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A Fourier series algorithm for the analysis of reflectance data

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Abstract. A simple Fourier series algorithm is presented for the determination of the phase, and hence the other optical constants, from measurements of the reflectance. The advantages of the proposed procedure and its mathematical equivalence with the Kramers–Kronig relations are discussed.

1. Introduction

Reflectance studies on solids provide one of the most valuable means by which the dispersion curves of the various optical constants can be determined. Relatively little work has been done to investigate different ways by which the key step in the determination of the optical constants, i.e., that of determining the phase, can be improved. The procedure which is currently employed to obtain the phase $\theta(\omega)$, from measurements of the reflectance $R(\omega)$, is the Kramers–Kronig relation (Velický 1961, Stern 1963)

$$\theta(\omega) = -\frac{\omega}{\pi} P\int_0^\infty \frac{\ln R(\omega')\mathrm{d}\omega'}{\omega'^2 - \omega^2}. \tag{1}$$

Recently, Peterson and Knight (1973) suggested that the Fourier allied integrals, which can be written as

$$f_\mathrm{i}(\omega) = \frac{2}{\pi}\int_0^\infty \mathrm{d}t \sin\omega t \int_0^\infty f_\mathrm{r}(\omega') \cos\omega' t\mathrm{d}\omega' \tag{2}$$

$$f_\mathrm{r}(\omega) = \frac{2}{\pi}\int_0^\infty \mathrm{d}t \cos\omega t \int_0^\infty f_\mathrm{i}(\omega') \sin\omega' t\mathrm{d}\omega' \tag{3}$$

where $f_\mathrm{r}(\omega)$ and $f_\mathrm{i}(\omega)$ are the real and imaginary parts of any generalised (complex) optical function, provide a more suitable means for inversion of optical data. Since very efficient algorithms for the rapid computation of Fourier integrals are available, the allied integral approach represents a useful alternative to the Kramers–Kronig method. In its present form, the allied integral approach cannot be employed for the reflectance. One requirement that must be satisfied in order to use equations (2) and (3),

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is that the function under consideration must have a suitable asymptotic behaviour. To obtain the phase from equation (2) would involve ln $R(\omega)$, which causes the integral to diverge.

2. Fourier series method

There is another method which is mathematically equivalent to the Kramers–Kronig relations. This is the Fourier conjugate series. It is this approach that will be discussed for the determination of the phase. The generalised reflectance $\tilde{r}(\omega)$ is

$$\tilde{r}(\omega) = R^{\frac{1}{2}}(\omega) \exp[\mathrm{i}\theta(\omega)]. \tag{4}$$

From equation (4), we have for the derivative,

$$-\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\tilde{r}(\omega) = \frac{\mathrm{d}\theta(\omega)}{\mathrm{d}\omega} - \mathrm{i}[2R(\omega)]^{-1}\frac{\mathrm{d}R(\omega)}{\mathrm{d}\omega}. \tag{5}$$

$R^{\frac{1}{2}}(\omega)$

The series algorithm is derived in terms of experimental data expressed in the form $[2R(\omega)]^{-1}\,\mathrm{d}R(\omega)/\mathrm{d}\omega$ for the following reason. To implement the Fourier series expansion, it is required that the function be bounded in the interval $(0, \infty)$. Since

$$R(\omega) = \mathrm{O}(\omega^{-4}) \qquad \text{as } \omega \to \infty$$

it is obvious that a Fourier series decomposition of $\ln R^{1/2}(\omega)$ is of no value. However the derivative $\mathrm{d}\ln R^{\frac{1}{2}}(\omega)/\mathrm{d}\omega$ serves the purpose. The function $\tilde{r}(\omega)$ is analytic in the extension to the upper half complex frequency plane, and arguments can be provided to show that $\ln\tilde{r}(\omega)$ is also analytic (Stern 1963) i.e., there are no zeros of $\tilde{r}(\omega)$ in the upper half plane. It follows immediately that $-\mathrm{i}\,\mathrm{d}\ln\tilde{r}(\omega)/\mathrm{d}\omega$ is also analytic in this domain.

It now proves to be highly convenient to carry out the conformal transformation

$$Z = (\omega - \mathrm{i})/(\omega + \mathrm{i}) \tag{6}$$

which carries the upper half plane in frequency space into the interior of the unit circle centred at the origin in Z-space. Therefore, we can now write

$$\begin{aligned} -\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\tilde{r}(\omega) &\to -\mathrm{i}\left[\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\tilde{r}(\omega)\right]_{\omega = -\mathrm{i}(Z+1)(Z-1)^{-1}} \\ &= \sum_{m=0}^{\infty} c_m Z^m \qquad \text{for } |Z| \leqslant 1. \end{aligned} \tag{7}$$

In writing the series expansion in equation (7), we have made use of the fact that $\mathrm{d}\ln\tilde{r}(\omega)/\mathrm{d}\omega$ in Z space is an analytic function in the unit circle. With the substitution

$$Z = \exp \mathrm{i}\Omega \tag{8}$$

equation (7) becomes

$$-\mathrm{i}\left[\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\tilde{r}(\omega)\right]_{\omega = -\mathrm{i}(Z+1)(Z-1)^{-1}} = \sum_{m=0}^{\infty} c_m \cos m\Omega + \mathrm{i}\sum_{m=1}^{\infty} c_m \sin m\Omega. \tag{9}$$

Introducing the definitions

$$\bar{R}(\Omega) = \left[\frac{1}{2R(\omega)}\frac{\mathrm{d}R}{\mathrm{d}\omega}\right]_{\omega = -\cot\Omega/2} \tag{10}$$

$$\bar{\theta}(\Omega) = \left[\frac{\mathrm{d}\theta(\omega)}{\mathrm{d}\omega}\right]_{\omega = -\cot\Omega/2} \tag{11}$$

and employing equations (5) and (8) leads to the result

$$-\mathrm{i}\left[\frac{\mathrm{d}}{\mathrm{d}\omega}\ln\tilde{r}(\omega)\right]_{\omega = -\mathrm{i}(Z+1)(Z-1)^{-1}} = \bar{\theta}(\Omega) - \mathrm{i}\bar{R}(\Omega). \tag{12}$$

The Fourier expansions of $\bar{R}(\Omega)$ and $\bar{\theta}(\Omega)$ in the interval $(-\pi, \pi)$ are

$$\bar{R}(\Omega) = \sum_{m=1}^{\infty} a_m \sin m\Omega \tag{13}$$

$$\bar{\theta}(\Omega) = \tfrac{1}{2}b_0 + \sum_{m=1}^{\infty} b_m \cos m\Omega \tag{14}$$

and the restriction to single trigonometric functions in equations (13) and (14) follows from the symmetry properties

$$\bar{R}(-\Omega) = -\bar{R}(\Omega) \tag{15}$$

$$\bar{\theta}(-\Omega) = \bar{\theta}(\Omega) \tag{16}$$

which can be deduced from the known symmetry properties of $R(\omega)$ and $\theta(\omega)$. Comparing equations (9) and (12), with the substitutions given by equations (13) and (14), leads to the results

$$2c_0 = b_0; \qquad c_m = b_m \qquad m \neq 0 \tag{17}$$

$$c_m = -a_m \qquad m \neq 0 \tag{18}$$

and hence

$$b_m = -a_m \qquad m \neq 0. \tag{19}$$

From the asymptotic condition

$$\lim_{\omega \to \infty}\left(\frac{\mathrm{d}\theta(\omega)}{\mathrm{d}\omega}\right) = 0 \tag{20}$$

we have that

$$\lim_{\omega \to \infty}\left(\frac{\mathrm{d}\theta(\omega)}{\mathrm{d}\omega}\right) = \bar{\theta}(0)$$

$$= \tfrac{1}{2}b_0 + \sum_{m=1}^{\infty} b_m \tag{21}$$

and hence

$$b_0 = -2 \sum_{m=1}^{\infty} b_m. \tag{22}$$

Equation (14) can therefore be rewritten as

$$\bar{\theta}(\Omega) = \sum_{m=1}^{\infty} b_m[\cos m\Omega - 1]. \tag{23}$$

The derivative of the phase, $d\theta(\omega)/d\omega$, can now be determined from reflectance measurements. The function $[2R(\omega)]^{-1}dR(\omega)/d\omega$ is determined from the dispersion curves of the reflectance and the function $\bar{R}(\Omega)$ is then calculated using equation (10). The Fourier coefficients a_m can then be determined. Equation (19) and the asymptotic behaviour of $[d\theta(\omega)/d\omega]_{\omega\to\infty}$ determine $d\theta(\omega)/d\omega$.

We now show how the phase can be constructed. From equation (23) we have

$$\left[\frac{d\theta(\omega)}{d\omega}\right]_{\omega=-\cot\Omega/2} = \sum_{m=1}^{\infty} b_m\left[2^{m-1}\cos^m\Omega - 1 + \sum_{k=1}^{[m/2]} \beta_{km}\cos^{m-2k}\Omega\right] \tag{24}$$

where β_{km} is defined in terms of the binomial coefficient $\binom{x}{y}$ by

$$\beta_{km} = (-1)^k(m/k)2^{m-2k-1}\binom{m-k-1}{k-1} \tag{25}$$

and square brackets on the summation denote a limit equal to $\frac{1}{2}(m-1)$ if m is odd. Equation (24) can be re-expressed as

$$\frac{d\theta(\omega)}{d\omega} = \sum_{m=1}^{\infty} b_m\left[-1 + 2^{m-1}\left(\frac{\omega^2-1}{\omega^2+1}\right)^m + \sum_{k=1}^{[m/2]} \beta_{km}\left(\frac{\omega^2-1}{\omega^2+1}\right)^{m-2k}\right]. \tag{26}$$

Integration of equation (26) from $(0, \omega)$ and noting that $\theta(0) = 0$, yields

$$\theta(\omega) = \sum_{m=1}^{\infty} b_m\left[-\omega + 2^{m-1}I_m(\omega) + \sum_{k=1}^{[m/2]} \beta_{km}I_{m-2k}(\omega)\right] \tag{27}$$

where

$$I_m(\omega) = \int_0^{\omega}\left(\frac{\omega'^2-1}{\omega'^2+1}\right)^m d\omega'. \tag{28}$$

Evaluation of $I_m(\omega)$ leads to the result:

$$I_m(\omega) = \omega - \sum_{j=0}^{m-1} \frac{(-1)^j}{2^{j+1}}\binom{m}{j+1} \times \left(\binom{2j}{j}\tan^{-1}\omega + \sum_{k=0}^{j-1} \frac{1}{(j-k)}\binom{2j}{k}\sin[(2j-2k)\tan^{-1}\omega]\right): \tag{29}$$

Equation (27) represents an *exact* relation for the phase $\theta(\omega)$. The steps in the determination of the phase follow in a similar manner to that outlined above for $\mathrm{d}\theta(\omega)/\mathrm{d}\omega$. The measured reflectance allows $[2R(\omega)]^{-1}\mathrm{d}R(\omega)/\mathrm{d}\omega$ to be calculated and hence $\bar{R}(\Omega)$, from which the Fourier coefficients a_m can be determined. Noting the relation (19) allows the phase to be calculated from equation (27). Other optical constants can be determined from the standard formulae relating such constants to $\theta(\omega)$ and $R(\omega)$.

A simple example will clarify the procedure. Consider the function $[2R(\omega)]^{-1}\mathrm{d}R(\omega)/\mathrm{d}\omega$ to be given by

$$[2R(\omega)]^{-1}\frac{\mathrm{d}R(\omega)}{\mathrm{d}\omega} = \frac{-2\omega}{(1+\omega^2)^2}. \tag{30}$$

This particular form is chosen for reasons of simplicity, and we ignore detailed considerations of the asymptotic behaviour which the true phase should satisfy, provided equation (20) is satisfied and that $\theta(0) = 0$.

From equation (30) we have

$$\left([2R(\omega)]^{-1}\frac{\mathrm{d}R(\omega)}{\mathrm{d}\omega}\right)_{\omega=-\cot\Omega/2} = \tfrac{1}{2}\sin\Omega - \tfrac{1}{4}\sin 2\Omega. \tag{31}$$

The Fourier coefficients are determined by inspection to be

$$a_1 = \tfrac{1}{2}; \qquad a_2 = -\tfrac{1}{4}; \qquad a_m = 0 \qquad m > 2. \tag{32}$$

Making use of the values

$$I_0(\omega) = \omega$$

$$I_1(\omega) = \omega - 2\tan^{-1}\omega$$

$$I_2(\omega) = 2\omega(1+\omega^2)^{-1} - 2\tan^{-1}\omega + \omega$$

and using equations (32) and (19) gives

$$\theta(\omega) = \omega/(1+\omega^2) \tag{33}$$

which can be checked by other means to be the correct phase.

3. Discussion

The Fourier series method provides an easy and convenient means for analysing reflectance data. The wide availability of very fast algorithms for the machine computation of Fourier series makes this approach an attractive alternative to the Kramers–Kronig scheme.

Both the series approach and the Kramers–Kronig relation will provide identical results for the phase, when computed to the same level of accuracy. However, the number of computer operations involved in the evaluation of the Kramers–Kronig integral for an N-point mesh, will be N^2. The main step in the series method, that of determining the Fourier coefficients, which can be computed by the fast Fourier series algorithm (Cooley and Tukey 1965) involves $N \ln N$ operations. For large mesh size, the latter procedure is clearly favoured.

For experimental profiles which are band limited, which in essence will be the case if measurements over a sufficient spectral range are available, then equation (13) can be truncated with a resulting reduction in computational effort. Since the usual Kramers–Kronig inversion (equation 1) requires the evaluation of an integral over an infinite range, it is necessary to provide extrapolations for both the low-energy and high-energy regions, since these are usually less accessible to experimental determination. Various fitting procedures are required for this purpose, which involve semi-empirical parameters of one kind or another. In the present method, a single and straightforward Fourier analysis of the data is sufficient to determine the phase. This requires considerably less computational effort than that required in data extrapolation and computation of the Kramers–Kronig integral.

It is to be stressed that the result obtained for the phase is exact. Equations (13) and (14), which are known as conjugate Fourier series, provide one means of discussing the connection between the real and imaginary parts of an analytic function. Two other methods which are mathematically equivalent are the Kramers–Kronig relations (Hilbert transforms) and the allied Fourier integral approach (equations 2 and 3). For a given function with the appropriate asymptotic behaviour, all three procedures for relating the real and imaginary parts can be derived from the same assumption of analytic behaviour, the resulting forms are all equivalent. The generalised reflectance does not have the appropriate asymptotic behaviour for a series expansion. It is therefore necessary to examine the derivative of this function, and integrate the resulting differential equation in order to obtain an equivalent relation to the Hilbert transform expression for the phase.

The method employed in this work is general. It can be applied to determine the dissipative mode of any causal function, when the derivative of the dispersion curve is known. The only changes that need be made concern the boundary conditions (equation 21), and that involved in obtaining equation (27), i.e. $\theta(0) = 0$.

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