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Use of Grid Search Techniques to Extend the Use of a Least Squares Program for Analysis of Electron Spin Resonance Spectra

There exist a number of papers concerned with the analysis of electron spin resonance spectra by means of nonlinear least squares techniques [1–5]. These methods are very useful in deciding the assignment of an ESR spectrum but they suffer from the great disadvantage that the shape of the energy surface near the minimum is often such that, at points not far from the minimum, the maximum gradient in the negative direction is not towards the minimum energy. This means that unless the first estimate fed into the least squares program is very close to the minimum the least squares procedure will not converge. This is a serious failing in applying this technique to the analysis of ESR spectra since the amount of time required to obtain the preliminary estimate may be much longer than that required for the least squares procedure itself. To overcome this a grid search has been added to the least squares program to make the first estimate of the parameters less critical.

A least squares program, similar to that written by Gladney [4], which operates on a spin Hamiltonian of the form

$$\mathcal{H} = \beta H.g.S + S.D.S + S.A.I_N + S.A.I_L + I.Q.I + \frac{a}{6}[S_x^4 + S_y^4 + S_z^4] + \frac{F}{180}[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2] \quad (1)$$

where

I_N = nuclear spin of paramagnetic nucleus

I_L = nuclear spin of ligand nucleus

was written and used for test cases to see how accurate the initial estimate had to be to obtain convergence. This was variable but in many cases an error of 1 % or less in any of the parameters caused nonconvergence. A simple grid search was then added to the program[1] so that, if the least squares procedure did not converge after

[1] This program is available from the author on request.

a number of iterations, the grid search was entered and the parameters varied according to the rules given below. The results of the grid search were then scanned for the best fit, i.e., the smallest total standard deviation from the experimental data. The parameters used for this best fit set of data were then fed into the least squares procedure, and so on cyclically until either convergence was reached or until the number of iterations reached a specified number.

The grid search procedure used was a very simple one in which the parameters were varied one at a time by a specified amount which was variable. The parameters were both incremented and decremented by this amount, there being a condition as to which parameters could be varied. This crude procedure could certainly be improved by using a more sophisticated grid search technique and this possibility is being investigated at the present time. However, the time required for this may be prohibitive at the present. To give some idea of the time requirement: for the case of an $S = 1$, $I = \frac{3}{2}$ manifold with a spin Hamiltonian of this form:

$$\mathscr{H} = \beta H.g.S + S.D.S + S.A.I_N \tag{2}$$

and five varying parameters D, E, A_x, A_y, A_z with three least squares iterations, one complete cycle, i.e., one set of least squares iterations and one grid search took almost three hours on an ICL 1905E with a store cycle time of 1.8 μsec. It appears that some improvement in efficiency is required before this technique can be generally applicable, and some heuristic algorithms are being considered at the moment to assess their usefulness.

It is worth noting that if the assignments of the experimental spectrum were fairly certain at the start, a large saving in time could be obtained by only solving the Hamiltonian for the relevant energy levels near the resonance field instead of, as is programmed at the present, completing an extensive search for all possible transitions up to the maximum field and then finding the best fit and hence the assignment of the spectrum.

On a variety of test cases it has been shown that this program can save an appreciable amount of time in attempting to find the best fit parameter. It is anticipated that if it becomes feasible to increase the complexity of the grid search then the saving in time will be greater because this will allow a still greater margin of error in the initial estimate.

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