Moments of the optical rotatory power and circular dichroism for an isotropic medium

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The moments of the optical rotatory power and circular dichroism are determined for an isotropic nonconducting medium. The even moments of the optical rotatory power and the odd moments of the circular dichroism are determined by crossing-symmetry arguments to be zero. Formal expressions for the odd moments of the optical rotatory power and the even moments of the circular dichroism are also derived. The possible application of these moments as a necessary constraint on experimental data is discussed.

INTRODUCTION

It has been recognized for a long time that the analytic properties of the generalized optical rotatory power lead to fundamental interconnections between the real and imaginary parts of this quantity, that is, between the optical rotation and the circular dichroism. The relationships are referred to as Kramers-Kronig transforms. The analytic properties of the generalized optical rotatory power also serve as a basis for obtaining fundamental relationships that must be obeyed by the dissipative and dispersive modes. The purpose of this paper is to employ the analytic properties of the generalized optical rotatory power to obtain the moments of the optical rotatory power and circular dichroism.

The importance of obtaining constraints for a molecular property such as optical activity become apparent when the present status of the computational side of optical activity is examined. Accurate theoretical predictions of an optical rotatory dispersion curve are a long way from realization. The reasons for this situation are well known. Molecules exhibiting (natural) optical activity do not fit into "the few electron" category. Secondly, calculations of the rotational strength require a knowledge of the excited states which leads to extreme computational difficulties. Despite these problems, attempts are being made to provide accurate calculations of the rotational strength,[1] and this is likely to be a stimulating and challenging area for future molecular calculations.

The assumptions that form the basic input in this note are very general and fundamental and not restricted to the particular structure of a given material. The price paid for employing such general assumptions is that the moments apply only to the complete spectrum of data. That is, experimental measurements must be accessible in the frequency interval $(0, \infty)$.

The complex optical rotatory power for an isotropic medium is defined by

$$\Phi(\omega) = \phi(\omega) + i\theta(\omega) , \tag{1}$$

where $\phi(\omega)$ is the optical rotatory power and $\theta(\omega)$ the circular dichroism. In terms of the complex refractive index,

$$\Phi(\omega) = \frac{\omega}{2c}[N_+(\omega) - N_-(\omega)]$$

$$= \frac{\omega}{2c}[n_+(\omega) - n_-(\omega)] + \frac{i\omega}{2c}[\kappa_+(\omega) - \kappa_-(\omega)] . \tag{2}$$

The subscripts (+) and (−) denote left- and right-polarized modes.

DERIVATION OF MOMENTS

The moments fall into two distinct groups. The first consists of the even moments of the optical rotatory dispersion and odd moments of the circular dichroism. The second group consists of the remaining moments. The first group can be determined directly from the analytic properties and crossing-symmetry conditions on $\Phi(\omega)$. For the second group, only formal relationships can be obtained using analytic properties of $\Phi(\omega)$.

The important relation necessary for the derivation of moments in the first group is the crossing-symmetry relationship[2,3]

$$\Phi(-\Omega^*) = \Phi^*(\Omega) . \tag{3}$$

In this note, real and complex frequencies are denoted by ω and Ω, respectively. The real and imaginary parts of the complex index of refraction for an optically active medium satisfy

$$\begin{bmatrix} n_+(-\omega) \\ n_-(-\omega) \end{bmatrix} = \Gamma \begin{bmatrix} n_+(\omega) \\ n_-(\omega) \end{bmatrix} , \tag{4}$$

$$\begin{bmatrix} \kappa_+(-\omega) \\ \kappa_-(-\omega) \end{bmatrix} = -\Gamma \begin{bmatrix} \kappa_+(\omega) \\ \kappa_-(\omega) \end{bmatrix} , \tag{5}$$

where the matrix Γ is given by

$$\Gamma = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{6}$$

The two important crossing relations employed below are

$$\phi(-\omega) = \phi(\omega), \tag{7}$$

$$\theta(-\omega) = -\theta(\omega). \tag{8}$$

We now consider the function

$$F(\Omega) = \Omega^m \Phi(\Omega), \tag{9}$$

where m is an integer and evaluate the contour integral $\oint_\gamma F(\Omega)d\Omega$, where the contour γ includes the real axis $(-\infty, \infty)$ and a semicircular arc (radius R) in the upper half complex frequency plane, and we let $R \to \infty$. In the upper half plane $\Phi(\omega)$ is an analytic function. The values of m permitted are those that lead to *convergent* moments and that allow the contribution from the *semicircular arc to be discarded.* This point will be elaborated on below. It is also assumed that negative values of m are restricted by the condition that there be no singularity at $\omega \to 0$. Evaluation of the contour integral leads to

$$\int_{-\infty}^{\infty} \omega^m \Phi(\omega)d\omega = 0 \tag{10}$$

since there are no poles enclosed by the contour. Making use of the crossing-symmetry relations, Eq. (3) leads to

$$\int_0^{\infty} \omega^m [\Phi(\omega) + (-1)^m \Phi^*(\omega)]d\omega = 0. \tag{11}$$

Substituting Eq. (1) into Eq. (11) leads to the results

$$\int_0^{\infty} \omega^m \phi(\omega)[1 + (-1)^m]d\omega = 0, \tag{12}$$

$$\int_0^{\infty} \omega^m \theta(\omega)[1 + (-1)^{m+1}]d\omega = 0. \tag{13}$$

The moments for the first group are therefore determined immediately to be

$$\int_0^{\infty} \omega^m \phi(\omega)d\omega = 0, \quad m \text{ even} \tag{14}$$

$$\int_0^{\infty} \omega^m \theta(\omega)d\omega = 0, \quad m \text{ odd}. \tag{15}$$

The odd moments of the optical rotatory power and the even moments of the circular dichroism cannot be determined from the above integral $\oint_\gamma F(\Omega)d\Omega$. These moments turn out to be considerably more complicated, and only formal relationships can be obtained based on a knowledge of only the analytic properties of $\Phi(\Omega)$.

The complex optical rotatory power can be written in the form

$$\Phi(\omega) = \int_0^{\infty} e^{i\omega\tau} f(\tau)d\tau, \tag{16}$$

where $f(\tau)$ is a real function which depends on the properties of the medium. At purely imaginary frequencies (ω' real), we have

$$\Phi(i\omega') = \phi(i\omega') + i\theta(i\omega') = \int_0^{\infty} e^{-\omega'\tau} f(\tau)d\tau. \tag{17}$$

It follows from Eq. (17) that at purely imaginary frequencies

$$\theta(i\omega') = 0. \tag{18}$$

We now consider the contour integral $\oint_{\gamma'} F(\Omega)d\Omega$, where the contour γ' is the real axis $(0, R)$, a circular arc radius R (center the origin), and the imaginary axis $(R, 0)$, and we examine the limit $R \to \infty$. Then we obtain

$$\int_0^{\infty} \omega^m \Phi(\omega)d\omega = i^{m+1} \int_0^{\infty} \omega^m \Phi(i\omega)d\omega. \tag{19}$$

Separating into real and imaginary parts gives

$$\int_0^{\infty} \omega^m \phi(\omega)d\omega = \mathrm{Re}(i^{m+1}) \int_0^{\infty} \omega^m \phi(i\omega)d\omega, \tag{20}$$

$$\int_0^{\infty} \omega^m \theta(\omega)d\omega = \mathrm{Im}(i^{m+1}) \int_0^{\infty} \omega^m \phi(i\omega)d\omega, \tag{21}$$

where Re and Im denote the real and imaginary parts respectively, and Eq. (18) has been employed. Equations (14) and (15) are recovered for even values of m in Eq. (20) and odd values of m in Eq. (21). From Eq. (20) we have

$$\int_0^{\infty} \omega^m \phi(\omega)d\omega = (-1)^{(m+1)/2} \times \int_0^{\infty} \omega^m \phi(i\omega)d\omega \text{ for } m \text{ odd}, \tag{22}$$

and from Eq. (21)

$$\int_0^{\infty} \omega^m \theta(\omega)d\omega = (-1)^{m/2} \times \int_0^{\infty} \omega^m \phi(i\omega)d\omega \text{ for } m \text{ even}. \tag{23}$$

DISCUSSION

Some special cases of the above moment formulas have been derived recently by Smith.[3] For the optical rotatory power, Smith has obtained the special cases of Eq. (14) for $m = -2$ and $m = 0$. Smith has also derived two moments for the circular dichroism. He has given the special case of Eq. (15) for $m = -1$. Smith has also calculated the result for $m = 1$, and reports the result

$$\int_0^\infty \omega\theta(\omega)d\omega = \frac{8\pi^2}{3\hbar}\mathfrak{N}\sum_b \omega_{ba}^2 R_{ba}, \tag{24}$$

where $\mathfrak{N}$ is the number of optically active molecules per unit volume, and R_{ba} is the rotational strength. Emeis *et al.*[4] have also reported the special case $m=-1$ for Eq. (15).

Equation (24) is not in agreement with the result derived above using crossing-symmetry arguments. The origin of this discrepancy is not difficult to find. The method employed by Smith is based on an examination of the asymptotic behavior of the appropriate dispersion relation for the circular dichroism. This technique has been usefully employed by a number of workers to obtain sum rules for optical constants and scattering amplitudes.[5-9] One important prerequisite for employing the asymptotic expansion technique is that a precise knowledge of the asymptotic behavior for the relevant property is required, since moments are obtained by comparison of asymptotic expansions. Smith argued that the appropriate asymptotic behavior could be obtained from the Rosenfeld equation

$$\phi(\omega) = \frac{8\pi}{3\hbar c}\mathfrak{N}\sum_b \omega^2 \frac{R_{ba}}{\omega_{ba}^2 - \omega^2}. \tag{25}$$

Smith assumes the validity of Eq. (25) for determining the limit $\omega \to \infty$ for both conducting and nonconducting media. Now it is well known that one of the fundamental approximations involved in obtaining the Rosenfeld equation in the above form is that the wavelength of light must be much greater than the molecular dimensions of the optically active species. With this constraint, it is *not* possible to determine the limit $\omega \to \infty$ of the optical rotatory power and circular dichroism from the Rosenfeld formula.

To ascertain which moments are convergent requires a detailed knowledge of the asymptotic behavior for both the high- and low-frequency limits. For the case of an *isotropic* medium, Tobias, Brocki, and Balazs[10] have recently considered a generalization of the Rosenfeld formulation, in which the restriction to the long wavelength limit is removed. The result obtained by Tobias *et al.* is

$$\phi(\omega) = \frac{2\pi\hbar^2\mathfrak{N}}{c^2}\sum_{m,i,j}\frac{(e_i e_j/m_i m_j)E_{mn}^{(0)}\Phi_{mn,ij}}{E_{mn}^{(0)2} - \hbar^2\omega^2}, \tag{26}$$

where

$$\Phi_{nm,ij} = \int dq \int dq' u_n^*(q)u_m^*(q)(\sin kR_{ij} - kR_{ij}\cos kR_{ij}) \times (kR_{ij})^{-3}\vec{R}_{ij}\cdot[\mathrm{grad}_{x_j'} u_n(q')\times \mathrm{grad}_{x_i} u_m(q)] \tag{27}$$

with $\vec{R}_{ij} = \vec{x}_i - \vec{x}_j$, and $u_n(q)$ are the eigenstates of the molecule. The other symbols have their usual meaning.

The number of convergent moments for negative values of m can be determined using the low-frequency limit obtained from the Rosenfeld equation. For $\omega \to 0$, optical activity vanishes like ω^2.[11] The only negative moments which converge subject to the constraints of the Rosenfeld equation are therefore

$$\int_0^\infty \omega^{-2}\phi(\omega)d\omega = 0, \tag{28}$$

$$\int_0^\infty \omega^{-1}\theta(\omega)d\omega = 0. \tag{29}$$

For positive moments, the Rosenfeld and Tobias-Brocki-Balazs generalization lead to different conclusions. In the Rosenfeld formulation, the optical activity vanishes as $\sim\omega^{-2}$ for $\omega \to \infty$. This restricts Eq. (14) to the single positive value $m=0$. As we noted above, however, the limit $\omega \to \infty$ cannot be obtained from the Rosenfeld equation. From the expression of Tobias *et al.*, Eq. (26), it is possible to show that the optical activity vanishes somewhat faster than $O(\omega^{-2})$ for $\omega \to \infty$.[12] If this result had been employed by Smith,[3] his derivation would lead to a result in agreement with Eq. (15) for $m=1$. The upper limit of m for which Eqs. (14) and (15) converge awaits further publications in this area.

The moment formulas obtained in this work can serve as a useful constraint for testing experimental data. Of course, it is possible with formulas of this kind that compensating errors at different spectral frequencies may occur, yet the moment formulas are still satisfied. The moment formulas therefore serve only as a *necessary* criterion on the quality of experimental data. The major limitation of the moment formulas is the necessity for having experimental data available over an infinite frequency range, and difficulties are to be expected for data sets on limited spectral ranges. To make use of the moment formulas for testing data, one of the following two assumptions may be employed. The experimental data to be tested are assumed to be band limited, that is, outside some spectral range (ω_1, ω_2), $\phi(\omega)$ and $\theta(\omega)$ are zero. The second approach is to assign an appropriate expression for the asymptotic behavior of $\phi(\omega)$ and $\theta(\omega)$ as $\omega \to \infty$ and $\omega \to 0$.

The moment formulas involving complex frequencies are purely formal results and, for practical purposes, would seem to be less useful in testing experimental data. The last and perhaps

most important comment is that the assumptions employed in this work are rather general and fundamental without regard to any specific material. Therefore, the convergent moment formulas derived in this work are valid for *any* isotropic nonconducting system.

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[1]A. Rauk, J. O. Jarvie, H. Ichimura, and J. M. Barriel, J. Am. Chem. Soc. 97, 5656 (1975).

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

[3]D. Y. Smith, Phys. Rev. B 13, 5303 (1976).

[4]C. A. Emeis, L. J. Oosterhoff, and G. de Vries, Proc. R. Soc. A297, 54 (1967).

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

[6]A. Villani and A. H. Zimmerman, Phys. Rev. B 8, 3914 (1973).

[7]K. Furuya, A. H. Zimmerman, and A. Villani, J. Phys. C 9, 4329 (1976).

[8]F. W. King, J. Phys. B 9, 147 (1976).

[9]F. W. King, J. Math, Phys. 17, 1509 (1976).

[10]I. Tobias, T. R. Brocki, and N. L. Balazs, J. Chem. Phys. 62, 4181 (1975).

[11]In the limit $\omega \to 0$, the factor depending upon kR_{ij} in Eq. (27) simplifies to $\frac{1}{3}$, and in this limit Eqs. (27) and (26) reduce back to the Rosenfeld expression, Eq. (25); see Ref. 10.

[12]M. Brockman, private correspondence.