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Moment Analysis of Magnetic Resonance Signals*

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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 α, β, and the region R of integration are arbitrary,

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

Then the nth moment

$$\Phi_n=\int_{-\infty}^{\infty}y^n\Phi(y)dy$$

can be expressed as a linear combination of the nth and lower moments of ψ; i.e.,

$$\Phi_n=\sum_{j=0}^{n}C_{nj}\psi_j, \quad (2)$$

where the coefficients are given by

$$C_{nj}=\binom{n}{j}\int_R\cdots\int\alpha^{n-j}(x_1,\cdots,x_r)\beta(x_1,\cdots,x_r)dx_1\cdots dx_r \quad (3)$$

and are independent of ψ. Equations (2) and (3) are readily verified by writing Φ_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 ψ into Φ 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.[2–5] 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 ω the angular frequency of the modulating field. The effects of amplifier response and synchronous demodulation can then be represented by a function β in the transformation (1), where $\Phi(h)$ is the observed output of the spectrometer. Since the amplifier does not pass dc, the coefficients C_{nn} vanish, leaving only lower moments of ψ in the expressions for Φ_n. In particular, Φ_0 must vanish and Φ_1, the first moment of the observed curve, is directly proportional to the product of H_m and ψ_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_{nj} to vanish for $n-j$ even. A proportionality similar to the foregoing

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[1] The relations (1)–(3) have been given by Flynn and Seymour[6] for the case when $\alpha(x)=x$, and R is $-\infty<x<\infty$, i.e., a convolution transform. It can be shown that every transformation of the form (1) can be written as a convolution, in which case the relations (2), (3) take on a simpler form: If $f*g$ denotes the convolution of f and g, then

$$(f*g)_n=\sum_{j=0}^{n}\binom{n}{j}f_jg_{n-j},$$

where the subscripts denote moments, as before. However, in practical application it may be easier to write the transformation in the more general form (1) than to obtain an equivalent convolution transform.

[2] M. M. Perlman and M. Bloom, Phys. Rev. **88**, 1240 (1952).
[3] E. R. Andrew, Phys. Rev. **91**, 425 (1953).
[4] O. E. Myers and E. J. Putzer, J. Appl. Phys. **30**, 1987 (1959).
[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.
[6] C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) **75**, 337 (1960).
[7] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1958).
[8] W. Anderson and H. M. McConnell, J. Chem. Phys. **26**, 1496 (1957).

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 ψ_j. For example, in spectrometers with very narrow band pass the second moment correction inferred by Andrew[3] 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^{n-j}, 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 Φ_n to polynomials in H_m. Alternatively, the response of the spectrometer to a δ-function input may be determined as suggested by Spry.[9] It can easily be shown that C_{nj} is just the $(n-j)$-th moment of the response of the system to a δ-function input.

As a test of practical applicability, we have studied EPR spectra of a powdered DPPH sample with a Varian Associates Model V-4500 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, $\frac{1}{7}$, and $\frac{1}{10}$ 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-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.

[9] W. J. Spry, J. Appl. Phys. **28**, 660 (1957).

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

H	1.00	8.33	15.8	31.2
G_1/H	3.26	3.21	3.18	3.12

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.