

Analysis of Nuclear Magnetic Resonance Wide Line Spectra

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Dedicated to Professor Ole Lamm on his 60th birthday

It is attempted, by the use of a formal mathematical analysis of NMR wide line spectra, to throw some light on the well-known difficulties associated with the experimental and theoretical determination of line moments.

The analysis is based on the observation that the squared fundamental eigenfunction of the harmonic oscillator represents a Gaussian distribution, a correction to which may be obtained by the addition of the subsequent squared eigenfunctions in a series expansion of expected rapid convergence. This expectation is confirmed by the present investigation and it is shown that, in general, a spectral line may be optimally approximated with a maximum of 5 terms in the expansion. It is further shown that the method may be successfully applied to the analysis of complex spectra when the overlap between the spectral components satisfies certain conditions and that the accuracy of the analysis is satisfactory. Several applications and conclusions are treated in the text.

The theoretical treatment of NMR wide line spectra for crystalline systems represents, at the present stage of development, a formidable mathematical task, permitting only rough approximations to the solution of the problem. These difficulties have led to certain limitations in the practical application of the nuclear magnetic methods to the study of solid systems. On the other hand, the magnetic resonance methods are in several respects indispensable for the detailed study of coupling mechanisms and molecular motions in hydrogels and hydrogen bonded high polymers and other solids which makes it very desirable to improve and extend the now available methods for the analysis of wide line spectra¹.

The above-mentioned mathematical difficulties derive from the coupling effects between the individual nuclear moments which occur in crystalline spin systems. While an ensemble of uncoupled spins may be described by means of a statistical operator matrix of the order $(2I + 1)(2I + 1)$ where I is the

spin quantum number, the coupled spin system compels one to treat the whole observed system of N nuclear spins as *one* element in a statistical ensemble, the description of which leads to an operator of the order $(2I + 1)^N (2I + 1)^N$. The coupling between the nuclei occurs in several ways; one dominant term in the spin energy function may be described as a classical dipole-dipole coupling between the magnetic moments of the nuclei, and is assumed in the following discussion to elucidate the analytical problem.

The dipole coupling may be regarded as a perturbation of the Zeeman effect and the individual contribution to the coupling energy from two interacting nuclei may be split in six components characterised by their varying influence on the magnetic quantum number of the energy function.

If we confine the calculation to first order perturbations, only two components are of interest, namely those which lead to unchanged total magnetic quantum number. One of these terms represents simultaneous re-orientations of anti-parallel spins. It is accordingly only operative when the interacting spins have commensurable frequencies of rotation, which usually implies like spins in fields of comparable magnitude. A strong quadruple coupling in a distorted lattice, leads for instance to the inhibition of this contribution to the dipole coupling, due to the relative changes in rotational frequency of the nuclei affected by the quadrupole fields. The remaining terms of the dipole coupling operator lead, in addition, to secondary and tertiary resonances which, as a rule, are associated with intensities too low to permit direct observation, but which may contribute significantly to the integrated intensity if included in the energy operator. We shall presently return to this question.

The coupling between the nuclei leads to an energy exchange and a relaxation mechanism the time dependence of which may be described by a function $G(t)$. The normalized Fourier transform

$$f(\omega) = \kappa \int_0^{\infty} G(t) \cos \omega t \, dt$$

characterizes the shape of the absorption band as a function of the angular velocity $\omega = 2\pi\nu$ of the radio-frequency field. The shape of the absorption band may, on the other hand, be connected with the n th moment, M_n , defined by the equation

$$M_n = \int_{-\infty}^{+\infty} f(\omega)(\omega - \omega_0)^n d\omega$$

where M_0 represents the area, A , under the absorption curve proportional to the number of nuclei which contribute to the resonance, M_1 the static moment of the area, with respect to the reference point ω_0 etc. If $f(\omega)$ is symmetrical with respect to ω_0 , all odd moments disappear.

The moments M_n may, as has been shown by Van Vleck², be calculated from primary data without a knowledge of the eigenvalues of the energy operator by means of the expansion of $G(t)/\cos \omega_0 t$ in a power series of t . The coefficients of the series may indeed be determined independently of the choice of base functions in the matrix elements of the corresponding operators. If,

accordingly, a representation is chosen in which the individual spin quantum numbers of the nuclei characterize the operators for the coupling energy and the resonance magnetisation, it is possible to circumvent the at present insoluble problem of finding the eigenfunctions and eigenvalues for the energy operator of the coupled spin system.

One of the weaknesses of the method depends on the circumstance that all coupling effects which commute with the transversal angular momentum may modify the shape of the absorption band without influencing the second moment which, accordingly, cannot be uniquely correlated with the coupling and relaxation mechanisms. In order to evaluate the deviation from the signal amplitude distribution, supposed Gaussian, of the uncoupled system, it is desirable to calculate the fourth moment and the ratio M_4/M_2^2 which takes the value 3 for a pure Gaussian distribution. This, however, emphasizes a fundamental difficulty associated with the experimental determination of moments, namely, that the essential contributions to the higher moments derive from the wings of the absorption band which usually are unobservable due to the general background of noise. The effect is obviously of extreme importance in the practical application of the method of moments to the study of molecular re-orientations and chain motion in solids where, as a rule, the observable part of the second moment varies, while the total second moment remains invariant with respect to the lattice motions.

For a comparison between the theoretical calculated moments and the experimental ones, it is desirable to find a satisfactory method for the indirect determination of the unobservable wings of the spectral band, while leaving out the terms in the energy operator which are responsible for the satellites in the theoretical calculation of moments.

We believe that it is possible to throw some light on these problems by the expansion of the experimental resonance line in a rapidly converging series of suitable functions for the description of the line shape and of the deviation from the Gaussian distribution. The adaptation to the experimental spectral band is performed in the frequency range where the signal to noise ratio is favourable and the moments of the spectral line are then calculated by the integration of the analytical expression so obtained. In the present paper our investigation is confined to the methodological aspect of the problem and no attempt has been made to connect the results with the current theories of the line width. The possibility to characterize the line shape with the aid of the expansion parameters as a function of the composition and the physical state of the system under investigation, is of great practical use in wide line spectrography.

As suitable functions for the series expansion, we have chosen the eigenfunctions of the harmonic oscillator, the squared fundamental of which represents a Gaussian distribution. The following expansions then have been used for the description of a single absorption band:

$$\varphi = \sum_k a_k \Phi_k^2 \text{ and } \varphi = \sum_k a_k \Phi_k$$

where

$$\Phi_k = H_k(\sqrt{ax}) \exp(-\frac{1}{2}ax^2)$$

$H_k(\sqrt{\alpha}x)$ are Hermite polynomials, α representing the magnetic field intensity or the corresponding frequency. The function Φ_k is an even function for even k , and odd for odd k . The first series can therefore be applied to even functions only, whereas the second one can be used for asymmetrical functions. Although the electronic computer programme has been worked out for both cases, the application of the method will be illuminated by a few examples of even functions only.

Proton resonance spectra of an organic solid containing water, as a rule, consist of a broad band superimposed by a narrow band. The derivatives of both bands are centrosymmetrical with respect to a common centre of inversion. The broad band usually derives from:

- (a) hydrogens attached to a carbon chain and which only slowly take part in exchange processes,
- (b) hydrogens attached to nitrogen or oxygen included as heteroatoms in the carbon chain and which can be exchanged with relative ease for deuterium *via* an adjacent liquid or gaseous phase,
- (c) hydrogen atoms attached to oxygen belonging to water, which is either included in the crystalline lattice or, otherwise, appears as an adsorbed phase.

The narrow band usually derives from hydrogen in water with approximately normal coordination and proton exchange frequency, so-called "free" water, although the line width may display great variations with the degree of freedom. In reality, the width of the narrow band is determined by so many boundary conditions that the term "free water" is rather inadequate.

A partial exchange of hydrogen against deuterium modifies the shape of the bands and their intensities and the detailed study of these changes makes possible, in principle, an identification of the contributions from the different proton containing groups. In all the cases where the individual line shapes are unknown, spectra of this kind, therefore, have to be expanded as the superposition of two distinct series. The expansion takes, in this case, the following form:

$$\varphi = \sum_k a_{k1} \Phi_{k1}^2 + \sum_k a_{k2} \Phi_{k2}^2$$

$$\Phi_{k1} = H_k(\sqrt{\alpha_1}x) \exp(-\frac{1}{2}\alpha_1 x^2)$$

$$\Phi_{k2} = H_k(\sqrt{\alpha_2}x) \exp(-\frac{1}{2}\alpha_2 x^2)$$

Both α_1 and α_2 are estimated from experimental data and chosen for the best fit, each series representing a complete description of an even function. When the difference in width between the two bands is great, the calculation can easily be carried out with a finite number of terms in each band, the two series being fitted to each part of the experimental band, one in comparative independence of the other. When, on the other hand, the overlap between the two bands becomes great, the conditions for the unique determination of the two series are insufficient, especially in the case when a greater number of terms are involved. With increasing overlap between the two bands, the calculation must accordingly be carried out with a decreasing number of coefficients. The applicability of the method has been tested in some simple cases corresponding to these conditions.

DESCRIPTION OF THE PROGRAMME

The programme has been worked out for the Swedish electronic computer Facit at the Swedish Board for Computing Machinery (MNA) in Stockholm, where it is available under designation 41095.

Taking the inversion centre of the symmetric absorption line derivative as origin, a sufficient number of equidistant amplitudes are measured and tabulated. The two branches of the curve are treated in the same way, and for both of them abscisses (x_i), as well as ordinates (y_i) are expressed as positive numbers

$$\begin{aligned} x_i &= hi & \text{for } i = 0, 1, 2, \dots, q \\ x_i &= hq + hp(i-q) & \text{for } i = q + 1, q + 2, \dots, n \end{aligned}$$

where h is the step length and q denotes the point from which the step length is increased to ph , p being an integer.

From the observed derivative (x_i, y_i) the absorption band, $F(x)$ is computed by numerical integration.

Putting $x = hj$ we have

$$F(hj) = h \int_0^{\infty} y dj - h \int_0^j y dj$$

$$\text{and } \int_0^j y dj = z_i = y_1 + y_2 + \dots + y_{i-1} + \frac{1}{2} y_i = z_{i-1} + \frac{1}{2} (y_{i-1} + y_i)$$

$$\text{for } i = 1, 2, 3, \dots, q$$

$$\begin{aligned} \text{and } z_i &= y_1 + y_2 + \dots + y_{q-1} + \frac{1}{2} y_q + \frac{1}{2} p y_q + p y_{q+1} + \dots + p y_{i-1} + \frac{1}{2} p y_i = \\ &= z_{i-1} + \frac{1}{2} p (y_{i-1} + y_i) \end{aligned} \quad \text{for } i = q + 1, q + 2, \dots, n.$$

When both parts of the curve are registered, a zero-line correction can be applied. In making this correction, a quantity ε is subtracted from the y_i -values of the first branch of the curve and added to the y_i -values of the second branch. The z -values are, in other words, substituted by G -values defined as follows for the branch I

$$G_i = z_i - \varepsilon i \quad \text{for } i = 0, 1, 2, \dots, q.$$

$$G_i = z_i - \varepsilon \{q + p(i-q)\} \quad \text{for } i = q + 1, q + 2, \dots, n$$

$$\text{and for branch II } G_i' = z_i' + \varepsilon i \quad \text{for } i = 0, 1, 2, \dots, q.$$

$$G_i' = z_i' + \varepsilon \{q + p(i-q)\} \quad \text{for } i = q + 1, q + 2, \dots, n.$$

ε is determined by the conditions $G_n = G_n'$ and

$$\varepsilon = \frac{z_n - z_n'}{2\{q + p(n-q)\}}$$

The integral $\int_0^{\infty} y dj$ is approximated by z_n or G_n , respectively, and the

absorption line is approximated by

$$\varphi_i = \frac{G_n - G_i}{G_n}$$

where $F(hj) = hG_n\varphi_i$.

The area under the φ -function is computed by numerical integration

$$\int_0^\infty \varphi_i dj = B_0 = \frac{1}{2}\varphi_0 + \varphi_1 + \varphi_2 + \dots + \varphi_{q-1} + \frac{1}{2}\varphi_q + \frac{1}{2}p\varphi_q + p\varphi_{q+1} + \dots + p\varphi_n$$

In the following, this sum is abbreviated as

$$B_0 = \sum'_{i=0}^n t_i \varphi_i$$

the prime indicating the preceding convention to be observed.

The area under the absorption line, computed by direct numerical integration will then be

$$A_0 = h^2 G_n B_0$$

The serial expansion takes the form

$$\varphi_i = \sum_{kl} a_{kl} \Phi_{kl}^2$$

where

$$\Phi_{kl} = H_k(\sqrt{\alpha_i}x) \exp(-\frac{1}{2}\alpha_i x^2)$$

and

$H_k(\sqrt{\alpha_i}x)$ are the Hermite polynomials.

The programme allows computation of one-, two- or three-component lines (summation over l from 1 to max. 3). The number of terms in each component can be chosen from 1 to max. 7 (summation over k for 0 to max. 6).

For ease of calculation the parameter α_i is transformed to a shape parameter m_i

$$\alpha_i = 1/2h^2m_i^2$$

$$\alpha_i x^2 = j^2/2m_i^2$$

When the absorption line is dominated by the Gaussian, the absciss of the maximum point of the registered derivative is $x_m = hm_i$. In the spectra considered here, the values of m_i have been roughly estimated from the abscisses of the derivative maxima.

The overdetermined equation system takes the form

$$\varphi_i = \sum_{\nu=1}^{\nu_m} x_\nu f_\nu(i) \quad \text{where } i = 0, 1, 2, \dots, n$$

$$\text{and } n < \nu_m$$

Introducing

$$\nu = k + 1 \quad \text{for } l = 1$$

$$\nu = k_m + 1 + k + 1 \quad \text{for } l = 2$$

$$\nu = 2(k_m + 1) + k + 1 \quad \text{for } l = 3$$

where $k_m + 1$ is the number of expansion coefficients in each component line, we can write $a_{kl} = x_\nu \Phi_{kl}^2 = f_\nu$

This system is solved to make the total square deviation attain a minimum and to obtain a uniform adaptation over the whole range of the line.

$$M = \frac{1}{2}(\varphi_0 - \varphi_0^b)^2 + (\varphi_1 - \varphi_1^b)^2 + \dots + (\varphi_{q-1} - \varphi_{q-1}^b)^2 + \frac{1}{2}(\varphi_q - \varphi_q^b)^2 + \frac{1}{2}r(\varphi_q - \varphi_q^b)^2 + r(\varphi_{q+1} - \varphi_{q+1}^b)^2 + \dots + r(\varphi_n - \varphi_n^b)^2 = \sum_{i=0}^n t_i \left\{ \varphi_i - \sum_{\nu} x_\nu f_\nu(i) \right\}^2$$

where φ_i^b is computed from $f_\nu(i)$ and the resolved values of x_ν .

The condition of minimum

$$\frac{\partial M}{\partial x_\eta} = -2 \sum_{i=0}^n t_i \{ \varphi_i - \sum_{\nu} x_\nu f_\nu(i) \} f_\eta(i) = 0$$

gives the equation system

$$\sum_{\nu} x_\nu \sum_{i=0}^n t_i f_\nu(i) f_\eta(i) = \sum_{i=0}^n t_i \varphi_i f_\eta(i)$$

from which the values of x_ν are determined.

Putting $r = p$ the sums $\sum_{i=0}^n t_i f_\nu(i) f_\eta(i)$ and $\sum_{i=0}^n t_i \varphi_i f_\eta(i)$ approximate to the integrals $\int_0^\infty f_\nu f_\eta dj$ and $\int_0^\infty \varphi_i f_\eta dj$.

φ_i^b and $\varphi_i - \varphi_i^b$ are computed and, if desired, printed.

The integral $\int_0^\infty f_\nu f_\eta dj$ may, in the case of $r = p$, be calculated analytically, leading to a considerable reduction of the machine time required for the computation.

Finally, the standard deviation is computed

$$s = \sqrt{\frac{M}{q + r(n-q)}}$$

assuming the number of coefficients to be small compared to n .

The coefficients a_{kl} are transformed to a series

$$b_{kl} = a_{kl} \frac{\int_0^\infty \Phi_{kl}^2 dj}{B_l} \quad \text{where} \quad B_l = \sum_k a_{kl} \int_0^\infty \Phi_{kl}^2 dj$$

$$\text{and} \quad \int_0^\infty \varphi_i dj = B = \sum_l B_l \sum_k b_{kl}$$

$$\sum_k b_{kl} = 1; \quad \sum_l B_l = B$$

Table 1. Expansion parameters for the ^1H -resonance in aqueous solutions of MnSO_4 .

(1)	b_0	b_1	b_2	(2) b_3	b_4	b_5	b_6	(3)	(4)	(5)
0.01	0.900	-0.040	0.092	0.020	0.023	0.000	0.005	20.18	20.02	1.9
0.1	0.810	-0.025	0.133	0.022	0.045	0.000	0.015	20.90	20.88	4.2
0.5	0.830	-0.010	0.120	0.015	0.035	0.000	0.008	20.68	20.56	14.5
2.0	0.820	-0.010	0.125	0.020	0.035	0.000	0.010	20.44	20.37	51.0

- (1) Molarity for the aqueous solutions of MnSO_4
 (2) Expansion coefficients.
 (3) The area under the absorption line (A)
 (4) The area under the absorption line computed by direct numerical integration (A_0)
 (5) Line width parameter m giving the best degree of adaptation.

The area under the absorption line computed from the analytical expression is

$$A = h^2 G_n B$$

The quantities G_n , B_0 , B , B_l/B , b_{kl} and s are given as the result of the evaluation. B_l/B denotes the fraction of the contribution from line number l to the area under the absorption line, and b_{kl} denotes the fraction of the contribution from function number k to the area under the absorption line of line number l .

APPLICATIONS TO EXPERIMENTAL DATA

The ^1H resonance of aqueous solutions of MnSO_4 in the concentration range 0.01 to 2.0 M has been evaluated, and the results used to demonstrate the general properties of the series expansion. The line width of these solutions is determined by the presence of the paramagnetic manganese ions.

The coefficients of the expansion, the standard deviation and the area under the absorption line are shown in Fig. 1 as functions of the line width parameter m for the aqueous solution of 0.5 M MnSO_4 . The remaining results, under conditions of closest fit, are summarized in Table 1. The coefficients turn out to be well reproducible for the two branches of the spectra and in the comparison between spectra recorded on different occasions.

The coefficients of the Gaussian dominate and the magnitude of the coefficients decreases rapidly with rising order. The degree of approximation to the experimental curve is characterized by the standard deviations. Plotted as a function of the line width parameter m , s generally shows a marked minimum. The minimum, however, is, as a rule, sufficiently flat to make the determination of m uncertain to about ± 2 to ± 5 %. The magnitude of the standard deviation, as well as the location of its minimum point, show a somewhat diminished reproducibility as compared to that of the coefficients.

When the expansion is extended to seven terms the two last terms are in all cases negligible at closest fit. An expansion to five terms accordingly gives

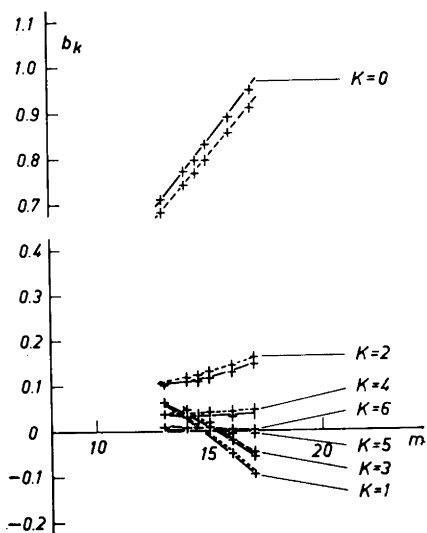


Fig. 1 a. The coefficients (b_k) of the ^1H -resonance of aqueous solution of 0.5 M MnSO_4 .
Part I of the curve ———
Part II of the curve - - - - -

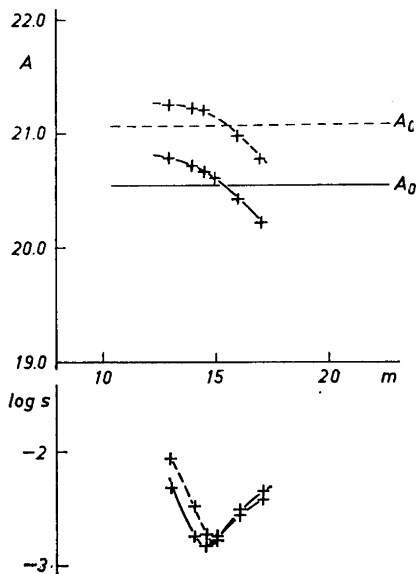


Fig. 1 b. The area under the absorption line (A) and the standard deviation (s) of the ^1H -resonance of aqueous solution of 0.5 M MnSO_4 .
Part I of the curve ———
Part II of the curve - - - - -

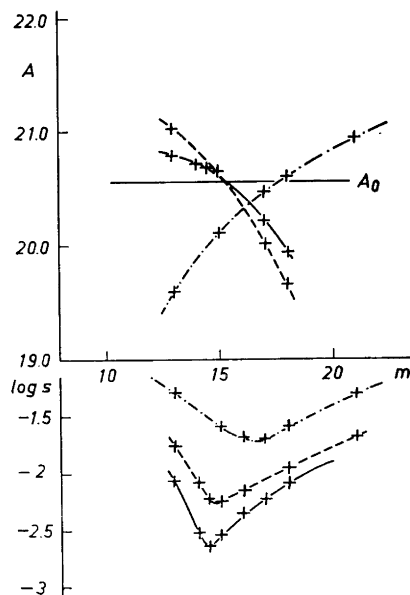


Fig. 1 c. The area under the absorption line (A) and the standard deviation (s) of the ^1H -resonance of aqueous solution of 0.5 M MnSO_4 . Part I of the curve
Evaluation using 7 coefficients ———
Evaluation using 5 coefficients - - - - -
Evaluation using 3 coefficients - · - · -

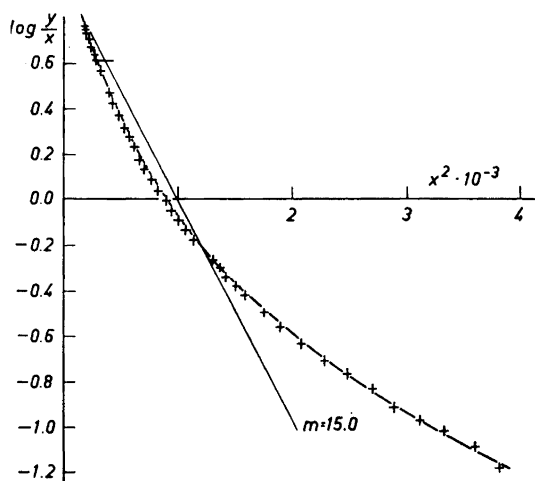


Fig. 2 a. The ^1H -resonance of aqueous solution of 0.5 M MnSO_4 .

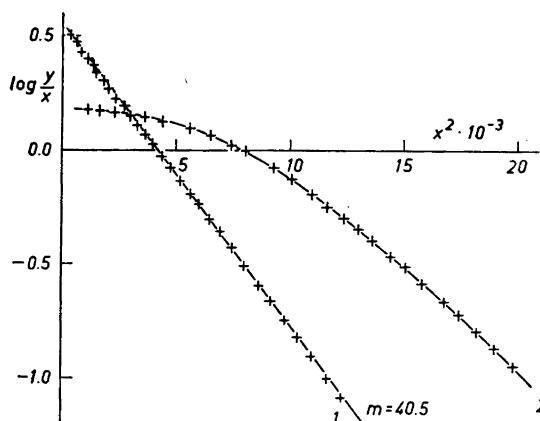


Fig. 2 b. 1) The ^1H -resonance of $(\text{NH}_4)_2\text{SO}_4$ powder. 2) The ^1H -resonance of NH_4Cl powder. In this diagram the Gaussian gives a straight line.

a satisfactory result and stationary values of the coefficients. The minima of the standard deviations coincide in the two cases. Using only three terms, the values of the expansion coefficients show considerable variation while the minimum of the root mean square deviation is displaced towards a somewhat higher m value.

The area A of the absorption band computed from the analytical functions is influenced by the number of terms in the expansion. As shown in Fig. 1c, the area becomes less dependent on m with an increasing number of terms. The uncertainty in the determination of the best fit thus introduces an error

less than $\pm 1\%$ of the A value at 5 or 7 terms. The area A_0 of the absorption band has also been determined by direct numerical integration. Fig. 1b shows that the difference between the two determinations of the A values is indeed small. The A values computed from the analytical functions at closest fit, usually exceed the corresponding A_0 values by 1 to 2%, which shows that for spectra of this type the area can be computed through direct numerical integration without serious disturbance from cut off effects. A values calculated for the different MnSO_4 solutions and corrected for the varying ^1H concentration, show a scattering of $\pm 3\%$. The A values computed from the analytical functions at closest fit show the same relative scattering as the A_0 values.

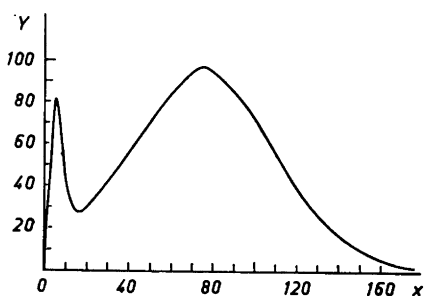


Fig. 3 a. Spectral line composed of the ^1H -resonances of an aqueous solution of 0.04 M MnSO_4 and an NH_4Cl powder.

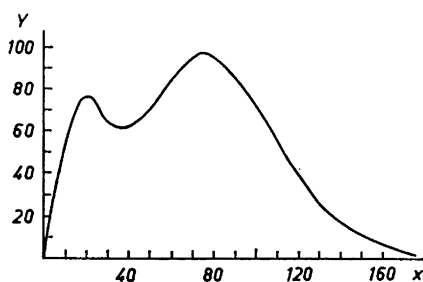


Fig. 3 b. Spectral line composed of the ^1H -resonances of an aqueous solution of 0.5 M MnSO_4 and an NH_4Cl powder.

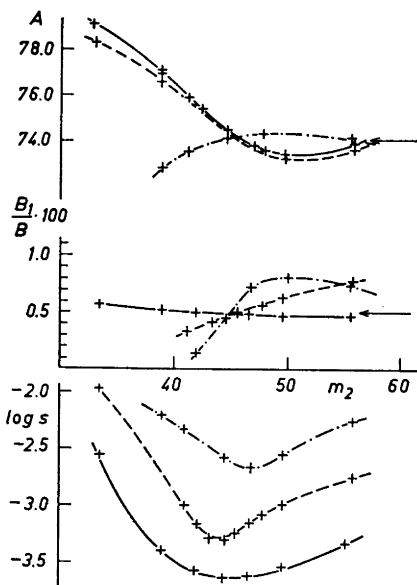


Fig. 4. The area under the absorption line (A), the fraction of the contribution from the narrow line to the area under the absorption line (B_1/B) and the standard deviation (s) for the spectrum in Fig. 3 a. Evaluation using 7 coefficients ——— Evaluation using 5 coefficients - - - - - Evaluation using 3 coefficients - · - · - The correct values are shown by the arrows.

In spite of the dominance of the Gaussian, the deviation from the Gaussian distribution is quite pronounced in these spectra. In Fig. 2 $\log y/x$ is plotted as a function of x^2 for a spectrum of 0.5 M MnSO_4 solution. In such a diagram a Gaussian is represented by a straight line. In the actual case the line is curved making it impossible to determine the m value from the inclination of the line. The adaptation to a Lorentz curve would, in this case, be considerably better but, even so, the approximation to a simple line shape is poor.

Spectra of some other substances have also been evaluated. Thus the absorption line of ^{19}F in teflon and of ^1H in the polysaccharide gum-arabic shows expansion coefficients which agree rather well with those for the spectra of MnSO_4 in aqueous solution. On the other hand, the spectra of NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ give rise to quite different expansion coefficients. In the spectrum of NH_4Cl , the Gaussian dominates together with the first harmonic, while for the spectrum of $(\text{NH}_4)_2\text{SO}_4$ the agreement with the Gaussian alone seems to be complete. These observations are detailed in Fig. 2b. The spectrum of NH_4Cl gives rise to a non-linear relationship, while the curve characteristic of $(\text{NH}_4)_2\text{SO}_4$ very accurately reproduces a straight line.

Some spectra artificially composed by the addition of two known components, consisting of two separately registered spectral bands, have been similarly studied to test the resolving power of the numerical analysis. The ^1H line of NH_4Cl has been used, while the ^1H lines of several aqueous solutions of MnSO_4 have been taken to represent the various narrow components. Figs. 3a and 3b show two such artificial spectra which have been subjected to a detailed analysis. The narrow bands of these spectra are somewhat overmodulated.

The results of these calculations are summarized in Fig. 4. In the part of the spectrum where the narrow band is dominating, the adaptation of the analytical form to the experimental curve is essentially determined by the value of m_1 , while in the part of the spectrum where the broad band dominates, the form of the analytical expression is principally determined by m_2 . The standard deviations for these two parts of the spectrum coincide rather well with the deviations of the spectral lines determined separately, and the m_1 and m_2 values corresponding to the closest fit can be accurately determined from the complex spectrum. When the m values are known, the remaining parameters determining the shape of the spectrum are easily found.

The use of 5 or 7 terms in the expansion for each band produces a good agreement with the results from the spectral bands registered separately. On the other hand, the use of 3 terms only, gives rise to considerable deviations, especially with regard to the ratio B_1/B leading, in this case, to an error of about 15 %. Similar difficulties are, however, also encountered in the analysis of the spectrum shown in Fig. 3b, where the overlap between the bands is considerable. Expansion to 7 terms in each band leads, as expected, to erroneous results, while an expansion to 5 or 3 terms, on the other hand, permits a separation of the band components at a corresponding loss of accuracy which is especially significant in the determination of B_1/B .

The calculations carried out show that the method can be safely applied when $m_2 > 8 m_1$. As a rule, this condition is fulfilled in a great many practical cases. It is, however, a matter of importance to be able to extend the use of

the method to spectra with large overlap, and some simple modifications of the method of calculation seem to make such an extension possible.

Acknowledgements. Thanks are due to Mrs. M. Andersson of the Swedish Board for Computing Machinery, who coded the programme. The free machine time granted by the *Swedish Board for Computing Machinery* and the financial support provided by the *Swedish Natural Science Research Council* and the *State Council of Technical Research* is gratefully acknowledged. The cost of the NMR spectrograph has been defrayed by a generous grant from the *Knut and Alice Wallenberg Foundation*.

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