

EXACT ANALYTIC SOLUTION OF THE SPIN 3/2 COMBINED ZEEMAN-QUADRUPOLE HAMILTONIAN

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ABSTRACT

The secular equation arising from the combined spin 3/2 Zeeman-quadrupole Hamiltonian has recently been solved in analytic form (refs. 1,2). Energy level and frequency expressions, valid for all magnetic field strengths, are derived in a form highly suitable for analysis of resonance patterns arising from rotation of a single crystal about an axis perpendicular to the magnetic field direction. Theoretical rotation patterns are presented for the six possible transitions. A simple method for measurement of the quadrupole parameters is discussed.

INTRODUCTION

Exact expressions of the energy levels of the combined Zeeman-quadrupole interactions ($I = 3/2$) have been obtained for particular orientations of the magnetic field with respect to the electric field gradient (efg) principal axes (refs. 3-5). Approximate solutions have been derived for arbitrary orientations (refs. 6-8). Recently, exact analytic solutions were derived for the general case, using spherical polar coordinates to specify the direction of the field relative to the efg principal axes (refs. 1,2). In this paper, exact equations are derived for energy levels and transition frequencies using Euler angles to specify the efg axes relative to the laboratory frame. This representation is particularly useful for analysis of patterns obtained by rotation of a single crystal about an axis perpendicular to the field direction.

SECULAR EQUATION

Using Euler angles, as defined by Goldstein (ref. 9), to specify the efg axes relative to the laboratory system, with the field H in the x-direction, the secular equation is:

$$E^4 - \frac{X}{4} E^2 - \frac{Y}{4} E + \frac{Z}{16} = 0; \quad (1)$$

$$X = 2\nu_Q^2(1 + \eta^2/3) + 10\nu_Q^2 \quad (2)$$

$$\begin{aligned} Y = & -2\nu_Q \nu_Q^2 \{ [3\sin^2\theta - \eta(1 + \cos^2\theta)\cos 2\psi] \cos 2\phi \\ & + 2\eta \cos\theta \sin 2\psi \sin 2\phi + 3\cos^2\theta - 1 - \eta \sin^2\theta \cos 2\psi \}, \quad (3) \end{aligned}$$

$$Z = \nu_Q^4 (1 + \eta^2/3)^2 + 2\nu_Q^2 \nu_0^2 \{ [3\sin^2\theta + 2\eta(1 + \cos^2\theta)\cos 2\psi - \eta^2\sin^2\theta] \cos 2\phi - 4\eta\cos\theta\sin 2\psi\sin 2\phi - 3\sin^2\theta + 1 + 2\eta\sin^2\theta\cos 2\psi - \eta^2\cos^2\theta \} + 9\nu_0^4 \quad (4)$$

The constant h has been omitted in the above equations, the energy levels will be in frequency units; ν_Q and η are the conventional quadrupole parameters, and $\nu_0 = \gamma H/2\pi$. If the field is chosen to be in the x-direction, rotation about an axis perpendicular to the field changes a single angle, ϕ .

ENERGY LEVELS AND TRANSITION FREQUENCIES

The secular equation yields energy levels of the form (ref. 1):

$$\begin{aligned} E_4 &= (R + D)/2 \\ E_3 &= (R - D)/2 \\ E_2 &= -(R - S)/2 \\ E_1 &= -(R + S)/2, \end{aligned} \quad (5)$$

where, if

$$\begin{aligned} \cos\beta &= -[X^3 - 36XZ - 54Y^2]/(X^2 + 12Z)^{3/2} \\ R &= 6^{-1/2}[X + (X^2 + 12Z)^{1/2}\cos(\beta/3)]^{1/2} \end{aligned} \quad (6)$$

$$D = [\frac{1}{2}(X + \frac{Y}{R}) - R^2]^{1/2} \quad (7)$$

$$S = [\frac{1}{2}(X - \frac{Y}{R}) - R^2]^{1/2} \quad (8)$$

We illustrate the nature of the solutions by considering the simple case of H parallel to the z' -axis of the efg. Although this is a situation for which the secular equation is readily solved (ref. 4), it leads to the most bizarre behavior of the elements R, D, and S. Fig. 1 shows graphs of R, D, and S as a function of ν_0 for two values of η .

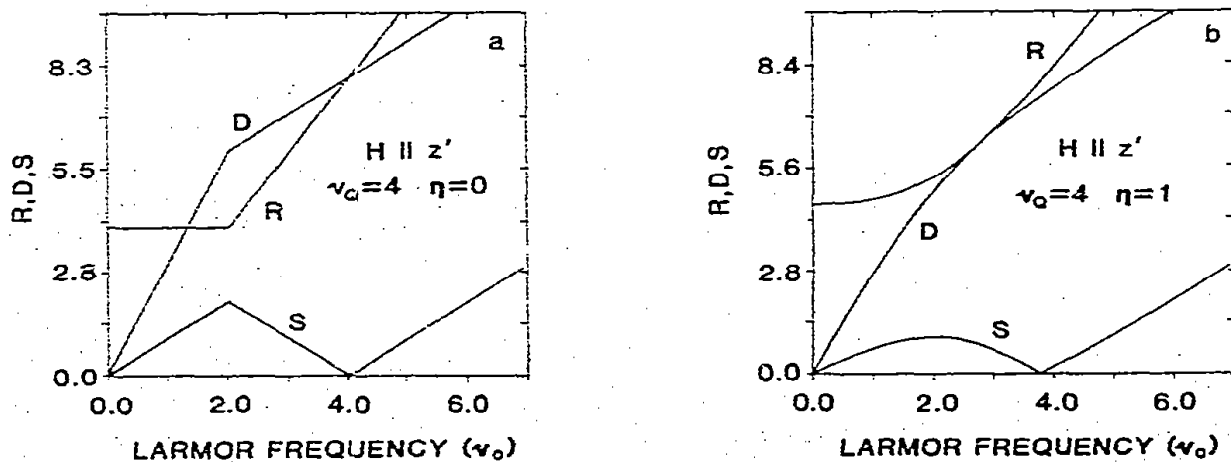


Fig. 1. Elements R, D, and S as a function of ν_0 for the case H parallel to z' with $\nu_Q = 4$. (a) $\eta = 0$ (b) $\eta = 1$.

The energy levels constructed from Eqns. 5 are shown in Fig. 2, with the same set of parameters used in Fig. 1. Referring to Fig. 2a, the levels can obviously be written as piecewise linear functions (refs. 4,5) with three separate regions; $\nu_0 \leq \nu_Q/2$, $\nu_Q/2 \leq \nu_0 \leq \nu_Q$, and $\nu_0 \geq \nu_Q$. With the notation of Eqns. 5, the ranking of levels is always automatically maintained $E_4 \geq E_3 \geq E_2 \geq E_1$. Thus, the energy levels may touch, but never cross.

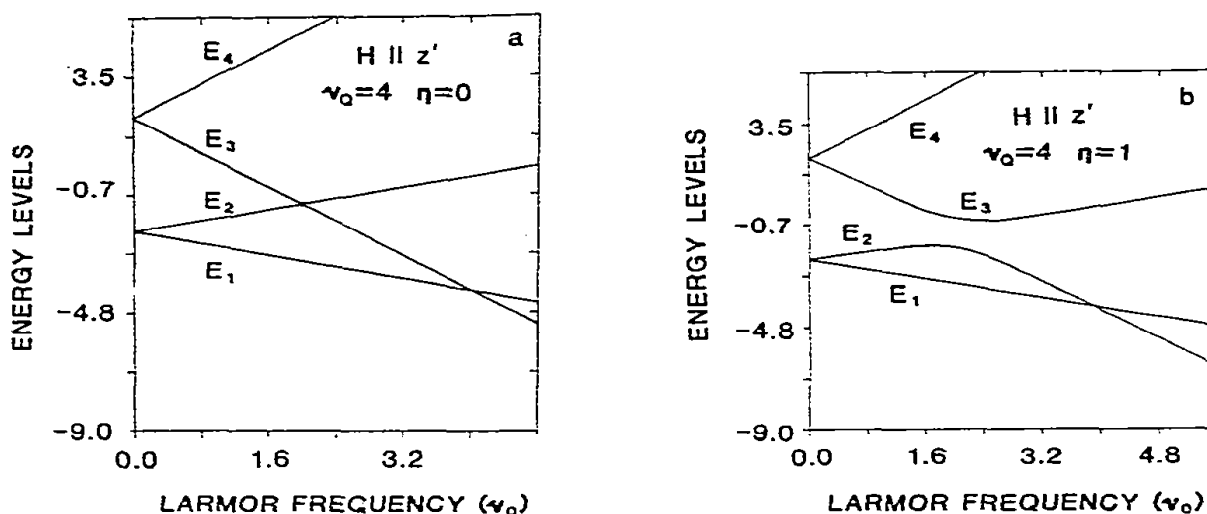


Fig. 2. Energy levels as a function of ν_0 for the case H parallel to z' with $\nu_Q = 4$. (a) $\eta = 0$ (b) $\eta = 1$.

The four Zeeman-quadrupole transitions, $\nu_4 = E_4 - E_1$, $\nu_3 = E_3 - E_1$, $\nu_2 = E_4 - E_2$, and $\nu_1 = E_3 - E_2$, are graphed for the same parameters in Fig. 3. The remaining transitions, the high field satellites, given by $\nu_6 = E_4 - E_3 = D$ and $\nu_5 = E_2 - E_1 = S$ are shown directly in Fig. 1.

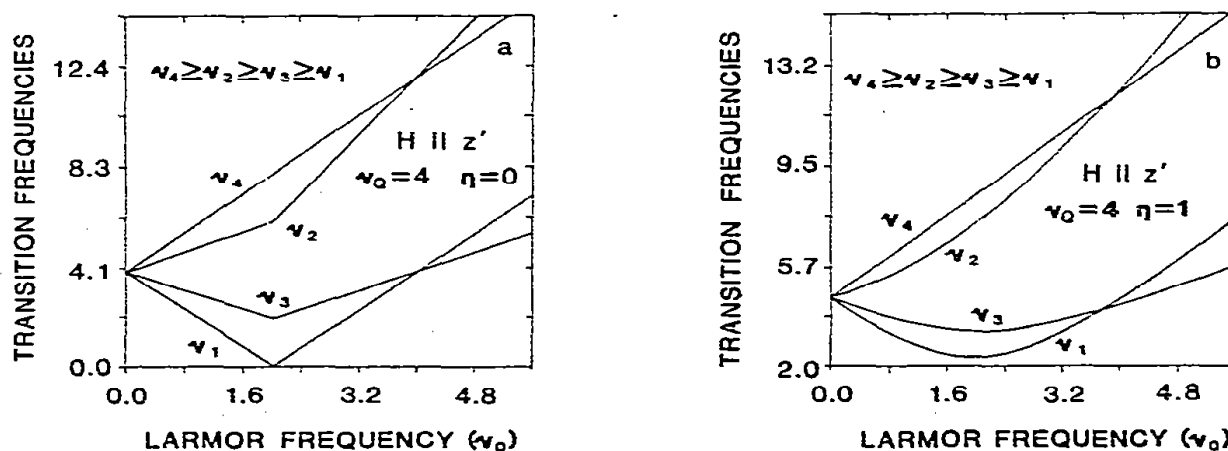


Fig. 3. Transition frequencies as a function of ν_0 for H parallel to z' with $\nu_Q = 4$. See text for notation. (a) $\eta = 0$ (b) $\eta = 1$.

SINGLE CRYSTAL ROTATION PATTERNS

Recently, experimental patterns of frequencies obtained by rotating a single crystal about an axis perpendicular to the field have been fit to theoretical patterns to extract values of the quadrupole parameters and efg directions (refs. 10, 11). Either perturbation theory or numerically calculated frequencies have been used. With the field chosen in the x-direction, the exact solutions are in a form highly suitable for the analysis of rotation patterns evolving from rotation of a crystal about an axis (z) perpendicular to the field. With this geometry, rotation of the crystal changes a single Euler angle ϕ with the other two, θ and ψ , remaining constant.

Theoretical rotation patterns of the energy levels and transition frequencies are shown in Fig. 4, for $\nu_Q = \nu_0 = 10$, $\eta = 1/2$, with the field in the y'z' - plane of the crystal. The exact solutions should prove useful in fitting routines where perturbation theory is not sufficiently accurate.

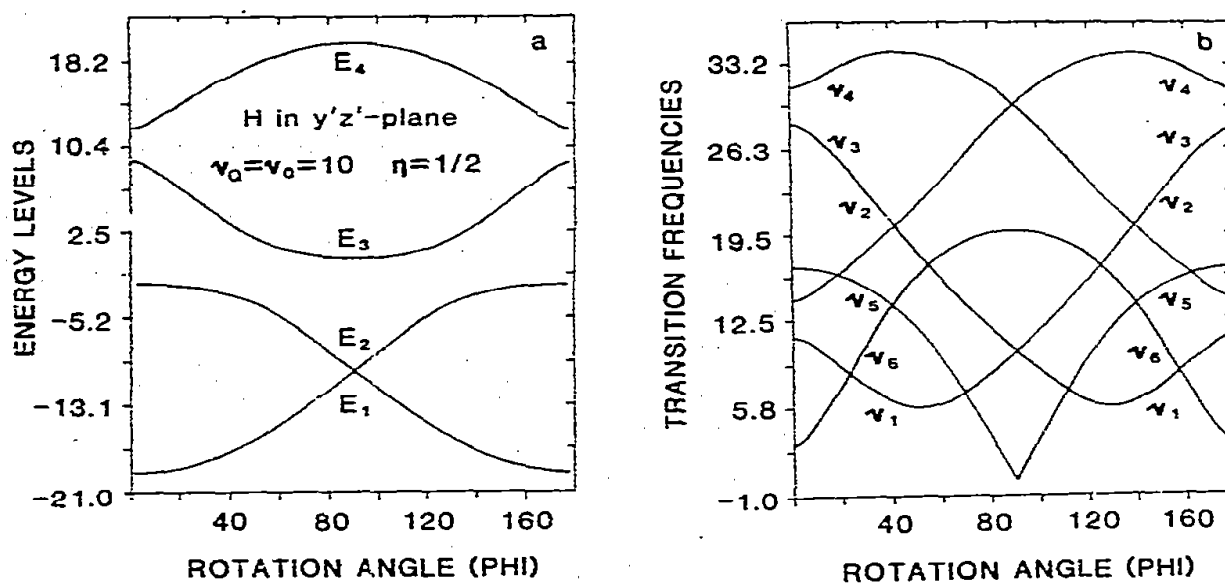
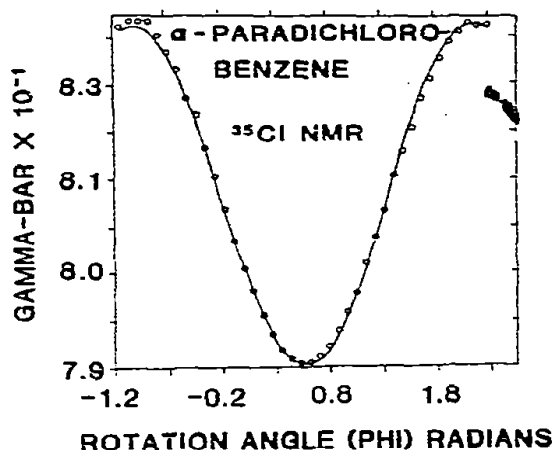


Fig. 4. Rotation patterns with H in the y'z' - plane of the efg system, (a) energy levels (b) transition frequencies.

We have reanalyzed room temperature single crystal rotation pattern data for the transition ν_5 between the two lower levels ($\pm 1/2$) in α -paradichlorobenzene. In the previous analysis (ref. 12), the transition frequency was calculated by diagonalization of the Hamiltonian matrix and compared to data in a three parameter fit (2 Euler angles and η), taking into account chemical shift effects. In the reanalysis, in which chemical shift effects have been ignored, the exact equation for ν_5 was compared to data in a five parameter fit (ν_Q , η , and the three Euler angles locating the efg axes relative to the sample tube). The fit is shown in Fig. 5.

Fig. 5. Rotation pattern of transition ν_5 in α - paradichlorobenzene. Solid line is theory, cross marks are data.



The fit gave $\eta = 0.0675$ compared to the previously obtained value of 0.0712 ± 0.005 , considered more accurate since chemical shift effects were taken into account. Reasonable agreement was obtained for the Euler angles; $\theta = -2.58^\circ$ compared to 0.8° , and $\phi + \psi = -32.3^\circ$ compared to 32.7° . Since θ is so small the angles ϕ and ψ are virtually indistinguishable, being rotations almost about the same axis, z . Ignoring chemical shift effects the sign of $\phi + \psi$ cannot be determined from a single rotation pattern.

QUADRUPOLE PARAMETERS FROM THREE ROTATIONS

The quadrupole parameters, ν_Q and η , and the three Euler angles specifying the efg axes relative to the lab axes can, in principle, be determined from measurement of the four Zeeman-quadrupole transitions at an initial arbitrary orientation followed by rotation of a single crystal by 45° and 90° about an axis perpendicular to H .

The coefficients Y and Z (eqns. 3, 4) can be written in terms of R , D , and S , which, in turn, can be written as functions of the four transition frequencies (three independent) using eqn. (5). For example, at the initial orientation ϕ_0 , from eqn. (3),

$$Y_0 = A \cos 2\phi_0 + B \sin 2\phi_0 + C, \quad (9)$$

where, A , B , and C are functions of ν_0 , ν_Q , η , θ , ψ and ϕ_0 . Using Y_1 and Y_2 for orientations of $\phi_0 + 45^\circ$ and $\phi_0 + 90^\circ$:

$$Y_1 = -A \sin 2\phi_0 + B \cos 2\phi_0 + C \quad (10)$$

$$Y_2 = -A \cos 2\phi_0 - B \sin 2\phi_0 + C. \quad (11)$$

Similar equations arise for the function Z . Thus, six equations, of which four are independent, are obtained. When combined with the known pure quadrupole frequency there are enough equations to solve for ν_Q , η , $\cos^2\theta$, $\cos 2\psi$, and $\cos 2\phi_0$. The Euler angles are only determined within the usual multiplicities.

This method is based on use of the intermediate equations arising in the exact solution. We know it will not be satisfactory for $\nu_0 \ll \nu_Q$ due to disappearance of information into round-off error, when frequencies are raised to the fourth power (eqn. 4). The method should be satisfactory for quick, but not highly accurate, measurements if ν_0 is a sizeable fraction of ν_Q .

Relationships similar to eqns. (9-11) arise if perturbation theory is used instead of exact theory. The parameters and angles enter into the coefficients A, B, and C in exactly the same form, and the quantities X, Y, and Z are functions of the transitions frequencies, but in simpler form since the frequencies are symmetrically disposed about the pure quadrupole frequency at low fields. It may be possible to devise a 3-rotation method which will be satisfactory to quickly measure the parameters and angles at low fields. We would not expect the results be nearly as precise as those obtained through fitting many data points to theory as in refs. (10) and (11).

If measurements are performed at high fields, magnetic shift effects should be incorporated into the theory since they may swamp effects from a small asymmetry parameter. Exact solution of the secular equation including shift effects is straight forward provided the efg and shift tensors are coincident. We intend to discuss this case in a future paper, in which the rotation method will be described in more detail using both exact and perturbation theory.

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