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## Variable-frequency electron paramagnetic resonance

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The principal sources of errors in the determination of parameters of the spin hamiltonian by conventional electron paramagnetic resonance (E.P.R.) experiments are identified. It is possible to circumvent these errors by performing an E.P.R. experiment in zero magnetic field, scanning the frequency. The benefits of zero-field (electron paramagnetic) resonance (Z.F.R.) and of combining E.P.R. and Z.F.R. techniques in a variable-frequency, variable-field experiment are listed and discussed. Such an approach offers a challenge to theorists to calculate the higher-order parameters which can now be obtained with high accuracy. Experimental advantages are also discussed.

### 1. Introduction

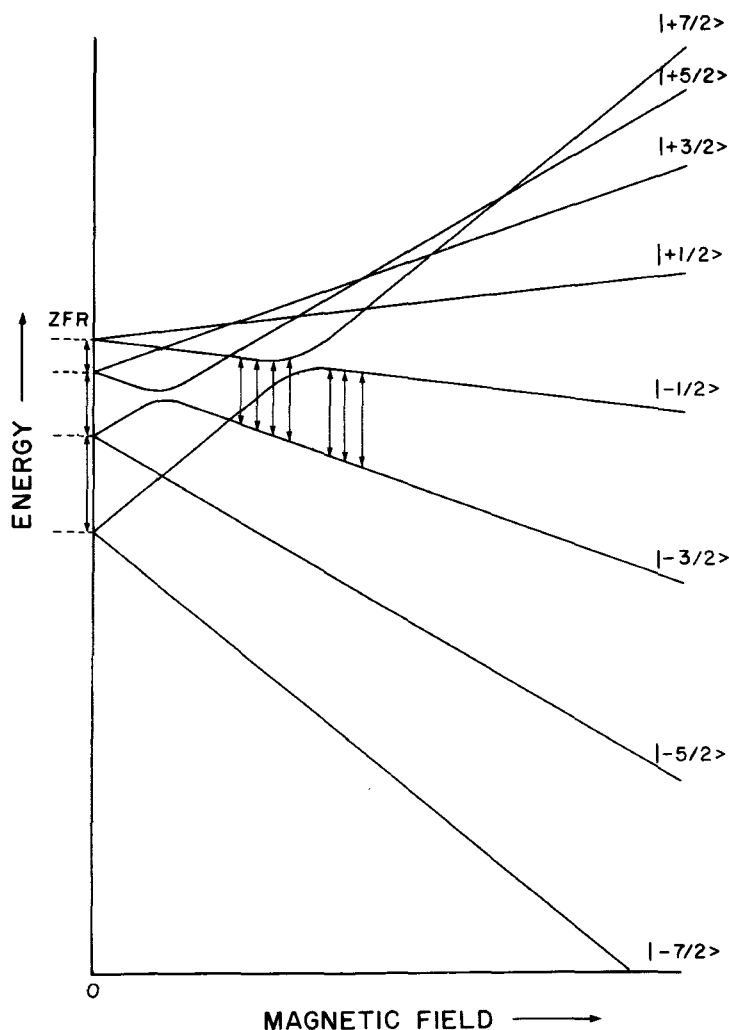
The interaction content of an electron paramagnetic resonance (E.P.R.) experiment resides in the hamiltonian or, in the form in which it is usually recast in terms of spin operators, in the spin hamiltonian. More specifically, it resides in parameters of these operators. Depending on site symmetry and on the various angular momenta and concomitant magnetic moments present, this hamiltonian generally contains many terms. Except in the simplest of molecular systems there may be several tensor interactions, each comprising independent components. With the exception of rarely detectable higher-order Zeeman terms, only the first-order Zeeman interaction depends on the laboratory-generated field,  $\mathbf{B}$ , in which all but a fraction of a per cent of E.P.R. experiments are performed. This latter interaction is parametrized by the  $\mathbf{g}$  tensor ( $\mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$ ),  $\mathbf{S}$  being the electron spin angular momentum. All the rest correspond to solely internal interactions amongst electrons and between electrons and nuclei, and a dispersed eigenvalue spectrum exists *in the absence of an external magnetic field*. That part of the spin hamiltonian may be written

$$H_S = \sum_{0 < k < 2S} \sum_{-k < q < k} B_k^q O_k^q + \sum_j \mathbf{I}_j \cdot \mathbf{A}_j \cdot \mathbf{S} \quad (1)$$

where the two terms selected correspond to (electronic) fine structure and (nuclear) hyperfine structure.  $\mathbf{I}_j$  is the spin angular momentum of nucleus  $j$  and  $\mathbf{A}$  is a tensor describing the electron spin-nuclear spin interaction.  $O_k^q$  is the  $q$ th component, polynomial function of electron spin operators of order  $k$ ;  $B_k^q$  is the corresponding parameter. As an example,

$$O_2^0 = 3S_z^2 - S(S+1) \quad (2)$$

The corresponding parameter  $B_2^0$  contains both the electron spin-electron spin dipolar interaction (for  $S \geq 1$ ) as well as the effect of electron spin-orbit interactions in non-cubic environments. (The present state of non-standardization of axes and notation in E.P.R. leaves much to be desired. Rather than raise that issue here we will use whatever parameter notation the original literature cited. This will cause no confusion since only



Zeeman diagram for an  $S=7/2$  ion in tetragonal symmetry, magnetic field parallel to the fourfold axis. Dominant transitions determined by variable frequency E.P.R. are shown on the diagram; strong zero-field resonances to the left.

one-for-one local comparisons are used. Some recent articles address these standardization problems (Rudowicz 1985 a, b, Rudowicz and Bramley 1985). The fact that a magnetic field is almost always used when the real interest may not lie in the Zeeman effect is a consequence of the early difficulties of varying the frequency of the microwave radiation and of allowing it to interact with the sample in frequency regions from UHF into the far infrared. In particular, in X band (around 10 GHz or  $0.3 \text{ cm}^{-1}$ ) it was the difficulty of both scanning the frequency and having frequency-independent microwave components that led to the traditional fixed-frequency, variable magnetic field spectrometers. These rely on the Zeeman effect to bring the various pairs of states into resonance with the radiation frequency. The first VHF experiments (Zavoiskii 1945) (around 130 MHz) were performed in fixed field by scanning the frequency. The very

first short-wave radio-frequency (12 MHz) experiments (Al'tshuler *et al.* 1944, Zavoiskii 1944) were performed in the reverse manner.

While none can deny the enormous detail that E.P.R. has probed in the traditional way, this has had some far reaching and little appreciated limitations which it is timely to remove now that appropriate microwave hardware is more readily available. The limitations of ordinary E.P.R. experiments are principally that only the low-order terms in the hamiltonian are easily obtained with reasonable accuracy; there is the inevitable trade-off between the precision of the results and the care and time taken with the experiment. These are the  $g$  tensor, the nuclear hyperfine interaction tensor  $\mathbf{A}$ , and the dominant ( $k = 2$ ) fine-structure terms. Even here, small anisotropies in  $\mathbf{A}$  may not be reliably determined. Except in the most precise work, all higher terms  $B_k^q$  for  $k = 4$  and 6 are rarely known with adequate precision. There are two main reasons for this. The first is now relatively trivial and relates to the early lack of adequate computational facilities and the necessary short cuts in the analysis of spectra by perturbation methods. Since, unlike in X-ray work, the primary data is rarely reported in E.P.R., all these are lost and experiments will often have to be repeated to get accurate anisotropies in the lower-order terms. The second reason is that field measurement *at the sample position* is not usually a sufficiently accurate procedure, and the orientation of that field with respect to the crystal or molecular axes is also not usually set with sufficient accuracy. Errors from this second source, when carried over into the analysis, end up as systematic errors in the many finer effects summarized in the spin hamiltonian and provide the essence of the limitation suffered by E.P.R. as normally performed.

Dispensing with the external field and recording the spectrum by scanning the frequency, removes these latter errors absolutely. It is assumed of course that significant residual fields in the laboratory are also removed. The result of doing this is much enhanced accuracy for all terms but those of the Zeeman effect. Nuclear hyperfine anisotropies now mean something and higher-order terms can be obtained much more accurately. Further advantages are that, for amorphous materials, all resonances occur at the same frequency for each transition. Without the external magnetic field there is no competition for the quantization of the magnetic moment. In E.P.R. a spread of magnetic fields is obtained and very often only the singularities, corresponding to the turning points in a single-crystal spectrum versus angle of rotation diagram, are observed. These advantages are particularly relevant for biological materials, mineralogical specimens, polymers, samples adsorbed on surfaces etc. A related advantage is that magnetic inequivalence is removed and the multiplicity of resonances from otherwise identical sites coalesce at the one frequency. Because many of the frequencies of interest are lower than those in X band, dielectric loss is less of a problem and excellent resonator filling factors can be obtained with dielectrically lossy solutions. The nuclear quadrupole interaction is a first-order effect at zero field, not second order as in high fields. It is a larger effect and obtainable with much greater precision that is normally done via the intensities of otherwise forbidden transitions observed in high fields. Hosts that are non-magnetic at zero field (e.g. triplets,  $\text{Ni}^{2+}$  etc.) give sharp spectra for guest species. Analysis is simpler for several reasons. The first is that frequency measurement is easy and frequency is directly proportional to energy. Only one solution of the secular determinant is needed (at zero field), not one for every field at which a resonance occurs. Non-magnetic levels give rise to a line-narrowing advantage over E.P.R. of one or two orders of magnitude. Finer effects are thus revealed, effects that would be missed in an E.P.R. experiment. In the analysis of spectra for low-

symmetry cases (Roitsin 1981), it cannot be assumed that the principal axes of the  $\mathbf{g}$  tensor coincide with those of the hyperfine, quadrupole or higher-order fine-structure terms. Removing the field at least eliminates the usual parallelism assumption about the  $\mathbf{g}$ -tensor alignment. Some of these advantages will now be illustrated, principally from some recent findings. (See Bramley and Strach (1983) for a recent review.)

## 2. Examples

### 2.1. Fine-structure terms

On the question of the relative precision and certainty of spin hamiltonian parameters determined at zero magnetic field, recent work on  $\text{Mn}^{2+}$  substituted into the  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  lattice provides a good example (Bramley and Strach 1981). Earlier E.P.R. work (Hayashi and Ono 1953, Janakiraman and Upreti 1971) had put the parameter  $D = 3B_2^0$  at 1200 and  $1154 \pm 14$  MHz with  $E = B_2^2 \approx 0$  and  $266 \pm 28$  MHz respectively. The zero-field spectrum predicted from either parameter set produced no obvious resemblance to the observed spectrum. Nuclear hyperfine is relevant with  $^{55}\text{Mn}$ , but that is not at issue here except to comment that the zero-field errors are one-tenth of the high-field errors for the components of  $\mathbf{A}$ . The zero-field spectrum is instead fitted with the fine-structure parameters  $D = 1181 \pm 2$ ,  $E = 183 \pm 2$  and the fourth-order term  $a = 12 \pm 3$  MHz, and a one-to-one correspondence between all the major features of the zero-field spectrum and the calculated spectrum is observed. The parameter  $a$  had not previously been determined from E.P.R. It is equivalent to  $24 B_4^4$  in this case.

### 2.2. Nuclear hyperfine structure

As an example of improved accuracy in anisotropy of a low-order term, consider the nuclear hyperfine term. A series of E.P.R. studies on the vanadyl ion in various salts had found values of  $|A_x - A_y|$  ranging from 3 to 41 MHz (Kasthuriangan and Soundararajin 1975, Kohin 1979). Zero-field studies (Strach and Bramley 1984), however, showed that this rhombic hyperfine anisotropy was relatively constant and ranged from 3.6 to 6.6 MHz only, with a standard deviation of 0.4 MHz.

A further feature of zero-field spectra is that the nuclear hyperfine splittings are often greater (e.g. by a factor of two or more) than in high-field spectra, imparting greater accuracy automatically to these parameters. Examples are to be found in work by Bramley and Strach (1981) on  $\text{Mn}^{2+} : \text{NH}_4\text{Cl}$ , and as calculated by them for  $\text{Cr}^{3+} : \text{Al}_2\text{O}_3$  (Bramley and Strach 1984), and also by Bernstein and Dobbs (1975) for  $\text{Gd}^{3+} : \text{LaEtSO}_4 \cdot \text{H}_2\text{O}$ .

### 2.3. Magnetic inequivalence

Magnetic inequivalence arises when the external magnetic field of a normal E.P.R. experiment lies at a different angle with respect to species which are otherwise crystallographically equivalent. Except with the magnetic field along symmetry axes of the crystal, a multiplicity of transitions appears which complicates analysis or makes it impractical to solve in many cases. An early example is in work by Symmons and Bogle (1962) on  $\text{Fe}^{3+}$  doped into  $\text{Al}(\text{acac})_3$ . The Z.F.R. showed clearly that there were three species, not related by symmetry, and that much of the spectral multiplicity that had frustrated E.P.R. analyses came from magnetic inequivalence.

#### 2.4. Line narrowing

Z.F.R. line-widths can in some cases be one to two orders of magnitude narrower than corresponding lines in the E.P.R. spectra. This has obvious sensitivity advantages for these situations. The effect arises wherever energy levels are second order in the magnetic field (from neighbouring magnetic ions and nuclei). And this is the case for levels which are non-degenerate in zero field. The effect occurs for some transitions of  $\text{VO}^{2+}$  in  $(\text{NH}_4)_2\text{SO}_4$ . The factor-of-ten narrowing in this case allowed resolution of three physically distinct sites whereas only one had been obvious from the E.P.R. spectrum (Bramley and Strach 1985). Similar effects are evident in the Z.F.R. spectra of  $-\text{CH}-$  radicals in organic molecules and the effect here is generally applicable and valuable for radicals containing no more than say four interacting nuclei. Beyond four, the advantage is swamped by the multiplicity of transitions (Cole *et al.*, 1963).

#### 2.5. Higher-order terms

Koster and Statz (1959) made the point that 'as accurate and more extensive experimental data become available, it will probably become necessary to use the present approach to describe adequately the experimental findings'. Their approach based on symmetry was a more general alternative to the 'microscopic' spin hamiltonian method originally due to Abragam and Pryce (for reviews, see e.g. Rudowicz 1978, 1981). The disadvantage of the former approach was the larger number of parameters that needed to be fitted. And as experimental data then were generally limited to a small part of the Zeeman diagram, dictated by one or at most two spectrometer frequencies, little challenge to the conventional spin hamiltonian could be mounted. Chamberlain and Syms (1964) took up this point in their Z.F.R. study of  $\text{Fe}^{3+}$  in  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ . By comparing the observed zero-field frequencies with those predicted from a careful E.P.R. study, they were able to get good agreement and to put an upper limit on the higher order Zeeman terms (other than the usual one) which are also linear in the magnetic field (the  $\text{BS}^3$  type).

However, while the conventional spin hamiltonian approach remains so successful and largely unchallenged, there are generally many higher-order terms in the non-Zeeman part of the hamiltonian. And these are frequently small enough to be reliable in only a few E.P.R. studies. It is regrettable that in many studies (often undertaken to get the larger lower-order terms) these higher-order terms ( $k=4,6$  in equation (1)) are little more than fitting parameters. Now that Z.F.R. can facilitate acquisition of spin hamiltonian parameters without convoluted field measurement and crystal orientation errors, the conjunction of Z.F.R. with E.P.R. experiments will allow both Zeeman and non-Zeeman parameters to be determined routinely with high accuracy. Non-linear Zeeman terms may also be revealed by parallel zero- and high-field studies.

#### 2.6. Nuclear quadrupole effects

In an E.P.R. spectrum, these are fine effects indeed, coming from small shifts of lines in the spectrum which are second order in the quadrupole interaction. An alternative route is from the effect this interaction has on the intensities of otherwise forbidden transitions. Both routes lead to estimates of the quadrupole coupling constant which are inaccurate. On the other hand, at zero field, the effect occurs in first order with much more accurately measurable shifts in line positions. Some recent work on  $\text{VO}^{2+}$  found a value for the quadrupole coupling constant that rivalled in accuracy results from atomic beam measurements (Strach and Bramley 1984).

### 3. Swept-frequency, swept-field E.P.R.

Some of the preceding discussion might suggest that unless the Zeeman effect is of interest, magnets and conventional E.P.R. can be discarded. This is not the case for a number of reasons. The case of  $\text{Cr}^{3+}$  ( $d^3$ ,  $S = \frac{3}{2}$ ) illustrates one reason. In symmetries lower than axial, the two-fine structure terms  $B_2^0$  and  $B_2^2$  give but one zero-field splitting which occurs at a transition energy of  $6\{3(B_2^0)^2 + (B_2^2)^2\}^{1/2}$ . Zeeman E.P.R. experiments are required to separate  $B_2^0$  and  $B_2^2$ . A similar situation occurs for  $\text{Fe}^{3+}$ , ( $d^5$ ,  $S = \frac{5}{2}$ ) where, ignoring nuclear spin again, only two main transitions occur whereas several parameters may appear in the fine-structure part of the spin hamiltonian for a low-symmetry situation. Generally speaking, E.P.R. and Z.F.R. studies have valuable complementarity. It is possible to combine them in a swept-frequency, swept-field E.P.R. experiment. This is illustrated in the figure for the case of an  $S = \frac{7}{2}$  ion in tetragonal symmetry. The non-crossing regions (Newman and Urban 1975) are the consequences of specific terms in the hamiltonian. Normal E.P.R. experiments cannot explore these regions unless the spectrometer frequency is fortuitously close. At these regions, the terms have their largest effect and very precise values for them can be obtained by varying spectrometer frequency and exploring the gap as a function of both field and frequency. We can conveniently distinguish this from E.P.R. and Z.F.R. as variable frequency E.P.R. (V.F.E.P.R.).

### 4. Prognosis

For the first time, the ready accessibility of microwave components spanning wide frequency bands will permit Z.F.R. and V.F.E.P.R. studies to reveal very accurate spin hamiltonian parameters, more accurately by more than an order of magnitude when compared with conventional E.P.R. All the higher-order terms can now be used intelligently via superposition theory (Newman and Urban 1975) for example, or other models, to get structural information and information on electronic interactions. It is hoped that this will stimulate a revival of interest in spin hamiltonian theory generally, of alternative approaches, and in the theory of the many higher-order terms which are now accessible.

### 5. Acknowledgments

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