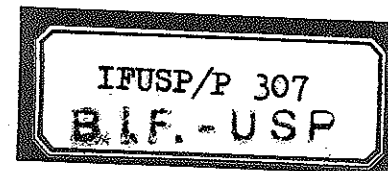


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preprint



IFUSP/P-307

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B.I.F. - USP

DEC/1981

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ABSTRACT

A new dispersion formula for the rotatory power is obtained in the framework of Kubo formalism for transport coefficients. Unlike the well known Rosenfeld-Condon dispersion law, our formula is consistent with the free electron gas asymptotic behavior.

I. INTRODUCTION

Natural optical activity constitutes an important tool in the study of the structure of asymmetric molecules. It can also give useful information on asymmetric crystals. It is, of course, not easy to translate optical activity measurements into relevant molecular structure information. This point will not be touched upon in the present paper. Our main task will be, instead, to obtain a general expression for the description of natural optical activity free of the problems that affect the, up to now, generally accepted Rosenfeld-Condon (RS) formula. These problems have to do with the high frequency asymptotic behavior of the RS formula.

Rosenfeld¹ obtained his rotatory power dispersion law over fifty years ago. It was generalized nine years later by Condon² and it was quite recently that its unsatisfactory behavior was pointed out³, apparently for the first time. The expression we will obtain looks very much like the RC formula except for the important power dependence on the frequency. Unlike the RC formula, our rotatory power dispersion law is consistent with the free electron gas like high frequency behavior that any electronic system is expected to have.

After a presentation of the fundamentals of natural optical activity in section II and a phenomenological description of optical rotatory power and circular dichroism⁴ in section III, the Rosenfeld-Condon theory is discussed in section IV, particularly in relation to the asymptotic behavior.

Our formula for the rotatory power will be derived from an analysis of the conductivity tensor in the framework of the Kubo formalism⁵ for transport coefficients. Thus, the very elegant Kubo approach is outlined in section V, where a familiar expression for the dielectric function is also obtained.

In section VI, our complex rotatory power dispersion law is derived from the antisymmetric part of the Kubo conductivity formula and its asymptotic behavior is discussed. We also present a sum rule which might be used, in conjunction with experimental data, to decide which of the dispersion formulae, RC's or ours, is the correct one. Finally, in section VII we briefly discuss local field corrections.

II. CONSTITUTIVE RELATIONS AND CONDUCTIVITY

Natural optical activity is the ability of certain substances to change the state of polarization of light.

The reaction of the medium through which light propagates, manifests itself in the appearance of the electric polarization vector \underline{P} and the magnetization \underline{M} . For non-active substances \underline{P} is proportional to the electric field \underline{E} while \underline{M} is proportional to the magnetic field \underline{H} and the polarization of the wave does not change except at boundaries. It should be clear that if \underline{P} and \underline{M} were each related to both \underline{E} and \underline{H} , the polarization of a wave could, in principle, change while traversing the medium.

That kind of response of the medium can be described in a somewhat different way. In a non-active isotropic (or cubic) material an electric field gives rise to an induced current⁶

$$\underline{j}(\underline{x}, \omega) = \sigma(\omega) \underline{E}(\underline{x}, \omega) = (i\omega/4\pi) [1 - \epsilon(\omega)] \underline{E}(\underline{x}, \omega) \quad (2.1)$$

where $\sigma(\omega)$ is the conductivity and $\epsilon(\omega)$ the dielectric function, both frequency dependent. The induced current is related to the polarizability $\underline{P}(\underline{x}, \omega)$ by

$$\underline{j}(\underline{x}, \omega) = \partial \underline{P}(\underline{x}, \omega) / \partial t = -i\omega \underline{P}(\underline{x}, \omega) \quad (2.2)$$

The situation changes in the case of optically active molecules. An example is provided by organic molecules that have helical structures. Consider electrons in such a molecule constrained to move on helical paths. In this case, there will be a term in the induced current parallel to the magnetic field acting on the molecule leading to

$$\begin{aligned} \underline{j} &= (i\omega/4\pi) [1 - \epsilon(\omega)] \underline{E} + \omega \xi(\omega) \underline{B} \\ &= (i\omega/4\pi) [1 - \epsilon(\omega)] \underline{E} + [c \xi(\omega)/4\pi] \underline{k} \times \underline{E} \end{aligned} \quad (2.3)$$

where, in obtaining the second line we have used Faraday-Maxwell equation⁶ for a plane wave field of the form

$$\underline{E}(\underline{x}, t) = \underline{E}_0 \exp i(\underline{k} \cdot \underline{x} - \omega t) \quad (2.4)$$

From Eq. (2.3) we see that the conductivity is now given by the tensor

$$\sigma_{\alpha\beta}(\omega, \underline{k}) = (i\omega/4\pi) [1 - \epsilon(\omega)] \delta_{\alpha\beta} - [c \xi(\omega)/4\pi] \epsilon_{\alpha\beta\gamma} k_{\gamma} \quad (2.5)$$

As before, the polarizability vector is related to the induced polarization charge density ρ and the induced current through

$$\partial \rho / \partial t = - \nabla \cdot \underline{j} = - \nabla \cdot (\partial \underline{P} / \partial t) \quad (2.6)$$

while the divergenceless part of the current, \underline{j}_M , is related to the magnetization by

$$\underline{j}_M = c \nabla \times \underline{M} \quad (2.7)$$

It is easy to see that the type of response described above is equivalent, to first order in the small parameter ξ , to a phenomenological theory based on the constitutive relations²

$$4\pi \underline{P}(\omega) = [\underline{D}(\omega) - \underline{E}(\omega)] = [\underline{\epsilon}(\omega) - 1] \underline{E}(\omega) + i\xi(\omega) \underline{B}(\omega), \quad (2.8)$$

$$4\pi \underline{M}(\omega) = [\underline{B}(\omega) - \underline{H}(\omega)] = -i\xi \epsilon^{-1}(\omega) \underline{D}(\omega). \quad (2.9)$$

The same parameter ξ appears in Eqs. (2.8) and (2.9) since both \underline{P} and \underline{M} originate from the same induced current (2.3).

In the following section the material (constitutive) relations will be used, together with Maxwell equations, in order to relate the measurable optical activity parameters to ξ . On the other hand, all the relevant information in relation to the response of the medium to an electromagnetic wave is also contained in the conductivity tensor (2.5) which will be studied in detail in sections V and VI.

III. COMPLEX ROTATORY POWER

Let us study the propagation of a right (left) circularly polarized plane wave in a nonmagnetic isotropic (or cubic) medium in which the relations (2.8) and (2.9) hold. The electric field of such a wave propagating in the z direction is

$$\underline{E}_{(-)}^{(+)} = E_0^{(+)} (\hat{e}_{x(-)}^{(+)} + i\hat{e}_{y(-)}^{(+)}) \exp i\omega [N_{(-)}^{(+)}(z/c) - t], \quad (3.1)$$

where $\hat{e}_{x(-)}^{(+)}$ and $\hat{e}_{y(-)}^{(+)}$ are unit vectors in the respective directions and

$$N_{(-)}^{(+)}(\omega) = n_{(-)}^{(+)}(\omega) + i\kappa_{(-)}^{(+)}(\omega), \quad (3.2)$$

are the complex refractive indices.

Adding equal amounts of right and left circularly polarized light we can form a linearly polarized incident wave. Since the material shows circular dichroism, i.e., the two circular components suffer different absorptions, the wave becomes elliptically polarized with an ellipticity given by²

$$\rho(\omega) = (\omega/2c) [\kappa_{+}(\omega) - \kappa_{-}(\omega)]. \quad (3.3)$$

At the same time, per unit path length, the main axis of the ellipse is rotated by an angle

$$\phi(\omega) = (\omega/2c) [n_{+}(\omega) - n_{-}(\omega)]. \quad (3.4)$$

$\phi(\omega)$ is also known as the rotatory power of the substance. Both the rotatory power and the ellipticity can be analysed together in terms of the complex rotatory power

$$\Phi(\omega) = \phi(\omega) + i\rho(\omega) = (\omega/2c) [N_{+}(\omega) - N_{-}(\omega)]. \quad (3.5)$$

From the constitutive relations (2.8) and (2.9), together with Maxwell equations⁶, one can derive

$$N_{\pm}(\omega) = [\sqrt{\epsilon(\omega)} \pm \xi(\omega)] [1 - \xi^2/\epsilon]^{-1} \approx \sqrt{\epsilon(\omega)} \pm \xi(\omega), \quad (3.6)$$

which, together with Eq. (3.5), leads to

$$\Phi(\omega) = \omega \xi(\omega)/c. \quad (3.7)$$

Thus, the complex rotatory power is simply related to the anti-symmetric part of the conductivity tensor (2.5). In section VI, an analysis of this antisymmetric part will allow us to derive a formula for the complex rotatory power.

IV. ROSENFELD-CONDON THEORY

The first quantum mechanical derivation of the rotatory power is due to Rosenfeld¹ who obtained

$$\phi^R(\omega) = (8\pi \eta \omega^2 / 3\hbar c) \sum_{\ell} R_{\ell 0} \left[\omega_{\ell 0}^2 - \omega^2 \right]^{-1} \quad (4.1)$$

Here, η is the number of optically active molecules per unit volume, $\omega_{\ell 0}$ is the transition frequency from the state ℓ to the ground state 0 and the rotational strength is related to the matrix element of the molecular (or active unit) electric dipole \underline{p} and magnetic dipole \underline{m} through

$$R_{\ell 0} = \text{Im} \left[\langle 0 | \underline{p} | \ell \rangle \langle \ell | \underline{m} | 0 \rangle \right] = -R_{0\ell} \quad (4.2)$$

It is easy to show that the rotational strengths satisfy the Kuhn sum rule^{7,2}

$$\sum_{\ell} R_{\ell 0} = 0 \quad (4.3)$$

As it stands, Eq. (4.1) is unable to describe a nonvanishing dichroism of a substance⁸. This fact prompted Condon² to modify Eq. (4.1) by the introduction of finite widths for the transitions thus obtaining the generalized complex rotatory power

$$\Phi^{RC}(\omega) = (8\pi \eta \omega^2 / 3\hbar c) \sum_{\ell} R_{\ell 0} \left[\omega_{\ell 0}^2 - \omega^2 - i\omega\gamma_{\ell 0} \right]^{-1} \quad (4.4)$$

This formula is generally accepted as giving a correct description of the natural optical activity phenomenon.

There is a problem, however, in that, in conjunction with Eqs. (2.5) and (3.7), the rotatory power (4.4) yields a conductivity tensor behaving asymptotically as

$$\sigma_{\alpha\beta}^{RC}(\omega) \xrightarrow{\omega \rightarrow \infty} (i\omega_p^2 / 4\pi\omega) \delta_{\alpha\beta} - (2\eta / 3\hbar\omega) \sum_{\ell} \gamma_{\ell 0} R_{\ell 0} \epsilon_{\alpha\beta\gamma} \hat{s}_{\gamma} \quad (4.5)$$

for a wave with $\underline{k} \rightarrow (\omega/c)\hat{s}$; \hat{s} being a unit vector and ω_p the free electron plasma frequency. The first term after the arrow in Eq. (4.5) is precisely the asymptotic form of the free electron gas conductivity. The second term, however, should be unacceptable³ according to the usual argument that being photon energies at very high frequencies much larger than electronic binding energies, any electronic system should respond, to first approximation, in the same way as a free electron gas.

More recently, Thomaz and Nussenzveig³ (TR) proposed for the complex rotatory power the formula

$$\Phi^{TN}(\omega) = (8\pi\eta / 3\hbar c) \sum_{\ell} \omega_{\ell 0}^2 R_{\ell 0} \left[\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2 \right]^{-1} \quad (4.6)$$

which does lead to a conductivity tensor having the free electron gas asymptotic behavior. However, Φ^{TN} does not vanish for $\omega \rightarrow 0$. Unless corrected, this is a serious drawback, as the authors themselves pointed out, since $\sigma_{\alpha\beta}(\omega)$, $\underline{P}(\omega)$ and $\underline{M}(\omega)$ being proportional to $\xi^{TN} = c\Phi^{TN}/\omega$ [see Eqs. (2.5), (2.8) and (2.9)] would develop a pole at the origin.

V. KUBO FORMALISM

As was already remarked, the complex rotatory power is closely related to the antisymmetric part of the conductivity tensor. Thus, a possible approach to the obtention of $\bar{\Phi}$ consists in the analysis of the conductivity.

Some time ago, Kubo⁵ developed a very elegant formalism for the study of transport coefficients in the context of the linear response approximation. For the particular case of the conductivity tensor of a medium where v_T is the total number of electrons per unit volume, the Kubo formula can be written as⁹

$$\sigma_{\alpha\beta}(\underline{k}, \omega) = -(v_T e^2 / im\omega) \delta_{\alpha\beta} + \sum_{\alpha\beta} \underline{\sigma}_{\alpha\beta}(\underline{k}, \omega) \quad (5.1)$$

with

$$\sum_{\alpha\beta} \underline{\sigma}_{\alpha\beta}(\underline{k}, \omega) = (1/\hbar\omega) \int_{-\infty}^{\infty} dt \theta(-t) \langle [\underline{j}_{\alpha}(\underline{k}, 0), \underline{j}_{\beta}(-\underline{k}, t)] \rangle_{AV} e^{-i\omega t} \quad (5.2)$$

Here, $(-e)$ is the electron charge, m its mass and $\theta(t)$ Heaviside's step function. The Fourier transform of the induced current in Eq. (5.2) is normalized according to

$$\underline{j}_{\alpha}(\underline{k}, t) = \int d^3x e^{-i\underline{k} \cdot \underline{x}} \underline{j}_{\alpha}(\underline{x}, t) \quad (5.3)$$

We are primarily interested in the study of natural optical activity which, as we will see, depends (in first order) on the interaction between the electric dipole \underline{p}^a and magnetic dipole \underline{m}^a of the active part a , summed over all parts per unit volume. We are talking about active parts or units because we want to be as general as possible. These parts could be atoms,

molecules, portions of a molecule, unit cells in a crystal, etc.. For simplicity all the n parts per unit volume will be assumed to be equal, each containing Z electrons. The total number of electrons per unit volume is $v_T = nZ$.

The subscript AV in Eq. (5.2) stands for an averaging process. In principle, two kinds of averages are involved¹⁰. One is a thermal average that has to do with the population of the active unit states with respect to which the expectation value of the retarded commutator is taken. For simplicity, our analysis will be done at zero temperature and only expectations with respect to the ground state will appear. The second kind of average, which is very important for our problem and will be done later on, is an average over the orientation of the active units in relation to the direction of wave propagation.

Next step is to approximate the current in Eq. (5.3) by the sum of its electric dipole $\underline{p}^a(t)$ and magnetic dipole $\underline{m}^a(t)$ terms according to⁶

$$\underline{j}(\underline{k}, t) = \sum_{a=1}^n [\partial \underline{p}^a(t) / \partial t + i \underline{k} \times \underline{m}^a(t)] \quad (5.4)$$

Neglecting the term quadratic in \underline{m} , Eq. (5.2) can be written as

$$\sum_{\alpha\beta} \underline{\sigma}_{\alpha\beta}(\underline{k}, \omega) = \sigma_{\alpha\beta}^{(p)}(\underline{k}, \omega) + \sigma_{\alpha\beta}^{(m)}(\underline{k}, \omega) \quad (5.5)$$

with

$$\sigma_{\alpha\beta}^{(p)}(\underline{k}, \omega) = (1/\hbar\omega) \sum_{a,b} \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(-t) \langle [\underline{p}_{\alpha}^a(0), \underline{p}_{\beta}^b(t)] \rangle_{AV} \quad (5.6)$$

$$\sigma_{\alpha\beta}^{(m)}(\underline{k}, \omega) = - (ick_{\gamma}/\hbar\omega) \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(-t) \left\{ \varepsilon_{\beta\gamma\lambda} \langle [\dot{p}_{\alpha}^a(0), m_{\lambda}^b(t)] \rangle - \varepsilon_{\alpha\gamma\lambda} \langle [m_{\lambda}^a(0), \dot{p}_{\beta}^b(t)] \rangle \right\}_{Av} \quad (5.7)$$

where, as usual, $\dot{p}_{\alpha}^a = \partial p_{\alpha}^a / \partial t$.

$\sigma_{\alpha\beta}^{(p)}$ is proportional to the dielectric function and will be studied in the present section. The analysis of $\sigma_{\alpha\beta}^{(m)}$ from which the rotatory power can be obtained, will be left to the following section. Integrations by parts transform Eq. (5.6) into

$$\sigma_{\alpha\beta}^{(p)}(\underline{k}, \omega) = (1/\hbar\omega) \sum_{a,b} \int_{-\infty}^{\infty} dt e^{-i\omega t} \left\{ \omega^2 \theta(-t) \langle [p_{\alpha}^a(0), p_{\beta}^b(t)] \rangle - i\omega \delta(t) \langle [p_{\alpha}^a(0), p_{\beta}^b(t)] \rangle - \delta(t) \langle [\dot{p}_{\alpha}^a(0), \dot{p}_{\beta}^b(t)] \rangle \right\}_{Av} \quad (5.8)$$

Since the electric dipole of the molecule (or active unit of the crystal) can be written in terms of the electronic positions x^i as

$$p_{\alpha}^a = -e \sum_i x_{\alpha}^{ai} \quad (5.9)$$

where the sum is over all electrons in the unit, an elementary calculation leads to

$$\delta(t) [p_{\alpha}^a(0), p_{\beta}^b(t)] = 0 \quad (5.10)$$

$$\sum_{a,b} \delta(t) [p_{\alpha}^a(0), \dot{p}_{\beta}^b(t)] = (iv_T e^2/m\omega) \delta_{\alpha\beta} \delta(t) \quad (5.11)$$

Eq. (5.8) then simplifies to

$$\sigma_{\alpha\beta}^{(p)}(\underline{k}, \omega) = (v_T e^2/im\omega) + \sigma_{\alpha\beta}^{(pl)}(\underline{k}, \omega) \quad (5.12)$$

with

$$\sigma_{\alpha\beta}^{(pl)}(\underline{k}, \omega) = (\omega/\hbar) \sum_{a,b} \int_{-\infty}^{\infty} dt e^{-i\omega t} \theta(-t) \langle [p_{\alpha}^a(0), p_{\beta}^b(t)] \rangle_{Av} \quad (5.13)$$

The first term on the right hand side of Eq. (5.12) cancels the corresponding term in Eq. (5.1) which comes from the contribution of the "diamagnetic current". The more interesting term, which we have called $\sigma_{\alpha\beta}^{(pl)}$, will lead us to an expression for the usual (nongyrotropic) dielectric function.

The averaging over all orientations of the p 's can be easily performed according to

$$\sum_{a,b} (p_{\alpha}^a p_{\beta}^b)_{Av} = \frac{1}{3} \sum_a |p_a^a|^2 \delta_{\alpha\beta} = \eta p_x^2 \delta_{\alpha\beta} = \eta p_x^2 \delta_{\alpha\beta} \quad (5.14)$$

We are trying to keep our formalism as general as possible so as to be able to describe the conductivity in different types of media. At this point it is convenient to introduce a complete set of intermediate states that for a solid, for instance, could be a complete set of electronic Bloch states summed over the band index and integrated over momentum. On the other hand, in the case of a molecular liquid, for instance, Bloch states are no longer appropriate and we will need a complete set of molecular states.

The best way to englobe, in a simple way, different media is to continue to assume they are composed of equal units. In each unit there are, at zero temperature, bound electrons in their equilibrium states labeled generically by 0, and conduction electrons in states labeled by their momenta q . Due to the

interaction with the electromagnetic field the electrons can occupy excited states. The states obey the completeness relation

$$\sum_{\underline{l}, (\underline{q})} |\underline{l}, (\underline{q})\rangle \langle \underline{l}, (\underline{q})| \equiv \sum_{\underline{l}} |\underline{l}\rangle \langle \underline{l}| + \sum_{\underline{q}} |\underline{q}\rangle \langle \underline{q}| = 1 \quad (5.15)$$

It is also convenient to use, for the step function in Eq. (5.13), the representation

$$e^{-i\omega t} \theta(-t) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\Omega \frac{e^{-i\Omega t}}{\Omega - \omega - is} \quad (5.16)$$

where the $s \rightarrow 0$ limit is implied. After all these steps are taken, Eq. (5.13) is transformed into

$$\begin{aligned} \sigma_{\alpha\beta}^{(pl)}(\underline{k}, \omega) &= \frac{\omega \eta \delta_{\alpha\beta}}{2\pi i \hbar} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} \frac{d\Omega}{\Omega - \omega - is} \sum_{\underline{l}, (\underline{q})} \\ &\times \left\{ \langle 0 | p_x(0) | \underline{l}, (\underline{q})\rangle \langle \underline{l}, (\underline{q}) | p_x(t) | 0 \rangle - \langle 0 | p_x(t) | \underline{l}, (\underline{q})\rangle \langle \underline{l}, (\underline{q}) | p_x(0) | 0 \rangle \right\} \end{aligned} \quad (5.17)$$

Next we use the operator relation

$$p_x(t) = e^{iHt/\hbar} p_x(0) e^{-iHt/\hbar} \quad (5.18)$$

where H is the Hamiltonian, and integrate with respect to t and Ω obtaining

$$\begin{aligned} \sigma_{\alpha\beta}^{(pl)}(\underline{k}, \omega) &= \frac{\eta \omega \delta_{\alpha\beta}}{i\hbar} \sum_{\ell \neq 0} \left| [p_x(0)]_{\ell 0} \right|^2 \left[\frac{1}{\omega_{\ell 0} - \omega - is} + \frac{1}{\omega_{\ell 0} + \omega + is} \right] + \\ &+ (\text{contribution from conduction electrons}) \end{aligned} \quad (5.19)$$

where $\omega_{\ell 0}$ are the frequencies for the transitions $\ell \rightarrow 0$. At this point it is customary to introduce the relaxation times $\tau_{\ell 0}$, or the widths $\gamma_{\ell 0} = 2/\tau_{\ell 0}$, by the replacement $s \rightarrow (\gamma_{\ell 0}/2)$ in each of the terms. It is also convenient to separate out the conduction term (intraband in solid state parlance). These steps transform Eq. (5.19) into

$$\sigma_{\alpha\beta}^{(pl)}(\omega) = \frac{i\omega_{pc}^2 \delta_{\alpha\beta}}{4\pi(\omega + i/\tau_c)} + \frac{2\omega \eta \delta_{\alpha\beta}}{i\hbar} \sum_{\ell \neq 0} \frac{\omega_{\ell 0} \left| [p_x(0)]_{\ell 0} \right|^2}{\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2} \quad (5.20)$$

where in the first term on the right hand side, ω_{pc} is the plasma frequency for the conduction electrons and τ_c their relaxation time. In the term arising from the contribution of the bound electrons (interband term) it is customary to introduce the oscillator strengths

$$f_{\ell 0} = (2m\omega_{\ell 0}/\hbar e^2 v_B) \left| [p_x(0)]_{\ell 0} \right|^2 \quad (5.21)$$

where v_B is the number of bound electrons in a unit. The $f_{\ell 0}$'s obey the well known Thomas-Reiche-Kuhn sum rule¹¹

$$\sum_{\ell} f_{\ell 0} = 1 \quad (5.22)$$

Eq. (5.20), together with Eqs. (2.5) and (5.21), yields the somewhat simplified but useful formula for the dielectric function

$$\epsilon(\omega) = 1 - \frac{\omega_{pc}^2}{\omega(\omega + i/\tau_c)} + \frac{4\pi e^2 (\eta v_B)}{m} \sum_{\ell} \frac{f_{\ell 0}}{\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2} \quad (5.23)$$

(ηv_B) is the number of bound electrons per unit volume.

Expressions like (5.23) are obtained, in similar or different ways, in several books and articles¹². Our purpose in going through that derivation again is twofold: First, we wanted to outline, in a more familiar context, a procedure that will be followed in the next section in order to obtain a formula for the rotatory power. And second, we want to make sure that we have the right normalization since in the next section we will get, for the rotatory power, a numerical factor twice as large as in the Rosenfeld-Condon formula.

VI. ROTATORY POWER FROM KUBO FORMULA

All the information on the natural optical activity of the substance is contained in $\sigma_{\alpha\beta}^{(m)}$ of Eq. (5.7), where integrations by parts yield

$$\sigma_{\alpha\beta}^{(m)} = \sigma_{\alpha\beta}^{(m1)} + \sigma_{\alpha\beta}^{(m2)} \quad (6.1)$$

with

$$\sigma_{\alpha\beta}^{(m1)}(\omega, \underline{k}) = \frac{ick_Y}{\hbar\omega} \sum_{a,b} \left\{ \epsilon_{\beta\gamma\lambda} \langle [p_\alpha^a(0), m_\lambda^b(0)] \rangle + \epsilon_{\alpha\gamma\lambda} \langle [m_\lambda^a(0), p_\beta^b(0)] \rangle \right\}_{Av} \quad (6.2)$$

and

$$\sigma_{\alpha\beta}^{(m2)}(\omega, \underline{k}) = -\frac{ck_Y}{\hbar} \sum_{a,b} \int dt e^{-i\omega t} \theta(-t) \left\{ \epsilon_{\beta\gamma\lambda} \langle [p_\alpha^a(0), m_\lambda^b(t)] \rangle + \epsilon_{\alpha\gamma\lambda} \langle [m_\lambda^a(0), p_\beta^b(t)] \rangle \right\}_{Av} \quad (6.3)$$

with p_α^a as in Eq. (5.9) and

$$m_\lambda^b = -(e/2c) \epsilon_{\lambda\alpha\beta} \sum_i X_\alpha^{bi} \dot{X}_\beta^{bi} \quad (6.4)$$

the commutators in Eq. (6.2) can be readily calculated with the result

$$\sigma_{\alpha\beta}^{(m1)}(\omega, \underline{k}) = -(e^2 v_T / 2m\omega) \langle X_\alpha^a k_\beta - k_\alpha X_\beta^a \rangle_{Av} = 0 \quad (6.5)$$

where v_T is the total number of electrons per unit volume and X_α^a a typical electronic coordinate.

In order to calculate Eq. (6.3) we first average over the orientations of the active units (molecules, etc.) according to

$$\sum_{a,b} \langle p_\alpha^a m_\lambda^b \rangle_{Av} = \frac{1}{3} \sum_a \langle p_\alpha^a m_\lambda^a \rangle \delta_{\alpha\lambda} = \frac{1}{3} n \langle p_\alpha^a m_\lambda^a \rangle \delta_{\alpha\lambda} \quad (6.6)$$

where in the last term we have dropped the unit label a since we will not need it in the following. The introduction of a complete set of intermediate states $|l\rangle$, the representation (5.16) for the θ -function and the inclusion of finite widths ($\gamma_{l0}/2$), together with Eq. (6.6), transform Eq. (6.3) into

$$\sigma_{\alpha\beta}^{(m)}(\omega, \underline{k}) = -\frac{cnk_Y}{3i\hbar} \sum_l \left\{ \epsilon_{\beta\gamma\alpha} \left[\frac{\langle 0 | p_\alpha | l \rangle \langle l | m_\beta | 0 \rangle}{\omega_{l0} - \omega - i\gamma_{l0}/2} + \frac{\langle 0 | m_\beta | l \rangle \langle l | p_\alpha | 0 \rangle}{\omega_{l0} + \omega + i\gamma_{l0}/2} \right] + \epsilon_{\alpha\gamma\beta} \left[\frac{\langle 0 | m_\alpha | l \rangle \langle l | p_\beta | 0 \rangle}{\omega_{l0} - \omega - i\gamma_{l0}/2} + \frac{\langle 0 | p_\beta | l \rangle \langle l | m_\alpha | 0 \rangle}{\omega_{l0} + \omega + i\gamma_{l0}/2} \right] \right\} \quad (6.7)$$

where $\underline{p} \equiv \underline{p}(0)$, $\underline{m} \equiv \underline{m}(0)$. Since, obviously,

$$\langle 0 | \underline{m} | \ell \rangle \langle \ell | \underline{p} | 0 \rangle = [\langle 0 | \underline{p} | \ell \rangle \langle \ell | \underline{m} | 0 \rangle]^* \quad (6.8)$$

using the rotational strengths defined in Eq. (4.2) we can write

$$\sigma_{\alpha\beta}^{(m)}(\omega, \underline{k}) = -\frac{4cn}{3\hbar} \epsilon_{\alpha\beta\gamma} k_\gamma \sum_{\ell} \frac{\omega_{\ell 0} R_{\ell 0}}{\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2} \quad (6.9)$$

Tracing this term back to Eqs. (5.1) and (5.5) we see that (6.9) is the complete antisymmetric part of the conductivity tensor. A comparison with Eqs. (2.5) and (3.7) immediately leads to the complex rotatory power formula

$$\Phi(\omega) = \frac{16\pi n\omega}{3\hbar c} \sum_{\ell} \frac{\omega_{\ell 0} R_{\ell 0}}{\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2} \quad (6.10)$$

Besides the numerical factor being twice as large as in the Rosenfeld-Condon expression (4.4), the asymptotic behavior is obviously different. The conductivity tensor

$$\sigma_{\alpha\beta}(\omega, \underline{k}) = (i\omega/4\pi) [1 - \epsilon(\omega)] \delta_{\alpha\beta} + \sigma_{\alpha\beta}^{(m)}(\omega, \underline{k}) \quad (6.11)$$

with the last term given by Eq. (6.9), has, to first order, the same asymptotic ($\omega \rightarrow \infty$) behavior as the free electron gas. Also, Eq. (6.10) vanishes, as it should, in the $\omega \rightarrow 0$ limit.

Several Kramers-Kronig like dispersion relations involving optical activity functions exist in the literature^{3,8,13}.

Of interest to us, is

$$\rho(\omega) = -\frac{2}{\pi} \omega P \int_0^{\infty} \frac{\phi(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (6.12)$$

Here, P stands for the principal value. Multiplying both sides by ω and taking the $\omega \rightarrow \infty$ limit, Rosenfeld-Condon dispersion formula (4.4), together with Eq. (6.12), leads to

$$\int_0^{\infty} \phi^{RC}(\omega) d\omega = \frac{4\pi^2 n}{3\hbar c} \sum_{\ell} R_{\ell 0} \gamma_{\ell 0} \quad (6.13)$$

Following the same procedure with our Eq. (6.10) [instead of 4.4] we get

$$\int_0^{\infty} \phi(\omega) d\omega = 0 \quad (6.14)$$

We wish we knew enough about the experimental possibilities to be able to suggest the sum rules (6.13) and (6.14) as a way to decide which dispersion law, RC or ours, is the correct one.

VII. LOCAL FIELD CORRECTION

Up to now we have, for simplicity, neglected the so-called local field correction. It was assumed that the local electric field \underline{E}' acting on the electrons was not much different from the external electric field \underline{E} . Relaxing this approximation, the induced current can be connected to either \underline{E} or \underline{E}' according to

$$\begin{aligned} j_{\alpha}(\omega, \underline{k}) &= \sigma_{\alpha\beta}(\omega, \underline{k}) E_{\beta}(\omega, \underline{k}) \\ &= \sigma'_{\alpha\beta}(\omega, \underline{k}) E'_{\beta}(\omega, \underline{k}) \end{aligned} \quad (7.1)$$

While the true conductivity tensor is $\sigma_{\alpha\beta}$, what we have actually calculated in sections V and VI are the symmetric and antisymmetric parts of $\sigma'_{\alpha\beta}$.

In the simple case of a medium with cubic symmetry, the local field correction is given by the Lorentz relation

$$\underline{\underline{E}}'(\omega) = \underline{\underline{E}}(\omega) + (4\pi/3) \underline{\underline{P}}(\omega) = \left[\frac{\epsilon(\omega)+2}{3} \right] \underline{\underline{E}}(\omega) \quad (7.2)$$

which immediately leads to

$$\sigma_{\alpha\beta}(\omega, \mathbf{k}) = \left[\frac{\epsilon(\omega)+2}{3} \right] \sigma'_{\alpha\beta}(\omega, \mathbf{k}) \quad (7.3)$$

Being proportional to the antisymmetric part of the conductivity tensor, the rotatory power is changed, by the local field correction, from (6.10) to

$$\underline{\underline{\Phi}}(\omega) = \frac{16\pi n \omega}{3\hbar c} \left[\frac{\epsilon(\omega)+2}{3} \right] \sum_{\ell} \frac{\omega_{\ell 0} R_{\ell 0}}{\omega_{\ell 0}^2 - (\omega + i\gamma_{\ell 0}/2)^2} \quad (7.4)$$

Since the local field correcting factor $(\epsilon+2)/3$ goes to one in the $\omega \rightarrow \infty$ limit, the asymptotic behavior of $\underline{\underline{\Phi}}$ remains unaltered by that correction. In particular, it is still true that the Rosenfeld-Condon rotatory power formula changes the asymptotic free electron conductivity by the addition of the second line of Eq. (4.5). Our expression (7.4) instead, has the correct behavior at both ends of the spectrum. While still going to zero in the $\omega \rightarrow 0$ limit, it does not modify the free electron like asymptotic response of the medium in the $\omega \rightarrow \infty$ limit.

FOOTNOTES AND REFERENCES

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- 5 - R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).
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- 8 - A. Moscovitz, in "Advances in Chemical Physics", vol. 4 (I. Prigogine ed., Interscience, New York, 1962).
- 9 - In almost this form, the Kubo conductivity formula can be found in Ref. 10.
- 10 - J. Callaway, "Quantum Theory of the Solid State", part B, (Academic Press, New York, 1974).
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- 12 - A derivation specially adapted to solids in terms of Bloch like states is given by H. Ehrenreich, in "The Optical Properties of Solids" (J. Tauc ed., Academic Press, New York, 1966).
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