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ABSTRACT - A new (Gaussian) type of sum rules (GSR) for several optical functions, are presented. The functions considered are: dielectric permeability, refractive index, energy loss function, rotatory power and ellipticity (circular dichroism). While reducing to the usual type of sum rules in a certain limit, the GSR contain in general, a Gaussian factor that serves to improve convergence. GSR might be useful in analysing experimental data.

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I - INTRODUCTION

Dispersion relations of the Kramers-Kronig type have been very useful in Optics as well as in other fields[1]. These dispersion relations are associated with Hilbert transforms between the real and imaginary parts of analytic function. In many cases the dispersion integrals are superconvergent allowing for the derivation of sum rules. In this way, several sum rules associated with Hilbert transforms have been obtained up to date[2-6]. These sum rules (of the Hilbert type), which have also proven to be very useful in general terms, are in some cases of rather slow convergence[7].

The present paper is devoted to the derivation of a different type of sum rules, Gaussian sum rules (GSR), in which the convergence is improved by the appearance of a Gaussian factor in the integral. Whenever the form of the dispersion law for a optical function is approximately known and in the complex frequency plane contains poles only, GSR can be explicitly derived. The general procedure for the obtention of GSR is described in section II. Then, in section III we apply that procedure for the particular case of the dielectric permeability function of an insulating medium.

The analyticity properties of the complex refractive index N are too complicated to allow a derivation of GSR. So, based on already known sum rules for N, we present in section IV our (plausible) conjectures on the possible forms of GSR for the index of refraction and the extinction coefficient.

The modifications that are required for the treatment of the dielectric permeability of a conductor are studied in section V where GSR for such materials are also derived. Then, we devote section VI to the dielectric response or energy loss function.

After a brief description of the phenomenon of natural optical activity[8], we derive in section VII, GSR for the rotatory power and the ellipticity function which is related to circular dichroism. Here, we base our treatment of the rotatory power on a formula obtained recently[9] that has the virtue of exibiting a correct limiting behavior at both ends of the frequency spectrum. At last, in section VIII, we indulge in a few concluding remarks.

II - GAUSSIAN SUM RULES

A new (Gaussian) type of sum rules for optical functions will be presented in this paper. Let $F(\omega_c)$ generically denote one of these functions depending on the complex frequency $\omega_c=\omega+i\nu$. Examples of $F(\omega_c)$ are $[\varepsilon(\omega_c)-1]$, where $\varepsilon(\omega_c)$ is the dielectric permeability function of an insulator, $[\varepsilon^{-1}(\omega_c)-1]$, or $[\phi(\omega_c)/\omega_c]$ where $\phi(\omega_c)$ is the complex rotatory power. In all these cases $F(\omega_c)$ fulfils the following conditions:

i) $F(\omega_c)$ is analytic everywhere in the upper ω_c plane including the real axis.

ii) On the real frequency axis, $F(\omega)\to 0$ for $\omega\to\infty$. By he Phragmën-Lindelöf theorem, this asymptotic behavior also holds uniformly in the upper plane as $|\omega_c|\to\infty$[1].

iii) $F(\omega_c)$ is real analytic, meaning that the crossing relation

$$F^*(\omega_c) = F(-\omega_c^*) \quad , \tag{1.1}$$

is satisfied.

In order to obtain our sum rule we will need representations of the function F for imaginary frequencies. One such representation is derived by Landau and Lifshitz[10] from the integral

$$\oint_c \frac{\omega F(\omega)}{\omega^2+\nu^2}\, d\omega \quad , \tag{2.2}$$

taken along the contour c consisting of the real axis and an infinite semicircle in the upper plane. It is easy to see that for a function satisfying the three conditions listed above, the integral (2.2) leads to

$$F(i\nu) = R_e F(i\nu) = \frac{2}{\pi}\int_0^\infty \frac{\omega \,\mathrm{Im}F(\omega)}{\omega^2+\nu^2}\, d\omega, \tag{2.3}$$

for $\nu>0$. $\mathrm{Im}F(i\nu)=0$ because of Eq. (2.1).

On the other hand, the integral

$$\oint_c \frac{F(\omega)}{\omega^2+\nu^2} d\omega \tag{2.4}$$

along the same contour c, yields

$$\frac{F(i\nu)}{\nu} = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{Re}F(\omega)}{\omega^2+\nu^2}\, d\omega, \tag{2.5}$$

still strictly for $\nu>0$.

In the following sections we will work with explicit forms for each optical function to be considered. These functions have only simple poles as singularities (no cuts) and can be analytically continued to the lower half plane in a straitforward way. In such a case Eqs. (2.3) and (2.4) can be extended to represent the even and odd parts of $F(i\nu)$ according to

$$\int_0^\infty \frac{\omega \,\mathrm{Im}F(\omega)}{\omega^2+\nu^2}\, d\omega = \frac{1}{4}\pi \left[F(i\nu) + F(-i\nu)\right] \tag{2.6}$$

and

$$\int_0^\infty \frac{\mathrm{Re}F(\omega)}{\omega^2+\nu^2}\,d\omega = (\pi/4\nu)\left[F(i\nu)-F(-i\nu)\right] \quad . \tag{2.7}$$

We can now derive Gaussian sum rules as follows. First, we take the derivative of order (m-1) with respect to ν^2 in Eq. (2.6), then we multiply by $\left[(-1)^{m-1}\ \nu^{2m}/(m-1)!\right]$ and finally we take the limit $m\to\infty$, $\nu^2\to\infty$ with $(\nu^2/m)=\Omega^2$ fixed. The result is

$$\mathrm{Lim}(m,\nu^2,\Omega^2)\frac{(-1)^{m-1}\ \nu^{2m}}{(m-1)!}\ \frac{\partial^{m-1}}{\partial(\nu^2)^{m-1}}\int_0^\infty \frac{\mathrm{Im}F(\omega)}{\omega^2+\nu^2}\,d\omega$$

$$= \int_0^\infty d\omega\ \omega e^{-(\omega^2/\Omega^2)}\,\mathrm{Im}(\omega)$$

$$= \mathrm{Lim}(m,\nu^2,\Omega^2)\frac{(-1)^{m-1}\ \nu^{2m}}{(m-1)!}\ \frac{\partial^{m-1}}{\partial(\nu^2)^{m-1}}\ \frac{1}{4}\ \pi\left[F(i\nu)+F(-i\nu)\right], \tag{2.8}$$

where

$$\mathrm{Lim}(m,\nu^2,\Omega^2) \equiv \lim_{\substack{m,\nu^2\to\infty \\ (\nu^2/m)=\Omega^2}} \quad . \tag{2.9}$$

As advertized, the new sum rules[11] contain a Gaussian factor that certainly will improve the convergence.

A similar procedure applied to Eq. (2.7) leads to

$$\int_0^\infty d\omega\ e^{-(\omega^2/\Omega^2)}\ \mathrm{Re}F(\omega) =$$

$$= \mathrm{Lim}(m,\omega^2,\Omega^2)\ \frac{(-1)^{m-1}\nu^{2m}}{(m-1)!}\ \frac{\partial^{m-1}}{\partial(\nu^2)^{m-1}}\quad (\pi/4\nu)\left[F(i\nu)-F(-i\nu)\right]. \tag{2.10}$$

III - GSR FOR THE DIELECTRIC PERMEABILITY OF AN INSULATOR

Let us consider the case of an insulating isotropic or cubic medium whose dielectric permeability function can be approximately described by[12]

$$\varepsilon(\omega) = 1 + \omega_p^2\ \sum_\ell f_\ell\left[\omega_\ell^2-\omega^2-i\gamma_\ell\omega\right]^{-1}, \tag{3.1}$$

where ω_ℓ is the frequency for the transition from the ground state to the state ℓ, γ_ℓ is the (line) width of that transition, ω_p is the plasma frequency, and the oscillator strengths f_ℓ obey the Thomas-Reiche-Kuhn sum rule[13]

$$\sum_\ell\ f_\ell = 1. \tag{3.2}$$

For imaginary frequencies, the dielectric permeability is, as it should be, purely real

$$\varepsilon(i\nu) = 1 + \omega_p^2\ \sum_\ell f_\ell\left[\omega_\ell^2+\nu^2+\gamma_\ell\nu\right]^{-1}.$$

We are now in a position to complete the calculation of the sum rules (2.8) and (2.10) for the case in which $F(i\nu)=\varepsilon(i\nu)-1$ For Eq. (2.10) we need the combination

$$(\pi/4\nu)\left[\varepsilon(i\nu)-\varepsilon(-i\nu)\right] = -\frac{1}{2}\pi\ \omega_p^2\ \sum_\ell f_\ell\gamma_\ell\left[(\omega_\ell^2+\nu^2)^2-\gamma_\ell^2\nu^2\right]^{-1}. \tag{3.4}$$

For the purpose of taking multiple derivatives with respect to ν^2, it is convenient to rewrite the right hand side of Eq. (3.4) as

$$i\ \frac{1}{4}\pi\ \omega_p^2\ \sum_\ell f_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{-1/2}$$

$$\cdot\left\{\left[\omega_\ell^2+\nu^2-\frac{1}{2}+i\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}\right]^{-1}-\left[\omega_\ell^2+\nu^2-\frac{1}{2}\gamma_\ell^2-i\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}\right]^{-1}\right\} \quad (3.5)$$

It is simple now to complete the calculation of Eq. (2.10) for this case and we obtain the sum rule

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] =$$

$$= -\frac{1}{2}\pi\omega_p^2\sum_\ell f_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{-1/2}\, e^{-(\omega_\ell^2-\frac{1}{2}\gamma_\ell^2)/\Omega^2}\sin\left[\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}/\Omega^2\right], \quad (3.6)$$

where we have assumed that the shifted frequencies are non-negative, i.e., $\omega_\ell^2 \geq \frac{1}{4}\gamma_\ell^2$.

Taking the frequency Ω high enough so that

$$\Omega^2 \gg \gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}, \quad \Omega^2 \gg (\omega_\ell^2-\frac{1}{2}\gamma_\ell^2), \quad (3.7)$$

for all ω_ℓ and γ_ℓ, Eq. (3.6) simplifies to

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = -\frac{\pi\omega_p^2\bar{\gamma}}{2\Omega^2}\xrightarrow[\Omega\to\infty]{} 0, \quad (3.8)$$

where we have introduced the "average width"

$$\bar{\gamma} \equiv \sum_\ell f_\ell\gamma_\ell. \quad (3.9)$$

A slightly different form for Eq. (3.8) is

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)}\,\mathrm{Re}\,\varepsilon(\omega) = \frac{1}{2}\sqrt{\pi}\,\Omega-\frac{1}{2}(\pi\omega_p^2\bar{\gamma}/\Omega^2). \quad (3.10)$$

An infinite set of sum rules can be obtained by taking succesive derivatives of Eq. (3.6) with respect to Ω^{-2}. The first derivative and the assumption that Eq. (3.7) holds, leads to

$$\int_0^\infty d\omega\,\omega^2 e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = \frac{1}{2}\pi\omega_p^2\bar{\gamma}, \quad (3.11)$$

while the second derivative yields

$$\int_0^\infty d\omega\,\omega^4 e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = \pi\omega_p^2\sum_\ell f_\ell\gamma_\ell(\omega_\ell^2-\gamma_\ell^2). \quad (3.12)$$

A $\bar{\gamma}$ independent sum rule can also be obtained from a combination of Eqs. (3.8) and (3.11), namely

$$\int_0^\infty d\omega\,(1+\frac{\omega^2}{\Omega^2})e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = 0 \quad (3.13)$$

From Eq.(2.8), with $F(i\nu)=\varepsilon(i\nu)-1$, we can obtain sum rules for $\mathrm{Im}\,\varepsilon(\nu)$. These sum rules depend on the combination

$$\frac{1}{4}\pi\left[\varepsilon(i\nu)+\varepsilon(-i\nu)-2\right] = \frac{1}{2}\pi\omega^2{}_p\sum_\ell\frac{f_\ell(\omega_\ell^2+\nu^2)}{(\omega^2+\nu^2)^2-\gamma_\ell^2\nu^2} \quad (3.14)$$

When written in a form analogous to Eq.(3.5), the multiple derivatives and the limiting procedure can be readily performed leading to

$$\int_0^\infty \omega\; e^{-(\omega^2/\Omega^2)}\,\mathrm{Im}\,\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2\sum_\ell f_\ell\; e^{-(\omega_\ell^2-\frac{1}{2}\gamma_\ell^2)/\Omega^2}$$

$$\left\{\cos\frac{\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}{\Omega^2}+\frac{1}{2}\frac{\gamma_\ell}{(\omega_\ell^2-\gamma_\ell^2)^{1/2}}\sin\frac{\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}{\Omega^2}\right\}, \quad (3.15)$$

which, when the relations (3.7) hold, reduces to

$$\int_0^{\infty} \omega e^{-(\omega^2/\Omega^2)} \, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2 \left[1 + \frac{\langle\gamma^2\rangle - \langle\omega^2\rangle}{\Omega^2}\right], \tag{3.16}$$

with

$$\langle\gamma^2\rangle \equiv \sum_\ell f_\ell \gamma_\ell^2 , \qquad \langle\omega^2\rangle \equiv \sum_\ell f_\ell \omega_\ell^2 . \tag{3.17}$$

The derivative with respect to Ω^{-2} of either Eq.(3.15) or Eq.(3.16) yields

$$\int_0^{\infty} \omega^3 e^{-(\omega^2/\Omega^2)} \, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2(\langle\omega^2\rangle - \langle\gamma^2\rangle), \tag{3.18}$$

which can be combined with Eq.(3.16) to give

$$\int_0^{\infty} \omega\left(1 + \frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)} \, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2 \tag{3.19}$$

IV - GSR FOR THE REFRACTIVE INDEX

For an isotropic nonmagnetic medium, the complex refractive index is $N=\sqrt{\varepsilon}$. Even when the medium is also insulating and ε has the simple form of Eq.(3.1), N has cuts in the lower half of the complex frequency plane. This fact prevented us from deriving GSR for N. Thus, the GSR for N that we will write down below are nothing more than proposals that we think are reasonable.

For $\omega\to\infty$ Eq.(3.1) gives

$$\varepsilon(\omega) \to 1 - \frac{\omega_p^2}{\omega^2} , \quad N = n+i\kappa = \sqrt{\varepsilon} \to 1 - \frac{1}{2}\frac{\omega_p^2}{\omega^2}, \tag{4.1}$$

where n is the (real) index of refraction and κ the extinction coefficient. It is well known that the asymptotic behavior of

Eq. (4.1) leads to the sum rules[2]

$$\int_0^{\infty} \omega \, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2, \tag{4.2}$$

and

$$\int_0^{\infty} \omega\kappa(\omega)\,d\omega = \frac{1}{4}\pi\omega_p^2. \tag{4.3}$$

We then advance the conjecture that corresponding to Eq.(3.16) we might have

$$\int_0^{\infty} d\omega\; e^{-(\omega^2/\Omega^2)} \omega\kappa(\omega) = \frac{1}{4}\pi\omega_p^2 \left[1 + \frac{\langle\gamma^2\rangle - \langle\omega^2\rangle}{\Omega^2}\right], \tag{4.4}$$

while corresponding to Eq.(3.19), the sum rule for $\kappa(\omega)$ might be

$$\int_0^{\infty} d\omega\left(1 + \frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)} \omega\kappa(\omega) = \frac{1}{4}\pi\omega_p^2. \tag{4.5}$$

Also, inspired in Eqs. (3.8) and (3.13) we propose

$$\int_0^{\infty} d\omega\; e^{-(\omega^2/\Omega^2)} \left[n(\omega)-1\right] = -\frac{\pi\omega_p^2\bar{\gamma}}{4\Omega^2}, \tag{4.6}$$

$$\int_0^{\infty} d\omega\left(1 + \frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)} \left[n(\omega)-1\right] = 0. \tag{4.7}$$

V - GSR FOR THE DIELECTRIC PERMEABILITY OF A CONDUCTOR

In the case of a conducting isotropic or cubic medium we have to add to Eq.(3.1) the free electron (intraband) contribution giving a dielectric permeability function[14]

$$\varepsilon(\omega) = 1 - \frac{\omega_{pc}^2}{\omega(\omega+i\gamma_c)} + \omega_{pb}^2 \sum_\ell \frac{f_\ell}{\omega_\ell^2 - \omega^2 - i\gamma_\ell\omega}, \tag{5.1}$$

where now, ω_{pb} is the plasma frequency associated with bound electrons while ω_{pc} is the plasma frequency of conduction electrons and $\gamma_c=1/\tau_c$ the inverse of their relaxation time.

Due to the pole at $\omega=0$ in the intraband term we cannot directly write dispersion relations for ε. The usual procedure is to work instead with the non-conducting part

$$\varepsilon_{nc}(\omega) = \varepsilon(\omega) + \frac{\omega_{pc}^2}{\omega(\omega+i\gamma_c)}, \tag{5.2}$$

which has the analyticity properties of the ε of an insulator. Thus, in the present case we have to take as the function F in section II, $F(i\nu) = \varepsilon_{nc}(i\nu) - 1$.

Then, Eq.(2.7) in the present case reads

$$\int_0^\infty \frac{[\mathrm{Re}\ \varepsilon_{nc}(\omega)-1]}{\omega^2+\nu^2}\,d\omega = (\pi/4\nu)\ \left[\varepsilon_{nc}(i\nu)-\varepsilon_{nc}(-i\nu)\right]. \tag{5.4}$$

The derivation leading to Eq.(3.6) can be repeated with the following differences: Firstly, in the second line ω_p^2 has to be replaced by ω_{pb}^2. Then, instead of the first line of Eq.(3.6) we now have

$$\int_0^\infty d\omega\ e^{-(\omega^2/\Omega^2)}\ \left[\mathrm{Re}\ \varepsilon_{nc}(\omega)-1\right] = \int_0^\infty d\omega\ e^{-(\omega^2/\Omega^2)}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right]$$
$$+\ \omega_{pc}^2 \int_0^\infty \frac{d\omega\ e^{-(\omega^2/\Omega^2)}}{\omega^2+\gamma_c^2}. \tag{5.5}$$

Putting everyting together we get, for a conducting medium, the sum rule

$$\int_0^\infty d\omega\ e^{-(\omega^2+\gamma_c^2)/\Omega^2}\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = 2\pi\sigma\ \left[\mathrm{erf}(\gamma_c/\Omega)-1\right]$$
$$-\ \frac{1}{2}\ \pi\omega_{pb}^2 \sum_\ell \frac{f_\ell}{(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}\ e^{-(\omega_\ell^2+\gamma_c^2-\frac{1}{2}\gamma_\ell^2)/\Omega^2}\ \sin\frac{\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}{\Omega^2}, \tag{5.6}$$

where

$$\sigma = \omega_{pc}^2/4\pi\gamma_c \tag{5.7}$$

is the dc conductivity and the erf denotes the error function

$$\mathrm{erf}(z) = (2/\sqrt{\pi})\ \int_0^z e^{-t^2}dt. \tag{5.8}$$

When conditions (3.7) and $\Omega^2 \gg \gamma_c^2$ are satisfied, Eq.(5.6) simplifies to

$$\int_0^\infty d\omega\ e^{-(\omega^2/\Omega^2)}\ \left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = -2\pi\sigma\left(1+\frac{\gamma_c^2}{\Omega^2}-\frac{4\gamma_c}{\pi\Omega}\right)$$
$$-\ \frac{\pi\omega_{pb}^2\bar{\gamma}}{2\Omega^2} + \mathcal{O}(\Omega^{-3}). \tag{5.9}$$

A sum rule free from $\bar{\gamma}$ can be obtained by taking the derivative of Eq.(5.6) and combining the result with Eq.(5.9),

$$\int_0^\infty d\omega\ e^{-(\omega^2/\Omega^2)}\left(1+\frac{\omega^2}{\Omega^2}\right)\left[\mathrm{Re}\,\varepsilon(\omega)-1\right] = -2\pi\sigma\left(1-\frac{2\gamma_c}{\pi\Omega}\right)+\mathcal{O}(\Omega^{-3}). \tag{5.10}$$

It would be interesting to plot the left hand side of this equation as a function of Ω^{-1} for a given material. The tangent to the curve at small Ω^{-1} should cross the Ω^{-1} axis at $\Omega = 2\gamma_c/\pi$.

Turning our attention to $\mathrm{Im}\,\varepsilon(\omega)$ we notice that for a conducting medium Eq.(2.6) leads to

$$\int_0^\infty \frac{\omega \,\mathrm{Im}\, \varepsilon_{nc}(\omega)}{\omega^2 + \nu^2}\, d\omega = \frac{1}{4}\pi \left[\varepsilon_{nc}(i\nu)+\varepsilon_{nc}(-i\nu)-2\right]. \qquad (5.11)$$

Taking the multiple derivatives followed by the limiting process of Eqs. (2.8) and (2.9) we now obtain, instead of Eq.(3.15),

$$\int_0^\infty \omega e^{-(\omega^2+\gamma_c^2)/\Omega^2}\, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_{pc}^2 \left[1-\mathrm{erf}(\gamma_c/\Omega)\right] +$$

$$+ \frac{1}{2}\pi\omega_{pb}^2 \sum_\ell f_\ell\, e^{-(\omega_\ell^2+\gamma_c^2-\frac{1}{2}\gamma_\ell^2)/\Omega^2}$$

$$\left\{\cos \frac{\gamma_\ell(\omega_\ell^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}{\Omega^2} + \frac{1}{2}\,\frac{\gamma_\ell}{(\omega_\ell^2-\gamma_\ell^2)^{1/2}}\,\sin\frac{\gamma_\ell(\omega^2-\frac{1}{4}\gamma_\ell^2)^{1/2}}{\Omega^2}\right\}. \qquad (5.12)$$

For a Ω high enough to satisfy relations (3.7) and $\Omega^2 \gg \gamma_c^2$, Eq. (5.12) is, approximately,

$$\int_0^\infty \omega e^{-(\omega^2/\Omega^2)}\, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2 + \frac{1}{2}\pi\omega_{pc}^2\left(\frac{\gamma^2}{\Omega^2} - \frac{4}{\pi}\frac{\gamma_c}{\Omega}\right) +$$

$$+ \frac{1}{2}\pi\omega_{pb}^2 \left(\frac{\langle\gamma^2\rangle\ \langle\omega^2\rangle}{\Omega^2}\right) + \mathcal{O}(\Omega^{-3}), \qquad (5.13)$$

where ω_p is the plasma frequency for all the electrons (bound + conduction) given by

$$\omega_p^2 = \omega_{pc}^2 + \omega_{pb}^2 . \qquad (5.14)$$

Again, it is straitforward to obtain, by taking the derivative with respect to Ω^{-2} and adding the result to Eq.(5.13), a $\overline{\gamma}$ independent

sum rule

$$\int_0^\infty \omega\left(1 + \frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)}\, \mathrm{Im}\varepsilon(\omega)\,d\omega = \frac{1}{2}\pi\omega_p^2 - \frac{\omega_{pc}^2\gamma_c}{\Omega} . \qquad (5.15)$$

A plot of the left hand side as function of Ω^{-1} should give a straight line for small Ω^{-1}. This line should cut the Ω^{-1} axis at $\Omega = 2\omega_{pc}^2\gamma_c/\pi\omega_p^2$.

VI - GSR FOR THE ENERGY LOSS FUNCTION

Let us discuss now the dielectric response (or energy loss) function $\varepsilon^{-1}(\omega,k)$ for a medium in which the formula

$$\varepsilon^{-1}(\omega,k) = 1 + \frac{4\pi e^2}{hk^2} \sum_\ell |(\rho_k^\dagger)_{\ell o}|^2 \left[\frac{1}{\omega-\omega'_{\ell o}+i\delta} - \frac{1}{\omega+\omega'_{\ell o}+i\delta}\right], \qquad (6.1)$$

as given for instance in Pines book[15], approximately holds. $(\rho_k^\dagger)_{\ell o}$ is the matrix element of the Hermitian conjugate of the Fourier transform of the local density operator that satisfies the Thomas-Reiche-Kuhn sum rule[16]

$$\frac{2m}{hk^2} \sum_\ell \omega_{\ell o}\, |(\rho_k^\dagger)_{\ell o}|^2 = N, \qquad (6.2)$$

where N is the number of electrons per unit volume. It is then convenient to introduce the oscillator strengths given by

$$(f_k)_{\ell o} = \frac{8\pi e^2}{hk^2\omega_p^2}\, \omega_{\ell o}\, |(\rho_k^\dagger)|^2 . \qquad (6.3)$$

It is also sensible to introduce finite widths for each transition by the replacement $\delta \to \frac{1}{2}\gamma_{\ell o}$ in each of the terms. With these modifications Eq.(6.1) can be rewritten as

$$\varepsilon^{-1}(\omega,k) = 1 - \omega_p^2 \sum_\ell (f_k)_{\ell o} \left[\omega_{\ell o}^2 - \omega^2 - i\omega\gamma_{\ell o}\right]^{-1} \tag{6.4}$$

Our purpose in the present paper is to derive Gaussian sum rules for function for which the form of the dispersion law is approximately known. We regard the discussion of problems like the simultaneous validity of a formula like (3.1) for ε and a formula (6.4) for ε^{-1}, as laying outside the scope of this paper. In section III we derived GSR for ε of a medium where Eq.(3.1) approximately holds. In the remainder of this section let us just list the various GSR for ε^{-1} of a medium where Eq.(6.4) is valid. These are:

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)} \left[\mathrm{Re}\,\varepsilon^{-1}(\omega,k)-1\right] = \frac{\pi\omega_p^2}{2\Omega^2}\left[\sum_\ell (f_k)_{\ell o}\gamma_{\ell o}\right], \tag{6.5}$$

$$\int_0^\infty d\omega\left(1+\frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)} \left[\mathrm{Re}\,\varepsilon^{-1}(\omega,k)-1\right] = 0\ , \tag{6.6}$$

$$\int_0^\infty d\omega\,\omega^4\, e^{-(\omega^2/\Omega^2)} \left[\mathrm{Re}\,\varepsilon^{-1}(\omega,k)-1\right] = -\pi\omega_p^2\left[\sum_\ell (f_k)_{\ell o}\gamma_{\ell o}(\omega_{\ell o}^2-\gamma_{\ell o}^2)\right]\ , \tag{6.7}$$

$$\int_0^\infty \omega e^{-(\omega^2/\Omega^2)}\, \mathrm{Im}\,\varepsilon^{-1}(\omega,k)\,d\omega = -\frac{1}{2}\pi\omega_p^2\left\{1-\Omega^{-2}\left[\sum_\ell (f_k)_{\ell o}(\omega_{\ell o}^2-\gamma_{\ell o}^2)\right]\right\}, \tag{6.8}$$

$$\int_0^\infty \omega\left(1+\frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)}\, \mathrm{Im}\,\varepsilon^{-1}(\omega,k)\,d\omega = -\frac{1}{2}\pi\omega_p^2. \tag{6.9}$$

VII - GSR FOR THE ROTATORY POWER

Let us consider a macroscopically isotropic substance that shows natural optical activity. Such a substance will have two comples refractive indices[8]; N_+ for right circularly polarized light and N_- for left polarization with

$$N_\pm(\omega) = n_\pm(\omega) + i\,\kappa_\pm(\omega)\ , \tag{7.1}$$

where $n_\pm(\omega)$ are the (real) indices of refraction and $\kappa_\pm(\omega)$ the extinction coefficients.

Linearly polarized light incident on the substance becomes elliptically polarized with an ellipticity given by

$$\rho(\omega) = (\omega/2c)\left[\kappa_+(\omega)-\kappa_-(\omega)\right]. \tag{7.2}$$

The main axis of the ellipse also rotates, per unit path length, an angle

$$\phi(\omega) = (\omega/2c)\left[n_+(\omega)-n_-(\omega)\right], \tag{7.3}$$

known as the (real) rotatory power. The complex rotatory power is defined by

$$\Phi(\omega) = \phi(\omega) + i\rho(\omega) = (\omega/2c)\left[N_+(\omega)-N_-(\omega)\right], \tag{7.4}$$

and contains all the information regarding the natural optical activity of the substance.

The theoretical expression generally used for the rotatory power is the classic Rosenfeld-Condon formula, first derived by Rosenfeld long time ago[17] and later generalized by Condon[8]. This formula could describe fairly well the behavior of Φ in the medium frequency range where most experiments are performed[18]. However, as it was recently pointed out, the asymptotic behavior of the Rosenfeld-Condon formula is not satisfactory[6,9].

In the framework of the Kubo formalism for the conductivity[19], a new dispersion law for the rotatory power, namely

$$\Phi(\omega) = \frac{16\pi n\omega}{3\hbar c} \sum_{\ell} \frac{\omega_{\ell o} R_{\ell o}}{\omega^2_{\ell o} - (\omega + i\gamma_{\ell o}/2)^2}, \tag{7.5}$$

was recently obtained[9]. n is the number of active molecules per unit volume, $\omega_{\ell o}$ the frequencies for the transitions $0 \to \ell$ while $\gamma_{\ell o}$ are their widths, and the rotational strengths are given by

$$R_{\ell o} = \mathrm{Im}\Big[\langle 0|\underset{\sim}{p}|\ell\rangle\langle\ell|\underset{\sim}{m}|0\rangle \Big] = -R_{o\ell},$$

where $\underset{\sim}{p}$ is the electric dipole moment of the active molecules while $\underset{\sim}{m}$ is the magnetic moment. It is easy to show that the rotational strengths satisfy the Kuhn sum rule[20]

$$\sum_{\ell} R_{\ell o} = 0. \tag{7.6}$$

Eq.(7.5) shows, unlike the Rosenfeld-Condon formula[8], an asymptotic behavior consistent with the asymptotic behavior of the free electron gas[9]. Based on Eq.(7.5) we will derive GSR for ϕ and ρ. For that, we can take as the function $F(\omega)$ in section , $F(\omega) = \Phi(\omega)/\omega$ and go through all the derivation of the sum rules. Or, more simply, notice that a comparison between Eq.(7.5) and (3.1) suggests the following translation dictionary between the parameters for ε in section III and the parameters for Φ:

$$\left.\begin{array}{l} (\varepsilon - 1) \\ \omega^2_{\ell} \\ f_{\ell} \\ \omega^2_p \end{array}\right\} \longrightarrow \left\{\begin{array}{l} \Phi/\omega = (\phi/\omega) + i\rho/\omega \\ \omega^2_{\ell o} + \frac{1}{4}\gamma^2_{\ell o} \\ \omega_{\ell o} R_{\ell o} \\ (16\pi n)/(3\hbar c) \end{array}\right. \tag{7.7}$$

The translation of the formulae in section III yields

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)} \frac{\phi(\omega)}{\omega} = -\frac{8\pi^2 n}{3\hbar c\Omega^2} \sum_{\ell} \omega_{\ell o} \gamma_{\ell o} R_{\ell o}, \tag{7.8}$$

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)} \omega\phi(\omega) = \frac{8\pi^2 n}{3\hbar c} \sum_{\ell} \omega_{\ell o} \gamma_{\ell o} R_{\ell o}, \tag{7.9}$$

$$\int_0^\infty d\omega \left(1 + \frac{\omega^2}{\Omega^2}\right) e^{-(\omega^2/\Omega^2)} \frac{\phi(\omega)}{\omega} = 0, \tag{7.10}$$

$$\int_0^\infty d\omega\, \omega^3 e^{-(\omega^3/\Omega^2)} \phi(\omega) = \frac{16\pi^2 n}{3\hbar c} \sum_{\ell} \omega_{\ell o}\gamma_{\ell o}R_{\ell o}\left(\omega^2_{\ell o} - \frac{3}{4}\gamma^2_{\ell o}\right), \tag{7.11}$$

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)} \rho(\omega) = \frac{8\pi^2 n}{3\hbar c} \left[1 - \Omega^{-2} \sum_{\ell} \omega_{\ell o} R_{\ell o}\left(\omega^2_{\ell o} - \frac{3}{4}\gamma^2_{\ell o}\right)\right], \tag{7.12}$$

$$\int_0^\infty d\omega\, e^{-(\omega^2/\Omega^2)} \omega^2 \rho(\omega) = \frac{8\pi^2 n}{3\hbar c} \sum_{\ell} \omega_{\ell o} R_{\ell o}\left(\omega^2_{\ell o} - \frac{3}{4}\gamma^2_{\ell o}\right), \tag{7.13}$$

$$\int_0^\infty d\omega e^{-(\omega^2/\Omega^2)} \left(1 + \frac{\omega^2}{\Omega^2}\right)\rho(\omega) = \frac{8\pi^2 n}{3\hbar c}. \tag{7.14}$$

All these expressions, (7.8) to (7.14), are valid when $\Omega^2 \gg \gamma_{\ell o}\omega_{\ell o}$ and $\Omega^2 \gg (\omega^2_{\ell o} - \frac{1}{4}\gamma^2_{\ell o})$.

VIII - CONCLUDING REMARKS

It is hoped that the Gaussian sum rules for the various optical functions presented in this paper might prove useful in analysing experimental data. We base our hope in the fact that the GSR are more general than the usual (Hilbert) kind of sum rules. While reducing to the usual type in the $\Omega\to\infty$ limit, for finite but large Ω, the GSR contain an adjustable Gaussian factor providing a much welcomed improvement in convergence. A related bonus, is the flexibility afforded by the appearance of the Ω parameter which makes it possible to plot the sum rules as a function of Ω^{-1} yielding more information on the system being studied.

The saturation of Gaussian sum rules using published experimental data with the kind of analysis described above is, at present, being considered.

FOOTNOTES AND REFERENCES

1 - See for instance, H.M.Nussenzveig, Causality and Dispersion Relations (Academic Press, New York, 1972).

2 - M.Altarelli et al., Phys.Rev. B6, 4502 (1972).

3 - M.Altarelli and D.Y.Smith, Phys.Rev. B9, 1290 (1974).

4 - A.Villani and A.H.Zimmerman, Phys.Rev. B8, 3914 (1973).

5 - D.Y.Smith, Phys.Rev. B13, 5303 (1976).

6 - M.T.Thomaz and H.M.Nussenzveig, preprint IFUSP/P-277 to be published in Ann.Phys. (N.Y.).

7 - T.Inagaki et al., Phys.Rev. B15, 3243 (1977).

8 - The classic reference for optical activity is the review article by E.U.Condon, Rev.Mod.Phys. 9, 432 (1937).

9 - I.Kimel, A New Optical Rotation Dispersion Formula, preprint IFUSP/P-307, December 1981.

10 - L.D.Landau and E.M.Lifshitz, Statistical Physics, third edition part 1 (Pergamon, Oxford, 1980), page 383.

11 - For Quantum Chromodynamics, similar sum rules have been proposed by M.A.Shifmand, A.I.Vainshtein and V.I.Zakharov, Nucl.Phys. B147, 385 and 448 (1979); and derived by S.Narison and E. de Rafael, preprint CPT-81/P.1287, Marseille.

12 - See, for instance, J.M.Ziman, The Principles of the Theory of Solids, (2nd. ed., Cambridge, 1972) p.265.

13 - Ref. 12, page 261.

14 - See, e.g., H.Ehrenreich, in Optical Properties of Solids, ed. by J.Tauc (Academic, New York, 1966) p.136.

15 - D.Pines, Elementary Excitations in Solids (Benjamin, N.York, 1964) p.126.

16 - Ref. 15 page 134.

17 - L.Rosenfeld, Z.Phys. 52, 161 (1928).

18 - See the articles by A.Moscowitz and I.Tinoco in Advances in

Chemical Physics, vol.4 (I.Prigogine ed., Interscience, N. York, 1962).

19 - R.Kubo, J.Phys. Soc.Japan 12, 570 (1957).

20 - W.Kuhn, Zeits. f. Physik.Chemie B4, 14 (1929).