Moment Analysis of Magnetic Resonance Signals
Peter H. Verdier, E. B. Whipple, and Verner Schomaker

Citation: The Journal of Chemical Physics 34, 118 (1961); doi: 10.1063/1.1731548
View online: http://dx.doi.org/10.1063/1.1731548
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/34/1?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Application of temporal moments and other signal processing algorithms to analysis of ultrasonic signals through melting wax
AIP Conf. Proc. 1706, 180006 (2016); 10.1063/1.4940636

Spherical tensor analysis of nuclear magnetic resonance signals

Mechanisms of signal loss in magnetic resonance imaging of stenoses
Med. Phys. 20, 1049 (1993); 10.1118/1.597001

Sum rule analysis of hyperon magnetic moments
AIP Conf. Proc. 95, 323 (1983); 10.1063/1.33873

Analysis of a Magnetic Resonance Spectrometer
Moment Analysis of Magnetic Resonance Signals*

PETER H. VERDIER, E. B. WHIPPLE, AND VERNER SCHOMAKER

Union Carbide Research Institute, Tuxedo, New York

(Received April 14, 1960)

A relation is given between the moments of a generalized convolution transform of a function, and the moments of the function itself. This relation is applied to the signal obtained with a field-modulated EPR spectrometer, a consequence being that the integrated intensity of an absorption line may be obtained from first moment measurements at any modulation amplitude, regardless of line shape or various instrumental nonidealities. This result has been verified experimentally to within a few percent with a Varian EPR spectrometer. Extension to measurement of higher moments is discussed.

Let two functions, \( \Phi(y) \) and \( \psi(y) \), be related by (1), where \( \alpha, \beta \), and the region \( R \) of integration are arbitrary,

\[
\Phi(y) = \int_R \cdots \int \psi[y - \alpha(x_1, \cdots, x_r)] 
	\times \beta(x_1, \cdots, x_r) \, dx_1 \cdots dx_r. \tag{1}
\]

Then the \( n \)th moment,

\[
\Phi_n = \int_{-\infty}^{\infty} y^n \Phi(y) \, dy
\]

can be expressed as a linear combination of the \( n \)th and lower moments of \( \psi \); i.e.,

\[
\Phi_n = \sum_{n=0}^{n} C_n \psi_n, \tag{2}
\]

where the coefficients are given by

\[
C_n = \binom{n}{j} \int_R \cdots \int \alpha^{n-j}(x_1, \cdots, x_r) \beta(x_1, \cdots, x_r) \, dx_1 \cdots dx_r \tag{3}
\]

and are independent of \( \psi \). Equations (2) and (3) are readily verified by writing \( \Phi_n \) in terms of (1), inverting the order of integration, and making the change of variable \( u = y - \alpha(x_1, \cdots, x_r) \).

The transformation (1) of \( \psi \) into \( \Phi \) may be used to represent the effect of a variety of distortions introduced into the measurement of a function \( \psi(y) \) by a linear apparatus. Examples are the effects of constant slit width in optical spectroscopy, arbitrary frequency response of linear electrical or mechanical networks, and certain types of modulation and demodulation.¹

The application to magnetic resonance spectrometers employing sinusoidal field modulation and synchronous detection is of considerable practical interest, since sensitivity limitations often require modulation amplitudes sufficient to distort the signals from their limiting derivative shapes.²⁻⁶ Analysis in terms of Eq. (2) is particularly appropriate to this problem, since many of the spectral parameters of principal interest can be obtained directly from the lower moments.⁶⁻⁸

If \( \psi(h) \) represents energy absorption as a function of magnetic field, the signal entering the spectrometer amplifier at fixed \( h \) is \( \psi(h - H_m \sin \omega t) \), where \( H_m \) is the amplitude and \( \omega \) the angular frequency of the modulating field. The effects of amplifier response and synchronous demodulation can then be represented by a function \( \beta \) in the transformation (1), where \( \Phi(h) \) is the observed output of the spectrometer. Since the amplifier does not pass dc, the coefficients \( C_n \) vanish, leaving only lower moments of \( \psi \) in the expressions for \( \Phi_n \). In particular, \( \Phi_0 \) must vanish and \( \Phi_1 \), the first moment of the observed curve, is directly proportional to the product of \( H_m \) and \( \phi_0 \), the integrated intensity, regardless of distortion due to modulation amplitude broadening, amplifier and detector response, detector misphasing, or main-field inhomogeneity. This proportionality is strictly independent of details of line shape and may, for example, be used to obtain the integrated intensity of partially resolved multiplets.

The expressions (2) for the higher moments are simplified by the symmetry of the modulating and demodulating functions, which causes \( C_{n+j} \) to vanish for \( n+j \) even. A proportionality similar to the foregoing practical application it may be easier to write the transformation in the more general form (1) than to obtain an equivalent convolution transform.

¹ Advanced Research Projects Agency support is gratefully acknowledged.

² M. M. Perlman and M. Bloom, Phys. Rev. 88, 1240 (1952).
⁵ A different approach has been formulated by Spry (footnote 9), who has applied the "unfolding" technique of Stokes [A. R. Stokes, Proc. Phys. Soc. (London) 61, 382 (1948)] to the analysis of magnetic resonance lines.
then exists between the experimental second moment and true first moment, which defines the centroid of the line. The method is readily extended in principle to a determination of the higher $\varphi_j$. For example, in spectrometers with very narrow band pass the second moment correction inferred by Andrew from a Taylor series expansion is verified for all $H_m$.

It is possible to obtain values of the coefficients in Eq. (2) experimentally, rather than analytically. Since $C_{nj}$ is proportional to $H_m^{-1}$, as may be seen from Eq. (3), the $C_{nj}$ may be determined by measuring each moment at several modulation amplitudes and fitting the resulting $\Phi_n$ to polynomials in $H_m$. Alternatively, the response of the spectrometer to a $\delta$-function input may be determined as suggested by Spry. It can easily be shown that $C_{nj}$ is just the $(n-j)$-th moment of the response of the system to a $\delta$-function input.

As a test of practical applicability, we have studied EPR spectra of a powdered DPPH sample with a Varian Associates Model V-4S00 EPR spectrometer using a V-4007 6-in. magnet system at 80 cps field modulation. Since demodulation is accomplished by a synchronous reversing switch, odd harmonics in the input contribute to the output. The spectrometer amplifier, tuned to 80 cps, was found to have relative gains of 1, 2, and 3 at 80, 200, and 400 cps.

The relative gains of the amplifier at different gain settings were determined by measuring dc output with a Leeds and Northrup Type K potentiometer. Ratios of modulation field strengths were obtained by measuring the voltage across the modulation coils with a Ballantine voltmeter.

The DPPH absorption was recorded at modulation ranging from one-quarter to eight times the peak-to-

---


---

TABLE I. Observed first moment $G_1$ vs relative field modulation amplitude $H$.

<table>
<thead>
<tr>
<th>$H$</th>
<th>1.00</th>
<th>8.33</th>
<th>15.8</th>
<th>31.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_1/H$</td>
<td>3.26</td>
<td>3.21</td>
<td>3.18</td>
<td>3.12</td>
</tr>
</tbody>
</table>

peak linewidth. The wings of the absorption curves were always recorded at higher gain than were the central portions. Zeroth and first moments were obtained for each modulation amplitude. The zeroth moments were always less than 4% of the respective half-curve areas.

The observed first moment $G_1$ is given in Table I for various relative settings of the modulation amplitude $H$. The ratio $G_1/H$, which in principle should be proportional to the total absorption intensity and independent of $H$, is constant to within 5% over the range of $H$ chosen. In particular, the values of $G_1/H$ at relative modulation amplitudes of 8.3 and 1, which are about twice and one-quarter the peak-to-peak linewidth, respectively, differ by less than 2%. Thus to this accuracy, the modulation amplitude for intensity measurements may be chosen anywhere between the small-amplitude derivative limit and the amplitude which yields maximum signal strength.

Attempts to obtain third moments revealed that the calculated integrals were not converging in the wings, although measurements ranged to thirty-six times the peak-to-peak linewidth, or four times the maximum modulation amplitude employed. In contrast, the first-moment integrals were clearly converging; the slight decrease of $G_1/H$ with increasing $H$ is probably a result of small losses in the wings. It is clear that measurement of third and higher moments will require spectra over a considerably wider range than has been employed here, in order to obtain convergence.