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Correlation Analysis of Electron Spin Resonance Spectra: the a-Spectrum

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An improved method of analysis of e.s.r. spectra is described, based on correlation methods. The most prominent line is identified by comparison of the experimental spectrum with a matching 'test spectrum,' which consists initially of a single Gaussian or Lorentzian derivative shape, but which includes a more and more complex pattern of lines as the analysis proceeds. A product function P (produced by correlation of the test spectrum with the experimental spectrum) is used as the criterion of improvement of fit. At each stage of the analysis, the product function is computed for a range of values for an additional coupling constant, a display of product function *versus* coupling constant constituting the a-spectrum. The coupling constant giving the biggest improvement in P is now incorporated in the test spectrum with the appropriate multiplicity, and the process is repeated until the a-spectrum shows a maximum at the origin, when the analysis is complete. The analysis allows coupling constants to be assigned with precision even in weak spectra; a unique analysis is often possible in a weak spectrum where few of the lines are recognizable by the naked eye. This feature should be especially valuable in identifying spectral satellites due to nuclei such as ^{13}C and ^{29}Si present in natural abundance. The benzyl and the 1-ethoxy-ethyl radical are analysed in detail, the latter being used in spectra with successively lower signal:noise ratios to demonstrate the power of the method, and finally the method is used to determine the position of the ^{29}Si satellites of the triethylsilyl radical.

Analysis of solution e.s.r. spectra of free radicals to extract the coupling constants is normally carried out by direct measurement of separations between lines of the spectrum, or by simulation, using guessed values for the coupling constants and varying these until the best agreement with the observed spectrum is reached. For complex spectra with many overlapping lines, there is often the possibility that although the best ' local ' fit has been obtained, the analysis is still in error, and that a completely different pattern of coupling constants is needed to give a correct analysis.

An alternative approach, the use of auto- and cross-correlation, was suggested by Allen [1] in 1962, tested on synthetic e.s.r. spectra [2] in 1964, and applied by Ziegler and Hoffmann in 1968 to the evaluation of coupling constants from a number of good quality e.s.r. spectra.[3] Relatively little use of correlation methods has been made since then:[4] this must be partly due to the fact that until recently, comparatively few e.s.r. spectrometers have been equipped with digital data systems, and it may also have been felt that the mathematical methods are too complex for general use. Other mathematical techniques which have been suggested include power spectrum analysis (significance plots)[5] and Fourier transform techniques.[6]

We describe here a slightly different approach to that of Ziegler and Hoffmann, still based on correlation, and show a number of practical applications. In favourable cases it is possible to show that the analysis of a spectrum is correct and complete. Once provisional analysis has been made, it is possible to search for new coupling constants by a variation on the correlation technique (the a-spectrum) and to use this to refine coupling constants and to determine whether there are new constants still to be determined. Information about linewidth and shape can also be obtained. Finally, we show that satisfactory analysis can be made on very poor quality spectra, a feature which is particularly useful in the determination of the positions of satellites in e.s.r. spectra due to species such as ^{29}Si and ^{13}C present in low natural abundance.

Correlation Analysis: a-Spectra.—The human eye can distinguish clearly features in a spectrum such as a Gaussian derivative shape even in the presence of a large amount of noise. It is less efficient in determining regularities in separ-

ations between such features, particularly if there are a large number of them, and if the spectrum is of poor quality. Correlation methods, in which information from all the points in the spectrum can be coalesced, offer a considerable advantage.

Cross correlation involves comparison of the experimental spectrum with a test spectrum or pattern. Perfect correlation can only be achieved when the test spectrum is identical in position and shape with the experimental spectrum. Goodness of fit is tested by summing the products of corresponding elements of the test and experimental spectra.

We illustrate our approach by considering a simple idealized six-line spectrum, before moving on to real examples. Two relatively simple computer programs MATCH and SEEK are involved. The simulated experimental spectrum has 36 points with a triplet coupling of 3 units and a doublet coupling of 10 units [Figure 1(a)].

Our analysis starts with a test spectrum consisting of a single simplified Gaussian derivative function, digitized as the numbers [-1 000, 0, 1 000] [Figure 1(b)]. The program MATCH is intended to locate initially the most intense line in the experimental spectrum. It does this by successively matching the experimental spectrum at all successive positions from left to right, giving at each point a product function P which is formed by summing the products of corresponding elements of the experimental and test spectra and multiplying by a scaling factor $S = (10^6/\Sigma x^2)^{\frac{1}{2}}$ in which x are the individual digitized numbers of the test spectrum. At position 2, the first available point, $P = [0 \times (-1\ 000)\ 0 \times 0 + 0 \times 1\ 000] \times (10^6/2 \times 10^6)^{\frac{1}{2}} = 0$. The process is repeated giving values of P for points 2—35 in the experimental spectrum; for example the first non-zero value is at position 8 [Figure 1(b)], where $P = [0 \times (-1\ 000) + 0 \times 0 - 1 \times 1\ 000] \times 0.707 = -707$. The maximum value of P corresponds to the most intense line of the spectrum. In this artificial spectrum, maxima will be found at points 13 and 23 [Figures 1(c) and (d)]. In real life one of the two peaks would usually be larger, due to noise; if two exactly equal maxima were found, the program would chose the left-hand one, in this case the peak centred at 13, with a corresponding product function of 2 828. This position is taken as the provisional centre of the spectrum.

The second program SEEK is now applied, to search for the first coupling constant. We look first for a possible doublet
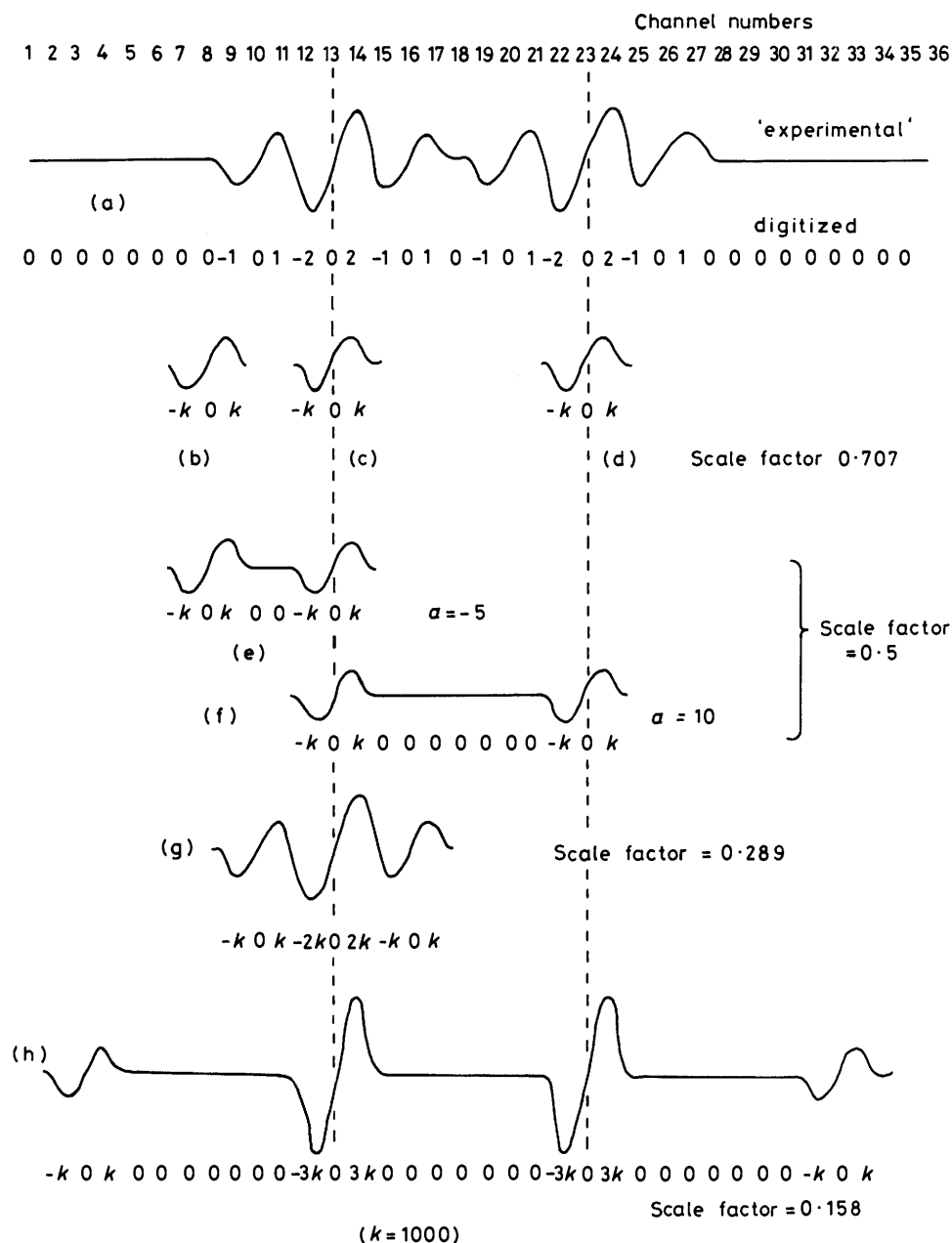
Figure 1. Illustration of procedure on simple idealized spectrum

splitting. The test spectrum now consists of two Gaussian derivative lines, one situated at the provisional centre of the spectrum, the other situated in a range of possible positions either to the left or to the right of the first line. The position of the ' movable line ' is varied systematically, and for each position a product function P is calculated. For example, for (e) with a coupling constant of -5 units, $P = 1\ 000\ (-1 + 2 + 2) \times 0.5 = 1\ 500$, for (f) with $a = 10$, $P = 1\ 000\ (2 + 2 + 2 + 2) \times 0.5 = 4\ 000$. The value of a which gives the highest value of P is considered as a possible new coupling constant. The a-spectrum, consisting of a plot of P against a [Figure 2(a)], shows maximum values at positions of a which may correspond to coupling constants of the system.

The procedure is repeated to search for possible triplet splittings: in this case, two lines of half the intensity of the central line are generated at positions equally to the left and to the right, and the coupling constant is again varied until

the best value of P is obtained [Figure 2(b)] at $a = 3$ and $P = 3\ 464$ corresponding to the test spectrum [Figure 1(g)]. Since the prospective doublet coupling constant of $+10$ gives a greater product function than the triplet, the doublet pattern [Figure 1(f)] is chosen for the next stage.

The first program MATCH is now used again to establish the new provisional centre (at point 18) and it is also checked at this stage if a quartet pattern [Figure 1(h)] would fit the experimental spectrum better than the doublet. Since the quartet gives a P value of only 3 795 compared with the doublet value of 4 000, the splitting is confirmed to be a doublet.

The procedure SEEK is followed once more, using the new test spectrum [Figure 1(f)] either as one part of a doublet pattern [Figure 2(c)], or as the central section of a triplet [Figure 2(d)]. In this way a triplet splitting of 3 units is found, giving a pattern identical with the experimental spectrum with
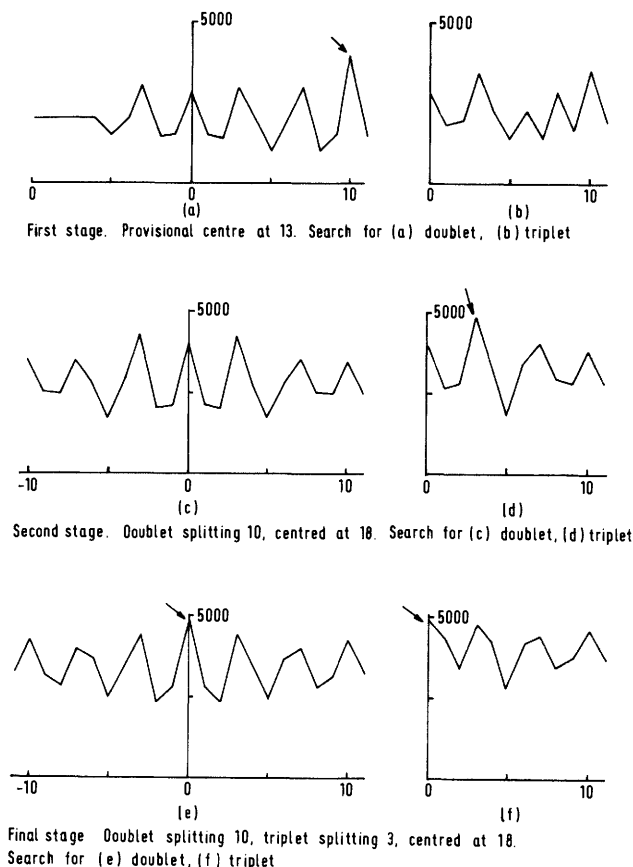
First stage. Provisional centre at 13. Search for (a) doublet, (b) triplet

Second stage. Doublet splitting 10, centred at 18. Search for (c) doublet, (d) triplet

Final stage. Doublet splitting 10, triplet splitting 3, centred at 18.
Search for (e) doublet, (f) triplet

Figure 2. a-Spectrum analysis of simple idealized spectrum. Plots are of product function P against coupling constant a

$P = 4\,899$. MATCH confirms that the centre is at 18 and that the new multiplet is a triplet rather than a quintet. SEEK discovers no new doublet or triplet coupling constant with a product function higher than 4 899 so the analysis is complete * [Figures 2(e) and (f)].

The normalization of the test spectrum at each stage means that the product function P must increase at each stage of the analysis as the test function more closely resembles the experimental spectrum, with P reaching a maximum value when the analysis is complete. We do not normalize the experimental spectrum, since it remains constant in a particular experiment. The final product function is thus a measure of the strength of the spectrum.

The simplified spectrum just considered exemplifies the method. A number of comments need to be made before real examples are considered. (1) In the simplified example, the lines had a ' width ' of 1 unit. In practice, lines will usually be considerably wider than this: the width will also be unknown at the outset. The desired ' width ' is fed into MATCH, which generates an appropriate Gaussian derivative pattern, normalized as close to 2 000 000 as is possible with integers. As stated above, for $w = 1$, the test spectrum values are $[-1\,000, 0, 1\,000]$; for $w = 5$, they are $[-9, -65, -282, -657, -696, 0, 696, 657, 282, 65, 9]$. In the analysis of a real spectrum, any (small) arbitrary value of w is taken, and the product function P corresponding to the most prominent line is calculated. The width is now varied to give a maximum value of P, at which

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* The ' experimental ' spectrum was padded with five leading and five trailing zeros for this stage of the analysis to allow the full range of possible new couplings to be explored.
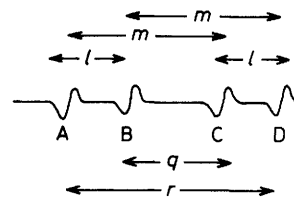

Figure 3.

point the test shape matches the experimental shape as well as possible. Lorentzian shapes can be calculated too, but for the examples used in this paper, Gaussian derivative shapes were used. If it is suspected that an ' impurity ' radical may be present, it is sometimes better to optimize the linewidths on a prominent line away from the centre.

Using a test spectrum consisting of a single Gaussian derivative shape of suitable width, a plot of P against position gives a second derivative type presentation of the spectrum with maxima at line positions. For noisy spectra, this is often an improvement over the original presentation.

(2) When the final assignment has been made, the assignments may be refined using MATCH by varying the coupling constants one at a time by one unit, until the maximum value of P is obtained. At this point, application of SEEK using all the coupling constants and multiplicities will give an a-spectrum showing no value for the product function higher than at the origin, and removal of the coupling constants one at a time followed by application of SEEK will present separately each of the couplings present in the molecule as a maximum in the a-spectrum.

(3) The selection of the first coupling constant can present difficulties, particularly in systems with many doublet splittings. For example, in the system shown in Figure 3, a doublet of doublets, suppose that although the theoretical intensity of each line is the same, the actual order was $B > C > A \sim D$. MATCH would identify B as the provisional centre of the spectrum, and SEEK would choose q as the first coupling constant rather than l or m. This problem is overcome, for the the first coupling constant only, by the use of TWINPEAK which searches for and sums coincidences of peaks y apart. In this example q and r would show up with only half the intensity of the two coupling constants l or m. Alternatively, AUTO-CORRELATION can be applied to the original spectrum (or its transform using MATCH with a suitable linewidth). This effectively uses the experimental spectrum as the test spectrum, with varying displacements as in MATCH. The auto-correlogram gives maxima corresponding to coupling constants, and also sums and differences. It is often impossible to identify all the coupling constants from an autocorrelogram, but our experience has been that in analysable spectra, even very weak ones, the highest value on the autocorrelogram away from the origin has always corresponded to a true coupling constant.

Our procedure is summarized in Figure 4. We show below its application to a number of known test systems, and conclude by using it to determine the (currently unknown) ^{29}Si coupling constant of the Et$_3$Si$\cdot$ radical.

The Benzyl Radical.—Benzyl radicals were obtained by photolysis of a mixture of toluene and di-t-butyl peroxide at $-30\,°C$. Maximum achievable gain was not used, but very similar figures were obtained from a more intense spectrum. MATCH showed the most intense peak (the right-hand line of the central doublet) to be located at 1 310 ($P = 225\,491$), and the width parameter w was optimized at 15 units. SEEK was used to determine the first coupling constant. The a-

```
                    ( Raw spectrum )
                            |
                            v
            MATCH finds position and width
            of most prominent line
                            |
                            v
            TWINPEAK or AUTOCORELLATION
            gives first coupling constant
                            |
                            v
            MATCH determines multiplicity    <----
            and finds new centre                 |
                            |                     |
                            v                     |
            SEEK produces a - spectrum           |
                            |                     |
                            v                     |
                  Is there a                      |
                  maximum in the                  |
               a-spectrum away from zero,  yes ---
               corresponding to a new
                  coupling constant?
                            |
                           no
                            |
                            v
                  Are refined              yes    Vary coupling constants
               values of the coupling    ----->   individually by 1 unit
                constants required?                to ensure best fit of
                            |                      spectrum (MATCH)
                           no |
                            v
                  Is final check           yes    Remove coupling constants
                of coupling constants    ----->    one at a time. SEEK gives
                     required?                     a display of the a-spectrum
                            |                      with a maximum
                           no |                    corresponding to the
                            v                      coupling constant removed
                  ( Analysis complete )
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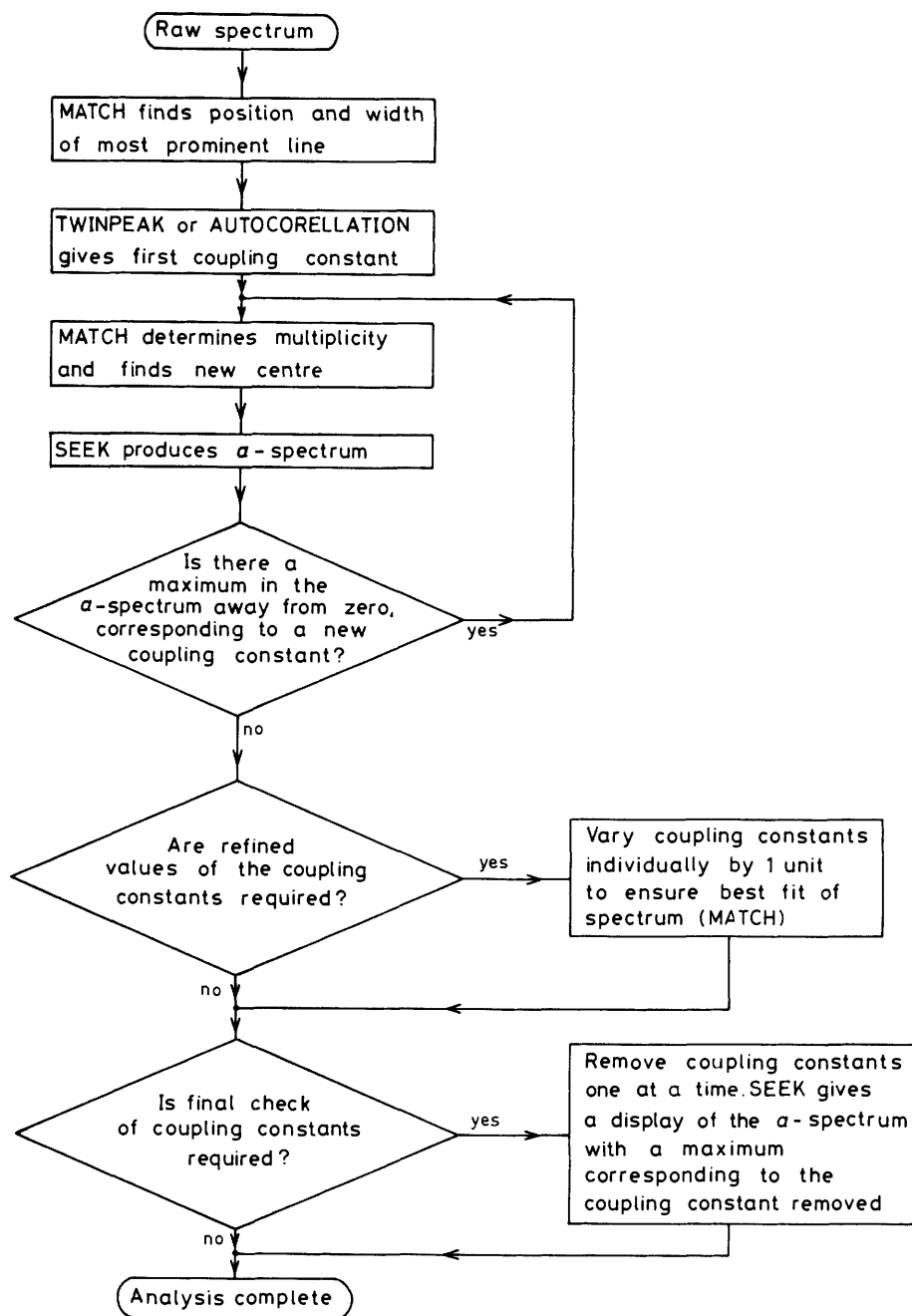
Figure 4.

spectra showed that a doublet at -140 ($P = 296\,703$) narrowly beat a triplet of 115 (296 403). (Next would have been a triplet of 40 units, but the final triplet coupling of 366 was well down the list of intensities.) MATCH confirmed this P value and gave the new centre as 1 240. The next run of SEEK gave a triplet of 115 ($P = 379\,037$). MATCH moved the centre marginally to 1 241. SEEK now gave a triplet of 40 units ($P = 502\,355$), and after MATCH confirmed the centre at 1 241, a fresh run of SEEK [Figures 5(a) and (b)] revealed the last triplet at 367, $P = 547\,031$. MATCH at this stage showed a better width factor of 16, confirming the centre as 1 241 units. The a-spectrum produced by SEEK [Figures 5(c) and (d)] showed that no further coupling constants are involved. A final optimization using MATCH and varying the parameters by 1 unit one at a time gave as best parameters a

doublet of 141 and triplets of 40, 116, and 367 units. The fit for a doublet of 140 is nearly as good as for 141 (and a repeat, more intense spectrum actually gave 140 for the doublet). Using SEEK without each of the coupling constants in turn, and interpolation near the maxima of the a-spectra thus produced, will give more precise coupling constants, though other errors are likely to make this refinement of marginal value. The values, shown in the Table, are in good agreement with the other recently determined values, particularly since the spectral width of 100 G needed to get all the lines on the chart does not lead to the greatest precision in evaluating small coupling constants.

The 1-Ethoxyethyl Radical.—A 3 : 1 mixture of di-t-butyl peroxide and diethyl ether was photolysed at $-39\,^{\circ}C$. Seven
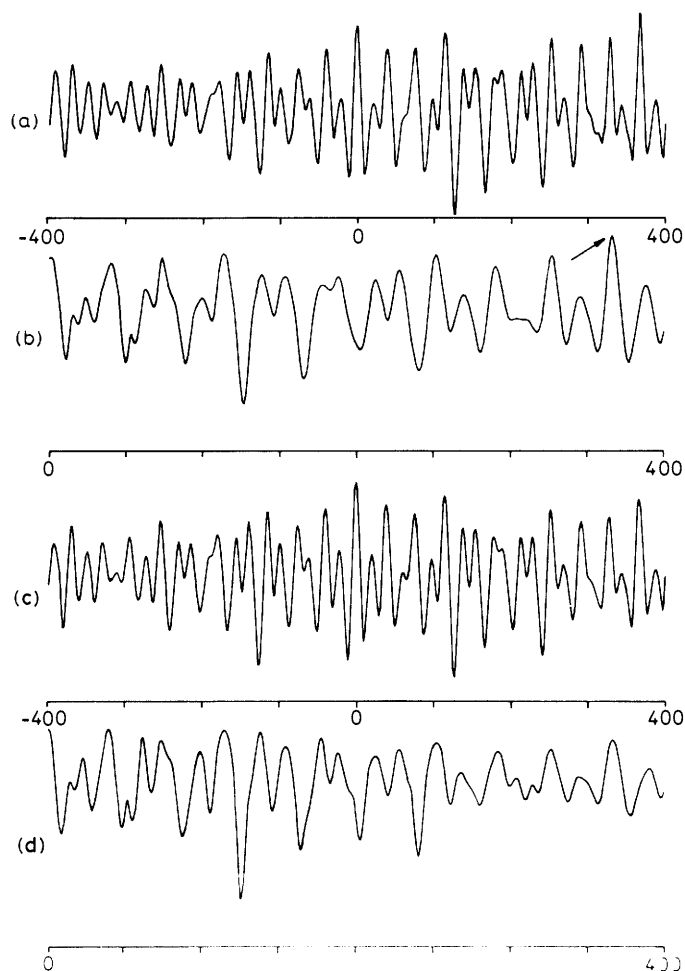
Figure 5. a-Spectra of the benzyl radical. Channel units: 22.45 units = 1 Gauss. (a) Penultimate assignment, search for extra doublet. (b) Penultimate assignment, search for extra triplet, maximum value of P at 367. (c) Final assignment, search for extra doublet, none found. (d) Final assignment, search for extra triplet, none found

Table Comparison of coupling constants for benzyl radicals (G)

H	Intense benzyl Whole nos.	Intense benzyl Interpolated	Weak benzyl Whole nos.	Weak benzyl Interpolated	Ref. 7
α	16.3_5	16.3_6	16.3_5	16.3_5	16.4_7
ortho	5.1_7	5.1_8	5.1_7	5.1_5	5.1_9
meta	1.7_8	1.7_8	1.7_8	1.7_8	1.7_7
para	6.2_4	6.2_2	6.2_8	6.2_6	6.2_4

The series of seven spectra of the 1-ethoxyethyl radical were used as a test of how weak a spectrum can be, whilst still allowing a full analysis. The analysis of each spectrum was started from scratch, with no assumptions about splittings or linewidths. It was found that a complete and unambiguous analysis could just be made for the fifth spectrum recorded at a modulation amplitude of 0.05 G [Figure 6(d)]. This is a very weak spectrum in which the position of only a very few lines can be established with any confidence. The signal to noise in (d) should be ca. 1/5 of the value of spectrum (b) (*i.e.* in proportion to the modulation amplitude [9]), since for both (b) and (d) the modulation amplitude is small compared with the value in (a) of 1 G which gives the maximum amplitude of the spectrum.

The sixth spectrum (modulation amplitude 0.025 G) could not be analysed from scratch, but if the pattern of couplings and the linewidth were supplied, the position of the centre could be established; hence in a spectrum of this intensity, some indication could be obtained about the presence of one out of several possible radicals, providing that the coupling constants were known. In the seventh spectrum (modulation amplitude 0.01 G), even this information could not be obtained.

[29]Si *Satellites of the Triethylsilyl Radical.*—A mixture of tri-ethylsilane and di-t-butyl peroxide (1 : 3 v/v) was photolysed at ca. -25 °C. A 200 G scan width was used, and two series of spectra were run, centred on 3 151 and 3 331 G respectively. In each series, a single 4 min scan was run to obtain the spectrum of the central septet, followed (with fresh samples) by two separate accumulations of 4 × 4 min scans. From the single scans at each wavelength, MATCH produced the septet splitting 64 units, 5.7_1 G (lit.,[10,11] 5.69, 5.73 G) with $w = 16$. MATCH was now used to find the position of the radical centre for all the spectra, and using this value, the nine scans (4 + 4 + 1) for each series of spectra were added to give overall accumulated spectra with the main spectrum on the right and left of the scan respectively. These spectra give an indication of satellite position [see Figures 7(a) and (c)] but little certainty.

MATCH was now applied to each wing of the spectrum separately; the resulting a-spectrum shows the centre of the satellite pattern to be 978 units downfield (87.02 G) and 923 units (82.66 G) upfield [see Figures 7(b) and (d)]. The centre of the $Et_3Si\cdot$ spectrum was estimated to be at ca. 3 222.7 G by comparison of its position with that of the DPPH standard, giving by application of the exact formula [+] $a_{29_{Si}} = 169.46$ (from lowfield satellites) or 169.68 (from highfield satellites) = $169._6$ G (average). This is somewhat smaller than the value of 181.1 or 183 G reported for the trimethylsilyl radical,[10,11] and

consecutive spectra were run with the sample changed after the third. The first was run with 1.0 G modulation, which gave the greatest signal intensity, though presumably at the expense of line distortion. The subsequent spectra were run at 0.5, 0.25, 0.1, 0.05, 0.025, and 0.01 G modulation with the other operational parameters left constant, to attain a controllable decrease in signal to noise.

The fourth sample [Figure 6(c), modulation 0.1 G] was chosen for initial analysis. MATCH found a prominent peak at 1 189, width parameter 15. SEEK suggested a doublet (172), $P = 137$ 161 just greater than a triplet 488 ($P = 136$ 718), but the triplet splitting was applied first on the basis of TWIN-PEAK or AUTOCORRELATION, which indicated 488 as the largest off-zero peak. MATCH indicated that the multiplicity of the 488 splitting was in fact a quartet. A doublet 316 and a triplet 37 were next identified. A final use of MATCH left the couplings unchanged, but showed a narrower linewidth $w = 14$. Checks for possible improvements in multiplicity and further coupling constants were carried out as far as possible, but were hampered in this case by the spectrum filling most of the array available, with very little base-line before and after. Calibration of the spectrum gave the quartet coupling as 21.8 G, the triplet as 1.65 G, and the doublet as 14.1 G [lit.,[8] 21.8, 1.67 and 14.1 G].

[+] $a = [2H_0(H_0 - H_k)/(2H_0 - H_k)] = [2H_0(H_l - H_0)/(2H_0 - H_l)]$ where H_0, H_k, and H_l are the field positions corresponding to the centre of the main spectrum, the lowfield satellites, and the highfield satellites, respectively.[12]
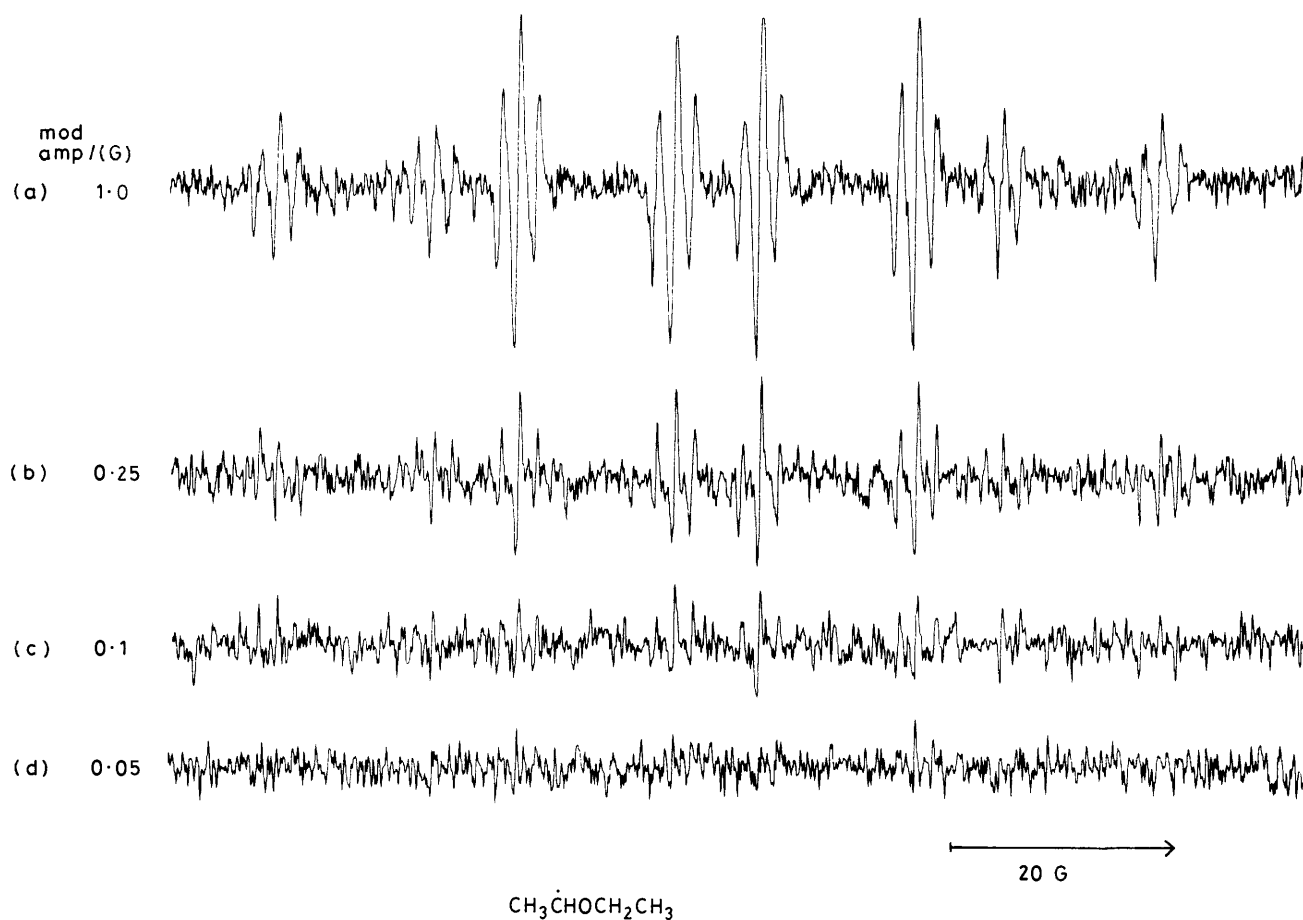
mod
amp /(G)

(a) 1·0

(b) 0·25

(c) 0·1

(d) 0·05

20 G

$CH_3\dot{C}HOCH_2CH_3$

Figure 6. Experimental e.s.r. spectra of $CH_3\dot{C}HOCH_2CH_3$. Modulation amplitude (a) 1.0, (b) 0.25, (c) 0.1, (d) 0.05 G

$Et_3Si\cdot$ satellites
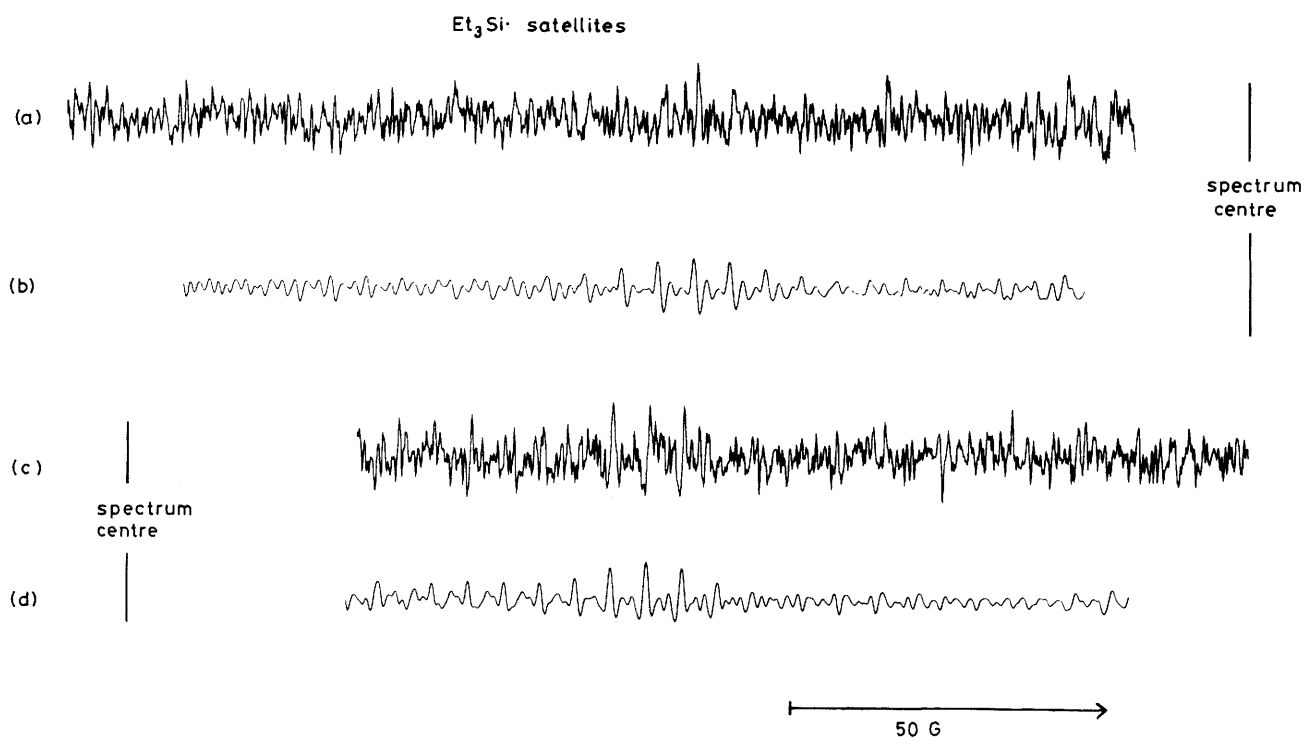
(a)

spectrum
centre

(b)

(c)

spectrum
centre

(d)

50 G

Figure 7. Satellites of $Et_3Si\cdot$. (a) Downfield, raw spectrum, 9 accumulations. (b) Downfield, a-spectrum. (c) Upfield, raw spectrum, 9 accumulations. (d) Upfield, a-spectrum

may indicate a slightly more planar geometry for the tri-ethylsilyl radical.

Conclusions.—The procedures outlined in this paper offer a convenient method of determining accurate coupling constant and linewidth data from e.s.r. spectra, even if the intensity is low. In structural studies, where the effect of a substituent is to be studied, a direct comparison between two compounds may allow a very high degree of precision in determination of relative coupling constants. The *a*-spectrum method should be particularly useful in identifying couplings due to satellites due to isotopes such as ^{29}Si and ^{13}C, present in small amounts in natural abundance. Even if complex splitting patterns are involved which spread out the spectral intensity, an *a*-spectrum using the parameter established for the main spectrum allows the satellite position to be determined more readily than from the raw spectrum itself.

Variations in this technique may well have applications in other forms of spectroscopy, particularly n.m.r.

Experimental

E.s.r. spectra were obtained by photolysis of samples in the cavity of a Varian E104A e.s.r. spectrometer as described previously.[7] Samples were made up in the approximate proportions of three volumes of di-t-butyl peroxide to one volume of other reagent. An 8 bit AD/DA convertor was connected to a DIGICO 16 computer for spectral accumulation. About 2 280 data points, each consisting of the average of 256 acquisitions could be collected during a 4 min scan. Application of the programs described here required a more powerful computer (a DEC VAX system).

The main features of MATCH and SEEK are described in the text. The normalizing routine scales the sums of squares of the elements of the test spectrum to 2 000 000 before comparison with the experimental spectrum. This ensures that an improvement in the product function with changes in multiplicity, coupling constant, or linewidth correspond to improvements in match with the experimental spectrum. (For high multiplicities, the product function ceases to be a sensitive test of multiplicity due to the dominance of the high intensity lines near the centre.) Since the experimental spectrum is not itself normalized, the product function of a completely analysed radical is a measure of its intensity.

TWINPEAK looks for coincidences of peaks with a particular separation by summing the product $S_x \cdot S_{x+l}$ (where S_x is a point on the digital spectrum, or more usually its transform by MATCH with an appropriate linewidth) over the whole range of x values in the spectrum. l is varied systematic-

ally, and values of l for which maxima occur correspond to coupling constants, or sums or differences of them. This procedure is similar to autocorrelation, but no normalization is carried out.

Both Gaussian and Lorentzian derivative line shapes were programmed; only Gaussian line shapes were used in this study. The peak–trough field separation ΔH_{pp} is related to the width parameter w used in this work by the relation $\Delta H_{pp} = 0.5657\ w$.

Calibration of the spectra was carried out by running an Mn^{2+} spectrum [13] (present as an impurity in SrO) immediately after the spectrum of interest. The line positions were obtained either by use of MATCH with an appropriate linewidth, or by autocorrelation of the spectrum to produce the separation directly.

References

1 L. C. Allen, *Nature (London)*, 1962, **196**, 663.
2 J. D. Swalen and H. M. Gladney, *I.B.M.J. Res. Dev.*, 1964, **8**, 515.
3 E. Ziegler and E. G. Hoffmann, *Z. Anal. Chem.*, 1968, **240**, 145.
4 *E.g.* E. Blanck, *Liebig's Ann. Chem.*, 1969, **724**, 56; K. D. Bieber and T. E. Gough, *J. Magn. Reson.*, 1976, **21**, 285; G. Grampp and C. A. Schiller, *Anal. Chem.*, 1981, **53**, 560.
5 S. Brumby, *J. Magn. Reson.*, 1979, **35**, 357; 1980, **39**, 1; 1980, **40**, 157.
6 R. H. Silsbee, *J. Chem. Phys.*, 1966, **45**, 1710; T. Nishikawa and K. Someno, *Anal. Chem.*, 1975, **47**, 1290; W. R. Dunham, J. A. Fee, L. J. Harding, and H. J. Grande, *J. Magn. Reson.*, 1980, **40**, 351.
7 S. Dinçtürk, R. A. Jackson, M. Townson, H. Ağirbaş, N. C. Billingham, and G. March, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1121.
8 I. Biddles, A. Hudson, and S. F. Wiffen, *Tetrahedron*, 1972, **28**, 867.
9 J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance: Elementary Theory and Practical Applications,' McGraw-Hill, New York, 1972, p. 454.
10 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938.
11 S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 1970, 348.
12 A. Hudson, M. F. Lappert, and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1976, 2369.
13 J. Rosental and L. Yarmus, *Rev. Sci. Instr.*, 1966, **37**, 381; H. M. Swarz, J. R. Bolton, and D. C. Borg, 'Biological Applications of Electron Spin Resonance,' Wiley, New York, 1972.