTION

Since virtually all experimental measurements relating to energy-band calculations involve a $\vec{k}$-space integration over the band energies $E_n(\vec{k})$ and the corresponding wave functions $\psi_{n\vec{k}}(\vec{r})$[1] (n is the band index), it has been a long-standing goal to devise a scheme capable of generating E and ψ fast enough to permit accurate integration over a fine $\vec{k}$-space mesh without losing any of the accuracy the most sophisticated methods can now provide at individual $\vec{k}$'s. This objective has for physically sound reasons led to the development of effective Hamiltonians, by which we mean empirical-pseudopotential theory[2] and the combined-d-plane-wave interpolation schemes[3] used in transition and noble metals. This paper describes a systematic generalization of effective-Hamiltonian theory with the following important practical virtues: (i) the secular matrix is as small, and often even smaller, than the corresponding effective Hamiltonian, (ii) the method is arbitrarily accurate, and (iii) problems which frequently complicate the fitting of effective Hamiltonians to E and ψ at particular $\vec{k}$'s in the Brillouin zone simply do not occur.

The outline of the paper is as follows. Section II isolates the physical considerations responsible for both the intuitive appeal and computational efficiency of effective-Hamiltonian theory and identifies and removes the fundamental approximation which limits its accuracy. Section III describes how this basic philosophy can be implemented in the context of the Korringa–Kohn–Rostoker (KKR) method of band calculation, and Sec. IV presents the results of numerical tests designed to measure the success of our approach. Section V presents our over-all conclusions and makes comments concerning the relevance of the procedure to molecular and other noncrystalline systems.

II. EFFECTIVE-HAMILTONIAN THEORY

The characterizing physical feature of the energy-band problem is that the electrons of interest have energies near, or greater than, all classical barriers which might seriously impede their motion. Thus, only in unusual circumstances are these electrons strongly scattered by the ions and it is on this fact that effective-Hamiltonian theory rests. The substantiation of this fact is most easily carried out in the language of multiple-scattering theory which tells us that the stationary states of an infinite system of scattering ions are given by the singularities of the reaction matrix K for the entire system, which is in turn given by the following relation:

$$K = k + kG'k + kG'kG'k + \cdots , \tag{2.1}$$

where the k's are the reaction matrices corresponding to the individual ions and G' describes free particle propagation between scattering events. (For spherically symmetric ionic potentials, k is diagonal in an angular momentum representation with elements proportional to the tangents of the scattering phase shifts.) In a periodic solid the