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NOTE

A Versatile Program for Computing Paramagnetic Resonance Spectra from a Parametric Spin-Hamiltonian*

PURPOSE

The resonance spectrum of a paramagnetic system of several spins is obtained after solving for the energy levels of the hamiltonian operator. In practice, one diagonalizes the matrix of an effective spin-hamiltonian, $\mathscr{H}_{\text{SPIN}}$, written in the basis of the direct product (uncoupled-particle representation) of single-spin eigenstates. The transition intensities are calculated in first order by using the eigenvectors generated at the current field strength.

The present program (MAGNSPEC) requires only the coefficients of $\mathscr{H}_{\text{SPIN}}$ in tensor form:

$$\begin{aligned}\mathscr{H}_{\text{SPIN}} = {} & -\beta_e \mathbf{H}_0 \cdot g_e \cdot \mathbf{S} + \beta_n \mathbf{H}_0 \cdot g_n \cdot \mathbf{I} + \mathbf{S} \cdot A \cdot \mathbf{I} \\ & + \mathbf{S} \cdot D \cdot \mathbf{S} + \mathbf{I} \cdot Q \cdot \mathbf{I} + J\mathbf{S} \cdot \mathbf{S}',\end{aligned}$$

the spin numbers considered, and their assignments to the given interactions. (The symbols have their customary meaning.) Adding more terms to the hamiltonian is a simple matter; so is changing the quantization axis, assumed here along the applied static field, or the direction of the radiation field, assumed here perpendicular to the static field.

ESR, NMR or NQR problems are treated equally. Output may be chosen as frequency spectra at given field values, or as a magnetic-field spectrum at a fixed radiation frequency. Various intermediate results may be selected. The program is complemented by a procedure (SPREAD) to broaden the discrete lines or generate a powder spectrum.

METHOD

The situation encountered in calculating magnetic resonance spectra has been described in detail [1]. Fundamentally, the method of the present program is

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straightforward. Its prominent feature is the flexibility of the operator approach to the spin-hamiltonian matrix generation. Having the spin operators in store allows the user to specify at will the hamiltonian algebraic form and the quantization axis, provided he includes the algorithms for selecting the proper operators. (The program supplies S_+, S_-, S_x, S_y, S_z, their bilinear cross products, and their squares, cubes and fourth powers. The "standard tensor option" actually relieves the user from specifying a scalar form, with the many unavoidable trigonometric functions.)

Once the spin hamiltonian matrix has been established and diagonalized for a given field value, the field range of interest is systematically scanned by the program. The diagonalization and eigenvectors are adjusted at each step, by finishing off the diagonalization, after transforming the hamiltonian matrix into the basis of eigenvectors defined at the preceeding step of the field. Whenever any transition frequency is found to have passed through resonance within the current field interval, its resonant field value is retrieved by successive quadratic interpolations. The Jacobi diagonalization method, used here, is known to be relatively slow. However, it alone yields the eigenvectors with sufficient accuracy and, especially, it keeps the ordering on successive applications. The ordering is necessary for bookkeeping purposes, and the eigenvectors are actually needed for computing the resonance intensity.

PROCESSING OF THE RESULTS

The main program generates single-crystal discrete spectra for given orientations of the magnetic axis in the crystal or molecular frame. Each discrete peak can be broadened to a chosen line shape. Also, the spectra at a few special orientations may form the roster for later interpolations to intermediate orientations. If the chosen orientations are evenly distributed in space, one will obtain a synthetic powder spectrum by cumulation of all spectra. For spin systems with axial symmetry, it is sufficient to calculate spectra at equal intervals of θ between 0° and 90°, and to weight each of them with $\sin\theta$. For other symmetries, however, a convenient set of orientations, that is practically evenly distributed in space, is furnished by the symmetry of the icosahedron (see Figure 1). For each of the triangular faces, the edge mid-points (projected onto the sphere surface) are apices of secondary triangles, which may in turn be divided, and so on.[1] In general, the characteristic orientations for a given problem are those in the hemisphere, but in

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[1] This scheme suggests itself as an advantageous short-cut to some Monte-Carlo calculations, when only averages (but no correlations) over random orientations are required. It has actually been used to simulate the motional narrowing of the n.m.r. doublet of a pair of spins $\frac{1}{2}$.

some cases those of the first octant may suffice. From resonance spectra calculated at these special orientations, a procedure for spherical interpolation, line-broadening, and cumulation produces the synthetic powder spectrum.

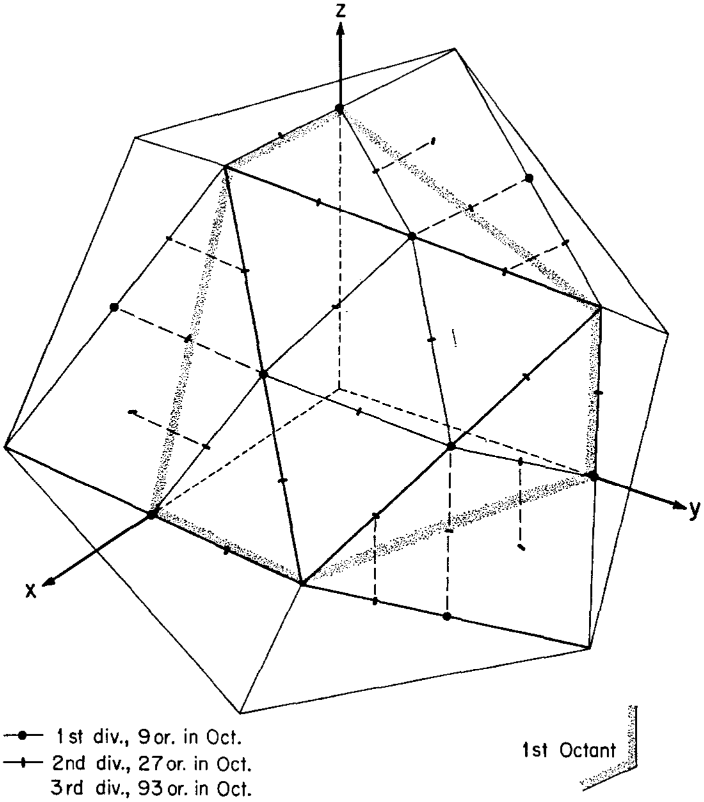

FIG. 1. The regular icosahedron and the scheme of edge division, which furnishes sets of orientations evenly distributed in space.

APPLICATIONS

(1) *The fine structure of* Cr^{+++} *in ruby*, already treated in great detail by Schulz-du Bois [2], is an excellent testing ground. The program reproduces all of his results directly and, in addition, computes transition intensities and cumulates the powder spectrum (see Figure 2).

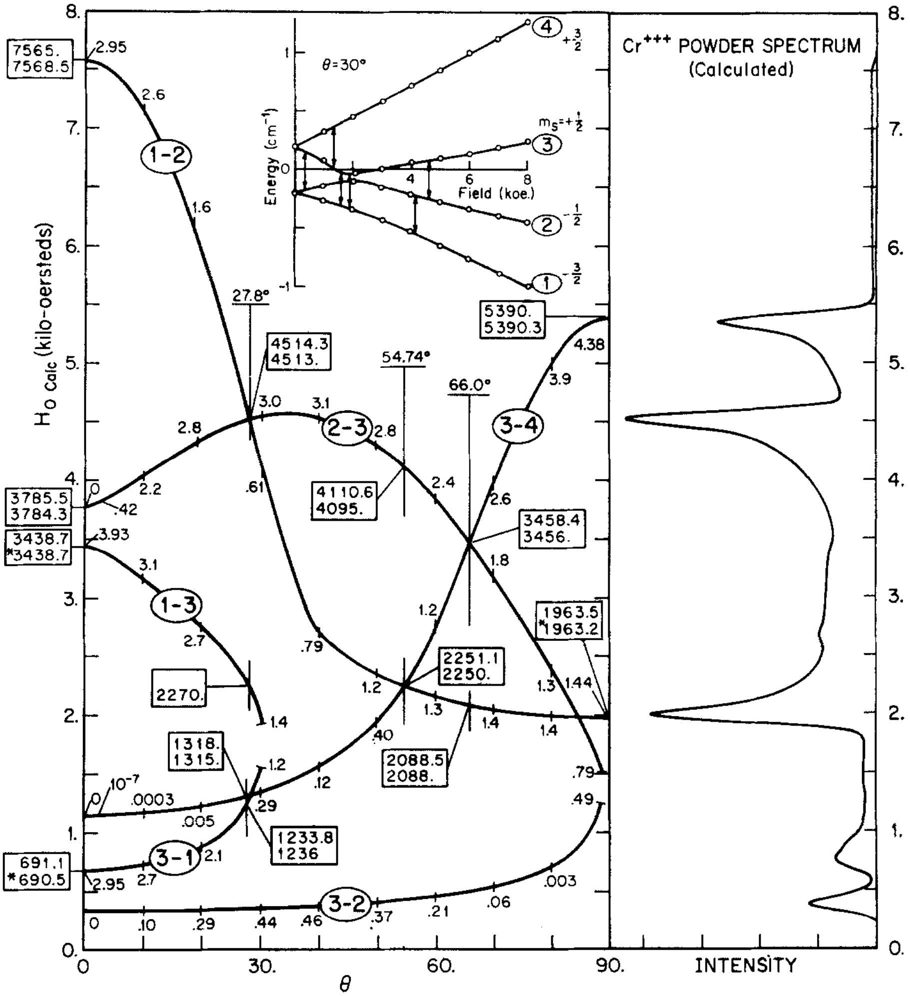

FIG. 2. Calculated magnetic spectrum of Cr+++ in ruby (cf. Ref. 2). The intensity, in arbitrary units, is indicated along the curves. Experimental resonance field values at 9540.5 MHz (Ref. 3) are compared with calculated values in the rectangles; the asterisks mark the resonances used for adjusting the parameters: $g_{\parallel} = 1.9822$, $g_{\perp} = 1.9841$, $D = -0.19110$. The inset shows the energy-level diagram at $\theta = 30°$. The cumulated powder spectrum is plotted at right (gaussian half-width $\sigma = 50$ gauss).

(2) *A nitrogen-related color-center in glass* [3] has a simple three-line hyperfine structure. The case of a glass resembles that of a powder, but a satisfactory fit to the experimental spectra at 9.5 and 16.3 GHz required not only anisotropy of the

parameters, but also a wide and skewed distribution of the g_{zz}-value. This distribution is consistent with the spectrum obtained at 35 GHz.

(3) *An aluminum-related color-center in quartz*, with g_e, g_n, A, and Q terms, motivated the general tensor formulation of the spin hamiltonian. The original parameters of Griffiths, Owen and Ward [4] were inadequate to reproduce experimental data at 77°K, and further adjustments were necessary [3].

(4) *Other applications* have included nuclear quadrupole resonance, simultaneous adjustment of D and E in the fine-structure tensor, and other color centers and metal-ion complexes in glasses and resins [3].

REFERENCES

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2. E. O. SCHULZ-DU BOIS, *Bell System Techn. J.* **38**, 271 (1959).
3. Results obtained at Mellon Institute; to be presented elsewhere. [A more complete description of the program and applications was given at the 19th Conference on Applied Spectroscopy, Cleveland, Ohio, March, 1968, and will be published in a monograph "ESR of Metal Chelates." The Fortran source decks and users guide have been sent to Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana.].
4. J. H. E. GRIFFITHS, J. OWEN, and I. M. WARD, Defects in crystalline solids. Report of Bristol Conference, The Physical Society, London, p. 81, (1955).

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