Predicting and Interpreting

Electron Paramagnetic Resonance Spectra.

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1. Introduction into Computer Simulation of Continuous Wave (CW) EPR Spectra

Multifrequency electron paramagnetic resonance (EPR) spectroscopy [1-7] is a powerful tool for characterising paramagnetic molecules or centres within molecules that contain one or more unpaired electrons. Computer simulation of the experimental randomly orientated or single crystal EPR spectra from isolated or coupled paramagnetic centres is often the only means available for accurately extracting the spin Hamiltonian parameters required for the determination of structural information [1,2,9-21].

2. Theory and Brief overview of XSophe

2.1 Theory used in Calculating a Simulated EPR Spectrum

EPR spectra are often complex and are interpreted with the aid of a spin Hamiltonian. For an isolated paramagnetic centre (A) a general spin Hamiltonian is [1,2,8]:

\[ \mathcal{H}_A = S \cdot D \cdot S + \beta B \cdot g \cdot S + S \cdot A \cdot I + I \cdot Q \cdot I - \gamma I \cdot (1 - \sigma) \cdot B \]  

(1)

where \( S \) and \( I \) are the electron and nuclear spin operators respectively, \( D \) the zero field splitting tensor, \( g \) and \( A \) are the electron Zeeman and hyperfine coupling matrices respectively, \( Q \) the quadrupole tensor, \( \gamma \) the nuclear gyromagnetic ratio, \( \sigma \) the chemical shift tensor, \( \beta \) the Bohr magneton and \( B \) the applied magnetic field. Additional hyperfine, quadrupole and nuclear Zeeman interactions will be required when superhyperfine splitting is resolved in the experimental EPR spectrum. When two or more paramagnetic centres \((A_i, i = 1, ..., N)\) interact, the EPR spectrum is described by a total spin Hamiltonian \((\mathcal{H}_{\text{Total}})\) which is the sum of the individual spin Hamiltonians \((\mathcal{H}_{A_i}, \text{Eq. [1]})\) for the isolated centres \((A_i)\) and the interaction Hamiltonian \((\mathcal{H}_{A_{ij}})\) which accounts for the isotropic exchange, antisymmetric exchange and the anisotropic spin-spin (dipole-dipole coupling) interactions between a pair of paramagnetic centres [1,9,10].

\[ \mathcal{H}_{\text{Total}} = \sum_{i=1}^{N} \mathcal{H}_{A_i} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \mathcal{H}_{A_{ij}} \]

\[ \mathcal{H}_{A_{ij}} = J_{A_{ij}} S_{A_i} \cdot S_{A_j} + d_{A_{ij}} S_{A_i} \times S_{A_j} + S_{A_i} \cdot D_{A_{ij}} \cdot S_{A_j} \]  

(2)

Computer simulation of randomly orientated EPR spectra is performed in frequency space through the following integration [1,22]

\[ S(B, \nu_c) = \sum_{i=0}^{M} \sum_{j=0}^{M} C \int_{\theta=0}^{\pi} \int_{\phi=0}^{\pi} |\mu_{ij}|^2 f[\nu_c - \nu_0(B), \sigma_\nu] d\cos \theta d\phi \]  

(3)

where \( S(B, \nu_c) \) denotes the spectral intensity, \( |\mu_{ij}|^2 \) is the transition probability, \( \nu_c \) the microwave frequency, \( \nu_0(B) \) the resonant frequency, \( \sigma_\nu \) the spectral line width, \( f[\nu_c - \nu_0(B), \sigma_\nu] \) a spectral lineshape function which normally takes the form of either Gaussian or Lorentzian, and \( C \) a constant which incorporates various experimental parameters. The summation is performed over all the transitions \((i, j)\) contributing to the spectrum and the integrations, approximated by summations, are performed over half of the unit sphere (for ions possessing triclinic symmetry), a consequence of time reversal symmetry [1,8]. For paramagnetic centres exhibiting orthorhombic or monoclinic symmetry, the integrations in Eq. [3] need only be performed over one or two octants respectively. Whilst centres exhibiting axial symmetry require integration only over \( \Theta \), those possessing cubic symmetry require only a single orientation.
2.2 Field versus Frequency Swept EPR

In practice the EPR experiment is a field swept experiment in which the microwave frequency ($\nu_c$) is kept constant and the magnetic field varied. Computer simulations performed in field space assume a symmetric lineshape function $f$ in Eq. [1] ($f(B-B_{\text{res}})$, $\sigma_B$) which must be multiplied by $d\nu/dB$ and a constant transition probability across a given resonance.[1,22] In fact Pilbrow has described the limitations of this approach in relation to asymmetric lineshapes observed in high spin Cr(III) spectra and the presence of a distribution of g-values (or g-strain broadening). The following approach has been employed by Pilbrow et al. in implementing Eq. [1] (frequency swept) into computer simulation programmes based perturbation theory [1,9]. Firstly, at a given orientation of $(\theta, \phi)$, the resonant field positions ($B_{\text{res}}$) are calculated with perturbation theory and then transformed into frequency space ($\nu(B)$). Secondly, the lineshape ($f(\nu_c - \nu(B)$, $\sigma_\nu$) and transition probability are calculated in frequency space across a give resonance and the intensity at each frequency stored. Finally, the frequency swept spectrum is transformed back into field space. Performing computer simulations in frequency space produces asymmetric lineshapes (without having to artificially use an asymmetric lineshape function) and secondly, in the presence of large distribution of g-values will correctly reproduce the downfield shifts of resonant field positions.[9]

Unfortunately, the above approach cannot be used in conjunction with matrix diagonalization as an increased number of matrix diagonalizations would be required to calculate $f$ and the transition probability across a particular resonance. However, Homotopy [46] which is in general three to five times faster than matrix diagonalization allows the simulations to be performed in frequency space.

2.3 Numerical Integration - Choice of Angular Grid

In numerical terms, computer simulation of randomly oriented EPR spectra involves the calculation of the resonant field positions and transition probabilities at all vertex points of a given partition for all contributing transitions. The simplest and most popular partition scheme is that of using the geophysical locations on the surface of the Earth for the presentation of world maps. However, the solid angle subtended by the grid points is uneven and alternative schemes have been invented and used in the simulation of magnetic resonance spectra. For example, in order to reduce computational times involved in numerical integration over the surface of the unit sphere, the igloo [19], triangular [24] and spiral [25] methods have been invented for numerical investigations of spatial anisotropy. In 1995, we described a new partition scheme, the SOPHE partition scheme [16] in which any portion of the unit sphere ($\theta \in [0, \pi/2]$, $\phi \in [\phi_1, \phi_2]$) or $\theta \in [\pi/2, \pi]$, $\phi \in [\phi_1, \phi_2]$) can be partitioned into triangular convexes. For a single octant ($\theta \in [0, \pi/2]$, $\phi \in [0, \pi/2]$) the triangular convexes can be defined by three sets of curves

$$\theta = \frac{\pi}{2} \cdot \frac{i}{N}$$

$$\theta \phi = \frac{\pi}{2} \cdot \frac{i-1}{N} (\phi_2 - \phi_1)$$

$$\theta \phi = \theta (\phi_2 - \phi_1) - \frac{\pi}{2} \cdot \frac{i-1}{N} (\phi_2 - \phi_1), (t = 1, 2, ..., N)$$

where $N$ is defined as the partition number and gives rise to $N+1$ values of $\theta$. Similar expressions can be easily obtained for $\theta \in [\pi/2, \pi]$, $\phi \in [\phi_1, \phi_2]$. A three dimensional visualisation of the SOPHE partition scheme is given in Figure 1b.
Figure 1. A schematic representation of the SOPHE partition scheme. (a) Vertex points with a SOPHE partition number $N = 10$; (b) the SOPHE partition grid in which the three sets of curves are described by Eq. [4]. (c) Subpartitioning into smaller triangles can be performed by using either Eq. [4] or alternatively the points along the edge of the triangle are interpolated by the cubic spline interpolation method [24] and each point inside the triangle is linearly interpolated three times and an average is taken.

As can be seen this method partitions the surface of the unit sphere into triangular convexes which resemble the roof of the famous Sydney Opera House. In SOPHE there are $N$ curves in each set with the number of grid points varying from 2 to $N+1$ in steps of 1. In order to produce simulated spectra of high quality, the unit sphere is often required to be finely partitioned, in other words, a large number of vertex points are required. Each triangle in Figure 1b can be easily subpartitioned into smaller triangles, referred to as tiny triangles. In Figure 1c, a selected triangle is further partitioned into 81 tiny triangles with a subpartition number $M=10$. The grid formed in such a subpartition can still be described by Eq. [4]. In this particular case, $\theta$ is stepped in a smaller step of $\pi/(2(N-1)(M-1))$ from $\theta = 45^\circ$ to $\theta = 54^\circ$, the two corresponding curves which bound the triangle (Figure 1c). A similar process is applied to curves in sets 2 and 3. Solid angles for these tiny triangles can be calculated from Eq. [5]. Alternatively, various interpolation schemes may be used for simulating randomly oriented EPR spectra [20,24-26]. Recently, we developed a highly efficient interpolation scheme, the SOPHE interpolation scheme [16].

The SOPHE interpolation scheme is divided into two levels of interpolation, a global interpolation using cubic spline [27] and a local interpolation using simple linear interpolation. Given the function values which may represent the resonant field position or the transition probability at the vertex points (Figure 1a), we use the cubic spline interpolation method to interpolate the function values at all other points on the curves described by Eq. [4] (Figure 1b). This is actually carried out in three different sets. In each set, there are $N$ interpolations with the number of knots (vertex points) varying from 2 to $N+1$. Although in two of the three sets (Eqs. 4b and 4c) both variables $\theta$ and $\phi$ are involved, variable $\phi$ can be treated as a parameter [16]. First derivative boundary conditions [27] have been employed in our program which has been proved to produce high-quality interpolated data [16].
After the global interpolation, the integration over the unit sphere can be viewed as integrating through individual triangularly shaped convexes. A second level of interpolation is carried out based on the values globally interpolated and this is schematically shown in Figure 1c. The resonant field position and transition probability are calculated at the vertices (tiny triangles) formed by linear interpolation (up to version 1.0.2) of the points on adjacent sides of the triangular convex. This is repeated for the other two pairs of sides of the triangular convex and the results averaged. Linear interpolation is based on a subpartition scheme and each triangular convex can be subpartitioned differently[16]. Intuitively speaking, the global cubic spline interpolation can be viewed as building up a “skeleton” based on the SOPHE grid and the local linear interpolation can be viewed as a “tile filling process”. In the early versions of XSophe we assume all the tiny triangles in a given triangle subtend the same solid angle. In version 1.0.4 of XSophe we calculate the exact areas and use cubic spline interpolation for the tile filling process.

An example demonstrating the efficiency of the SOPHE partition and interpolation schemes is shown in Figure 2 where we have calculated a randomly orientated spectrum for a high spin rhombically distorted Cr(III) ion for which an appropriate spin Hamiltonian is

\[
\mathcal{H} = g_e \beta B \cdot S + D(S_x^2 - \frac{1}{3}S(S+1)) + E(S_y^2 - S_z^2) + S_A I - g_n \beta B I \tag{5}
\]

The spin Hamiltonian parameters employed were \(g_e = 1.990\), \(D = 0.10\) (cm\(^{-1}\)), \(E/D = 0.25\), \(g_n = 1.50\), \(A_x = 120\), \(A_y = 120\), \(A_z = 240\) (10\(^{-4}\) cm\(^{-1}\)). A narrow line width was chosen (30 MHz) in order to demonstrate the high efficiency of these schemes. The unit sphere has to be partitioned very finely in order to produce simulated spectra with high signal to noise ratios when there is large anisotropy and the spectral linewidths are narrow. The simulated spectra without and with the SOPHE interpolation scheme with a partition number \(N=18\) are shown in Figures 2a and 2b respectively.

**Figure 2.** Computer simulations of the powder EPR spectrum from a fictitious spin system (\(S=3/2\); \(I=3/2\)) which demonstrates the efficiency of the SOPHE interpolation scheme. (a) Without the SOPHE interpolation scheme, \(N=18\), (b) With the SOPHE interpolation scheme, \(N=18\) and (c) Without the SOPHE interpolation scheme, \(N=400\). The computational times were obtained on a SGI O2 R5K (180 MHz). v=34 GHz; field axis resolution: 4096 points; an isotropic Gaussian lineshape with a half width at half maximum of 30 MHz was used in the simulation.
Without the SOPHE interpolation scheme, the spectral information is completely lost in the sea of computing noise (computational time was 29.36 sec.) whereas with the SOPHE interpolation scheme, a virtually noise-free spectrum was produced in 63.11 sec. In order to appreciate this better, a simulation without interpolation with a much larger partition number ($N=400$) produced a spectrum of lower quality (Figure 2c) and consumed 3 hrs. 47.94 min. of CPU time. To make the comparison in more detail, for Figure 2b an average of 5.6 million data points were generated through the SOPHE interpolation scheme for each of the 12 allowed transitions whereas for Figure 2c there were only 80,200 data points, a mere portion of the interpolated points. Clearly, spectra of comparable quality can be simulated with the SOPHE interpolation scheme at a significantly reduced computational time by approximately two orders of magnitude.

The use of the SOPHE interpolation scheme significantly reduces the time-consuming process of locating the resonance field positions and evaluation of the transition probabilities in the full matrix diagonalization. Having demonstrated the advantages of the SOPHE interpolation scheme, we should also point out its limitations. Firstly, the interpolation scheme will fail when there are multiple resonant field positions present at a given orientation ($\Theta, \phi$) and when looping transitions are present. We have implemented two solutions to solve these problems. The user can use the brute force matrix diagonalization or alternatively homotopy.[46]

2.4 Transition Searching - Field Segmentation

The very nature of EPR spectroscopy as a field-swept technique imposes a computational challenge to computer simulation of randomly oriented spectra. In essence, during an EPR experiment, the spin system under investigation is constantly modified through the Zeeman interactions as the magnetic field is swept. In a general situation where two or more interactions have comparable energies, search for resonance field positions is not a trivial task as the dependence of the energies of the spin states on field strength ($B_0$) can be very complex. The complication involved is best manifested by the presence of multiple transitions between a given pair of energy levels.

A number of search schemes have been used in the full matrix diagonalization approach for locating resonance field positions [14,20,28-30]. Generally, they can be grouped into two categories. In category I, the resonance field position is searched independently for every transition. Among the schemes belonging to this category, the so-called iterative bisection method is the safest but probably the most inefficient method [14]. Other more efficient methods such as the Newton-Raphson method have also been used [14]. In general, these search schemes are time-consuming as a large number of diagonalizations are normally required. The search schemes belonging to category II may be called segmentation methods. In these schemes, the field sweep range is divided equally into $K$ segments and for each segment, the whole energy matrix is diagonalised once for the centre field value of that segment. Thus only $K$ diagonalizations are performed for each orientation. A perturbation theory is then employed for determining the presence of a transition in each segment. This search scheme is still limited to situations where in each segment there is no more than one possible transition. However, if $K$ is not too small, the chance of having two resonances in a single segment is rare. Reijerse et al. [20] use a first-order perturbation approach for exploring transitions in each segment. However, from our experience, first-order perturbation theory cannot be guaranteed to produce resonance field positions with satisfactory precision. In Sophe we have adopted the second-order eigenfield perturbation theory originally developed by Belford et al. [31] in our program which has also been used by other groups[29]. The segment number, $K$, is a user-input parameter. We have found that second-order eigenfield perturbation theory used in conjunction with our segmentation scheme cannot only deal with complicated situations such as multiple transitions but also proved to be efficient and reliable for locating the resonance field positions in field-swept EPR spectra.
A saving factor in the segmentation method lies in the fact that full matrix diagonalization is only performed \( K \) times irrespective of the number of transitions involved. By contrast, in the other schemes, a few diagonalizations are required for each transition and for large spin systems this number can become very large. The precision of the resonance field positions normally depends on the segment number \( K \) as well as on the spin system. How large the segment number should be depends on the nature of the system under study. However, simulations can be performed with different segmentation numbers providing an easy test of precision.

### 2.5 Linewidth Models

A number of linewidth models originally developed for magnetically isolated paramagnetic species have been incorporated into the XSophe computer simulation software suite. For all the linewidth models discussed below the linewidth parameter, \( \sigma \), is given in energy units. In Sophe (field space version), \( \sigma \) is converted to a field-domain linewidth parameter \( \sigma_B \) through \( \sigma_B = |dB/dE_{ij}| \) \[1\,22\]. \( dB/dE_{ij} \) is calculated for each transition by using eigenfield perturbation theory \[31\]. The linewidth models incorporated into Sophe include:

- **Kivelson's linewidth model** [36] for isotropic spectra

  \[
  \sigma = a + b \mathcal{M}_1 + c \mathcal{M}_2 + d \mathcal{M}_3^3
  \]  

  The coefficients \( a, b, c, \) and \( d \) can be related to the solvent viscosity, correlation time, molecular hydrodynamics radius and the anisotropy of the spin system under study \[36\].

- **Angular variation of the g-values** [1].

  \[
  \sigma^2 = (\sigma_x^2 l_x^2 + \sigma_y^2 l_y^2 + \sigma_z^2 l_z^2)/g^2
  \]  

  where \( g^2 = g_x^2 l_x^2 + g_y^2 l_y^2 + g_z^2 l_z^2 \), \( \sigma_i \)'s \((i=x,y,z)\) are the input linewidth parameters and \( l_i \)'s \((i=x,y,z)\) are the direction cosines of the magnetic field with respect to the principal axes of the \( g \) matrix.

- A correlated \( g-A \) strain model which was originally developed by Froncisz and Hyde \[37\] and has been used successfully to account for the linewidth variations encountered in spin \( S=1/2 \) systems particularly in copper and low spin cobalt \( (S=1/2) \) complexes \[1,3,37\]. When expressed in the frequency-domain \[1,22\], the linewidth in this model is based on the formulae

  \[
  \sigma^2 = \left( \sum_{i=x,y,z} \left\{ \frac{\Delta g_i}{g_i} v_i(B) + \Delta A_i M_i^2 \right\} \right) / g^2
  \]  

  where the \( \sigma_{\hat{r}_i} \) \((i=x, y, z)\) are the residual linewidths due to unresolved metal and/or ligand hyperfine splitting, homogeneous linewidth broadening, and other sources, \( \Delta g_i \)'s and \( \Delta A_i \)'s are the widths of the Gaussian distributions of the \( g \) and \( A \) values. The \( g-A \) strain model involves nine parameters for a rhombically distorted metal ion site.

- Wenzel and Kim \[38\] have described a statistical \( D-E \) strain model. In their model, the distributions of \( D \) and \( E \) are assumed to be Gaussian and independent of each other with the resulting full width at maximum slope due to strain alone given by
where $\sigma_D$ and $\sigma_E$ are the half-widths at maximum slope of the distributions of $D$ and $E$ in energy units, respectively, and $\psi_i$ and $\psi_j$ are the wavefunctions associated with transition $i \rightarrow j$. A residual linewidth, $\sigma_R$, is convoluted with the $D-E$ strain effects.

$$\sigma_{DE}^2 = \sigma_D^2 \left\{ <\psi_i|S_z^2|\psi_i> - <\psi_j|S_z^2|\psi_j> \right\}^2 + \sigma_E^2 \left\{ <\psi_i|S_z^2 - S_y^2|\psi_i> - <\psi_j|S_z^2 - S_y^2|\psi_j> \right\}^2 \quad \text{(9)}$$

$$\sigma_i^2 = \sigma_{DE}^2 + \sigma_R^2 \quad \text{(10)}$$

2.6 Parallelisation

With the advent of multiprocessor computers and the new algorithms described above the simulation of EPR spectra from complex spin systems consisting of multiple electron and or nuclear spins becomes feasible with Sophe. Optimisation of the spin Hamiltonian parameters by the computer will also be possible for these spin systems. Parallelisation of the matrix diagonalization method has been performed at the level of the vertices in the Sophe grid. For example, if a computer has 5 processors then the number of Sophe grid points is divided into groups of five and each group is then processed by one of the processors with the resultant spectra being added to an array shared by the five processors. For the hypothetical Cr(III) spin system shown in Figure 2 a three-fold reduction in computational time is observed. Greater reductions are observed for more complex spin systems.

2.7 Optimisation Methods

A unique set of spin Hamiltonian parameters for an experimental EPR spectrum is obtained through minimising the goodness of fit parameter (GF)

$$GF = \left( \sum_{i=1}^{N} \left( Y_{exp} - S(B, \nu_c) \ast \sigma \right)^2 \right)^{1/2} / (N \ast \sigma) \quad \text{(11)}$$

where the experimental spectrum ($Y_{exp}$) has been baseline corrected assuming a linear baseline and the simulated spectrum has been scaled ($\sigma$) to $Y_{exp}$. $N$ is the number of points in common between the experimental and simulated spectra and $\sigma$ is the magnitude of noise in the spectrum. In the past minimising GF has been performed through a process of trial-and-error by visually comparing the simulated and experimental spectra until a close match was found. Recent progress in reducing computational times for computer simulations (Sections 3-7) and the improved speed of workstations allows the use of computer-based optimisation procedures to find the correct set of spin Hamiltonian parameters from a given EPR spectrum.

The most appropriate technique for optimising a set of spin Hamiltonian parameters is nonlinear least squares [40]. This method has the advantage that the differences ($Y_{exp} - S(B, \nu_c)$, Eq. 11) associated with the more extreme positive or negative values are exaggerated, which emphasises genuine peak mis-matching whilst tending to reduce the impact of noise. Unfortunately, evaluation of $S(B, \nu_c)$ can take a long time and as there is no analytic derivative information available, this method is not really an option for general spin systems. Consequently, we have considered three direct methods, the Hooke and Jeeve's [42], Simplex [43] and a Quadratic method based on the Hooke and Jeeves method and two simulated annealing approaches [46]. In addition there are several problems which need to be addressed, including (i) the sensitivity of scaling the various spin Hamiltonian parameters and the method chosen for comparing the experimental simulated spectra [46]. In Xsophe we allow the user to control the sensitivity of parameter adjustment throughout the optimisation procedure and secondly the user can compare the spectra directly or the Fourier transformed spectra. The latter method provides increased resolution through separating the high

\[
\sigma_{DE}^2 = \sigma_D^2 \left\{ <\psi_i|S_z^2|\psi_i> - <\psi_j|S_z^2|\psi_j> \right\}^2 + \sigma_E^2 \left\{ <\psi_i|S_z^2 - S_y^2|\psi_i> - <\psi_j|S_z^2 - S_y^2|\psi_j> \right\}^2
\]
and low frequency components [45]. As an aid to optimising the computer simulation XSophe/Xepr has the capability of displaying intermediate spectra (Magnetic Field vs. Intensity vs. Iteration Number) and the corresponding spin Hamiltonian parameters. Ideally, you would like to optimise a set of multifrequency EPR spectra with a single set of spin Hamiltonian parameters. Although this can be achieved in the current version of Xsophe, the methodology is not straightforward. Version 2.0 of XSophe currently under development will allow this and the optimisation of multi-component spectra.

2.8 Brief Product Overview of Xsophe [46,48]

XSophe-Sophe provides scientists with an easy-to-use research tool for the analysis of isotropic, randomly orientated and single crystal continuous wave (CW) EPR spectra. XSophe provides an X Windows interface (Figure 3) to the Sophe program allowing; the creation of multiple input files, the local and remote execution of Sophe and display of sophelog (output from Sophe) and input parameters/files.

Figure 3. The XSophe interface allows the creation and execution of multiple input files on the local or remote hosts. There are macro task buttons to guide the novice through the various menus and two button bars to allow easy access to the menus. For example the bottom bar (left to right), Experimental Parameters, Spin System, Spin Hamiltonian, Instrumental Parameters, Single Crystal Settings, Linershape Parameters, Transition Labels/Probabilities, File Parameters, Sophe Grid Parameters, Optimisation Parameters, Execution Parameters and Batch Parameters. (a) Main window, (b) Anisotropic hyperfine parameter dialog, (c) Single crystal parameter dialog.

XSophe allows transparent transfer of EPR spectra and spectral parameters between XSophe, Sophe and Xepr®, using state of the art platform independent Corba libraries. This interactivity allows the execution and interaction of the XSophe interface with Sophe on the same computer or a remote host through a simple change of the hostname. XSophe contacts the Sophe daemon, which if provided with a correct combination of username/password forks a Sophe which then performs the simulation. Sophe is a sophisticated computer simulation software programme written in C++ using the most advanced computational techniques, including: the SOPHE partition and interpolation schemes, field segmentation algorithm, homotopy, optimisation algorithms for optimising spin Hamiltonian parameters and parallelisation for reducing computational times. [16-18] The functionality of Sophe is shown below:
Experiments

- Energy level diagrams, transition surfaces, continuous wave EPR spectra, pulsed EPR spectra under development.

Spin Systems

- Isolated and magnetically coupled spin systems. An unlimited number of electron and nuclear spins is supported with nuclei having multiple isotopes.
- Interactions as listed in the following Table.

### Table 1. Spin Hamiltonian Interactions included in Sophe.

<table>
<thead>
<tr>
<th>Operator Form</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S.B \ (\beta^eS.g.B)$</td>
<td>Electron Zeeman</td>
</tr>
<tr>
<td>$I.B \ (\beta^n g_n I.B)$</td>
<td>Nuclear Zeeman</td>
</tr>
<tr>
<td>$S.D.S$</td>
<td>Fine structure</td>
</tr>
<tr>
<td>$S^4, S^6$</td>
<td>High-order fine structure*</td>
</tr>
<tr>
<td>$I.P.I$</td>
<td>Quadrupole</td>
</tr>
<tr>
<td>$S.A.I$</td>
<td>Hyperfine</td>
</tr>
<tr>
<td>$S_i \cdot J_{ij} \cdot S_j$</td>
<td>Dipole Dipole</td>
</tr>
<tr>
<td>$J_{ij} S_i \cdot S_j$</td>
<td>Exchange</td>
</tr>
</tbody>
</table>

*All high-order fine-structure terms taken from Table 1 in reference [8] have been incorporated into Sophe.

Continuous Wave EPR Spectra

- Spectra types: Solution, randomly orientated and single crystal
- Symmetries: Isotropic, axial, orthorhombic, monoclinic and triclinic
- Multidimensional spectra: Variable temperature, multifrequency and the simulation of single crystal spectra in a plane.

Methods

- Matrix diagonalization, sophe interpolation and homotopy. 1st order perturbation theory can be chosen for superhyperfine interactions.

Optimisation (Direct Methods)

- Hooke and Jeeves, Quadratic, Simplex, and Simulated Annealing.
- Spectral Comparison: Raw data and Fourier transform.

For nuclear superhyperfine interactions Sophe offers two different approaches; full matrix diagonalization or first order perturbation theory. If all the interactions were to be treated exactly, a Mn(II) (S=5/2, I=5/2) coupled to four $^{14}$N nuclei would span an energy matrix of 2,916 by 2,916. To fully diagonalise [23] a Hermitian matrix of this size, it would take some 13 hours on a Silicon Graphics O2 (R5K) workstation, let alone the memory requirement (~68 MB for a single matrix of this size with double precision). In fact, in most systems the electronic spin only interacts strongly with one or two nuclei but weakly with other nuclei and the latter approach of first order perturbation may be a satisfactory treatment which will ease the computational burden for large spin systems.
The specification of transition labels is not necessary in Sophe. In the absence of labels a threshold value for the transition probability is required. The program will then perform a search for all transitions which have a transition probability above this threshold value at a range of selected orientations. For a single octant the following orientations \(( \theta, \phi)\) are chosen: \((0^\circ,0^\circ), (45^\circ,0^\circ), (90^\circ,0^\circ), (45^\circ,90^\circ), (90^\circ,45^\circ), (90^\circ,90^\circ)\). The transitions found then act as "input" transitions.

The program is designed to simulate CW EPR spectra measured in either the perpendicular \((B_0 \perp B_1)\) or parallel \((B_0 \parallel B_1)\) modes, where \(B_0\) and \(B_1\) are the steady and oscillating magnetic fields, respectively. It can also easily generate single crystal spectra for any given orientation of \(B_0\) and \(B_1\) with respect to a reference axis system which is normally either the laboratory axis system or the principal axis system of a chosen interaction tensor or matrix in the spin Hamiltonian. Computer simulation of single crystal spectra measured in a plane perpendicular to a rotation axis can be performed by defining the rotation axis and the beginning and end angles in the plane perpendicular to this axis.

3. Role of frequency (and temperature) in extracting spin Hamiltonian parameters

3.1 Fine structure interaction

The effect of frequency and/or temperature can be seen in the following CW EPR spectra of a high spin system Fe(III), \(S=5/2\) centre \((D=-4.5\ GHz, E/D=0, g=2.0)\) found in sweet potato purple acid phosphatase

\[
\mathcal{H} = g \cdot \beta \cdot \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot D \cdot \mathbf{S} \tag{12}
\]

**Figure 4** Variable frequency CW EPR Spectrum

**Figure 5** Variable temperature CW EPR Spectra with \(D=-4.5\ GHz\), (red) \(D=4.5\ GHz\) (yellow)
Conclusions Concerning Choice of Microwave Frequency

- At very low frequencies (ν < D) there is insufficient energy to observe all transitions.
- Variable temperature experiments can be used to determine the magnitude and sign of the axial zero field splitting, D.

3.2 Isotropic and Anisotropic Exchange interactions

An example of an isotropically exchange coupled spin system is a nitroxide biradical

$$\mathcal{H} = \sum_{i=1}^{n} \{ g \beta \cdot S_1 + a S_1 \cdot I_1 \} - g_0 \beta_0 \cdot B \cdot I_1 \} + J_{iso} S_1 \cdot S_2$$  \hspace{1cm} (13)

where $g=2.00585$, $a=13.5 \times 10^{-4}$ cm$^{-1}$ and $J_{iso} = 40$ cm$^{-1}$. A variable temperature simulation of the experimental variable temperature spectrum can be used to extract the isotropic exchange coupling constant. However, if $J$ is large, then a combination of higher frequencies and/or higher temperatures is required to extract the exchange coupling constant.

**Figure 6** A variable X band simulation of of the nitroxide biradical.

If $J_{iso}$ is very small, for example 0.4 cm$^{-1}$, then the use of multifrequency EPR (Figure 7 opposite) can be used to measure $J_{iso}$. Conversely, if $J_{iso}$ is very large then a combination of frequency and temperature can be exploited to determine $J_{iso}$. 
3.3 Distributions of parameters

3.3.1 Distributions of g and A values - Examples - Low Spin Fe(III) and Co(II) Centres

Distributions of g values results in better spectral resolution at lower frequencies.

\[ \sigma_{v}^{2} = ( \sum_{i=x,y,z} \{ \sigma_{R_{i}}^{2} + \frac{\Delta g_{i}}{g_{i}} \nu_{0}(B) \} / g^{2} ) \]  

(14)

For example a low spin Fe(III) S=1/2, I=0 spin system, \( g_{x}=2.4, g_{y}=2.0 \) and \( g_{z}=1.5 \)

**Figure 8** Multifrequency EPR Simulation of a low spin Fe(III) spin system

Distributions of parameters (g and A values) can result in better spectra resolution at different frequencies

\[ \mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}(\text{Mo or Co}) - g_{n} \cdot \beta \mathbf{B} \cdot \mathbf{I}(\text{Mo or Co}) \]  

(15)

For example a low spin Co(II) with pyridine coordinated axially

\[ \sigma_{v}^{2} = ( \sum_{i=x,y,z} \{ \sigma_{R_{i}}^{2} + \left[ \frac{\Delta g_{i}}{g_{i}} \nu_{0}(B) + \Delta A_{i} M_{i} \right] g_{i}^{2} l_{i}^{2} \} / g^{2} ) \]  

(16)

**Figure 9** Co(II) S=1/2, I=7/2, \( g_{1}=1.972, g_{2}=2.180, A_{1}=77.5 \times 10^{4} \text{ cm}^{-1}, A_{2}=47.8 \times 10^{4} \text{ cm}^{-1}, \sigma_{R_{1}}=16.5 \text{ MHz}, \sigma_{R_{2}}=15.0 \text{ MHz}, \sigma_{g_{1}}/g_{1}=0.0016, \sigma_{g_{2}}/g_{2}=0.0034, \sigma A_{1}=5.8 \text{ MHz} \) \( \sigma A_{2}=16.6 \text{ MHz} \).  
(a) X-band (9.5962 GHz) EPR Spectrum (red), (b) S-band (2.3 GHz) CW EPR Spectrum (blue).
Conclusions Concerning Choice of Microwave Frequency

- For spin systems with no hyperfine coupling, the lower the frequency, the narrower the linewidth.
- For spin systems which contain nuclei, the optimum frequency for the best resolution of a given hyperfine resonance depends upon a quadratic in $M_i$ and the frequency. Generally lower frequencies (L to S-band are better).

### 3.3.2 Distributions of D and E values

An example of a spin system which exhibits a distribution of D and E values is the EPR spectrum of the high spin Fe(III) ($S=5/2$) centres (~10%) in the sweet potato purple acid phosphatase enzyme which contains a strongly antiferromagnetically coupled binuclear Fe(III) -μO-Mn(II) active site.

**Figure 10** (a) CW EPR Spectrum of the Fe(III)-apo and Fe(III)-Zn(II) centres in sweet potato purple acid phosphatase. Experimental (red) and computer simulated (green) spectra. (c) CW EPR spectrum as a function of E/D and (d) a transition surface where the colour map (decreasing from red to blue) corresponds to the distribution of E/D.
4. State Mixing

State Mixing occurs when one or more of the spin Hamiltonian interactions are of similar magnitude. This leads to energy level crossings and anticrossings (see below). When the Nuclear Hyperfine and Quadrupole Interactions are of a similar magnitude state mixing can lead to the observation of formerly forbidden \( \Delta M_I = \pm 2 \) and \( 3 \) transitions. At very low frequencies the Nuclear Hyperfine and Electron Zeeman Interactions become comparable (for example Figure 11a) leading to state mixing and complex spectra. Conversely state mixing can occur for high spin systems when the zero field splitting or exchange interactions are of a similar magnitude to the electron Zeeman interaction.

**Figure 11** A multifrequency EPR computer simulation of a VO(II) spin system. \( S=1/2, \ I=7/2, \ g_x=1.984, \ g_y=1.978, \ g_z=1.944, \Delta A_x=-49.2 \times 10^{-4} \ cm^{-1}, \Delta A_y=-58.5 \times 10^{-4} \ cm^{-1}, \Delta A_z=-163.2 \times 10^{-4} \ cm^{-1} \)
3.3.3 Energy level crossings and anticrossings and looping transitions

These affects are commonly observed in CW EPR spectra of high spin systems, for example Fe(III), $S=5/2$, $D = -4.5$ GHz, $E/D = 0$, $g = 2.0$

$$\mathcal{H} = g \cdot \beta \cdot \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$

(17)

**Figure 12** (a) S-band, 4.0 GHz, (b) X-band, 9.75 GHz,

(c) Q-band, 35.0 GHz, (d) W-band, 95.0 GHz

Conclusions Concerning Choice of Microwave Frequency

- CW EPR Spectra are simplified at higher frequencies
- At very low frequencies ($\nu < D$) there is insufficient energy to observe all transitions
4. Role of frequency in spectral resolution

Two examples include Mo(V) and Cu(II) dimer spectra.

![Figure 13 Multifrequency CW EPR spectra of [MoO(SPh),4]. (a,b) Solution spectra and (c,d) frozen solution spectra.](image)

\[ \sigma_v = a + b M_I + c M_I^2 + d M_I^3 \]  \hspace{1cm} (18)

The parameters a, b, c and d are dependent on the microwave frequency, the hydrodynamic radius, the solvent viscosity, temperature and the anisotropy of the g and A matrices.

\[ J_v^2 = \left( \sum_{i=x,y,z} \left\{ \sigma_{R_i}^2 + \left[ \frac{\Delta g_i}{g_i} \nu_0(B) + \Delta A_i M_I \right]^2 \right\} g_i^2 l_i^2 \right) / g^2 \]  \hspace{1cm} (19)

The narrower linewidths at lower microwave allow the observation of superhyperfine interactions [47] and redistributes the Mo hyperfine resonances providing a simpler interpretation.

The microwave frequency can be varied to separate multicomponent spectra. For example separation of two S=1/2 spin systems can be achieved by using higher frequencies. Another use of high frequencies is the separation of spectra from S=1/2 Cu(II) complexes from S=1 dipole-dipole coupled spectra, the latter being frequency independent.

5. Summary

In conclusion I hope I have demonstrated that a multifrequency approach in conjunction with computer simulation allows the accurate determination of spin Hamiltonian parameters which can be used to obtain structural information.

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7. Bibliography

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[41] Spin Hamiltonian parameters are constrained to a portion of $\mathcal{H}_p$-space as this will prevent the generation of a NULL spectrum.


