Computer Corner

EasySpin: *a Software Package for the Computation of EPR and ENDOR Spectra*

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During the last decade cheap and fast computers have become available. As a result, EPR spectroscopists can simulate their spectra on their desktop computer and no longer have to rely on large-scale computing facilities. This led to the emergence of several general simulation programs.

One of the first to become widely used was SimFonia for Windows, written by Ralph T. Weber (Bruker BioSpin) in the mid-1990s. Based on perturbation theory, it was not generally valid and its results had to be used with care. In 2000, Bruker BioSpin substituted SimFonia with XSophe, a significantly enhanced simulation suite now running under Linux. The program is developed by Graeme Hanson's group at the University of Queensland in collaboration with Bruker BioSpin.

Other general programs include the little known but highly useful DOS/Windows program SIM, developed by Høgni Weihe (University of Copenhagen), simpip (formerly QPOW) by Mark J. Nilges (Illinois EPR Research Center), and EPR-NMR, a long-standing project of John Weil (University of Saskatchewan) and Michael Mombourquette (Queen's University). Links to these programs and to other computational EPR software can be found on the internet at www.esr.ethz.ch or in the ESR software database (ESDB) at epr.niehs.nih.gov/software.html.

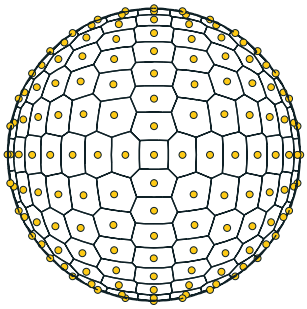
EasySpin

The spectrum simulation software with the most extensive functionality so far is EasySpin, developed in the EPR group at ETH Zurich (Switzerland). The software package grew out of an attempt to integrate theoretical computations, spectral simulations and data analysis on a single user platform. EasySpin consists of a collection of functions that add EPR analysis and spectral simulation functionality to the scientific computation and visualization environment Matlab (www.mathworks.com).

The latest release of EasySpin can be downloaded from www.esr.ethz.ch/easyspin. It requires Matlab 6.0 or later and runs on PC/Windows, PC/Linux, Sun/Solaris and SGI/IRIX. The software itself is free, but the source code is not yet available to the public.

Powder spectra

Although it offers a host of other features, the main purpose of EasySpin is the simulation of powder EPR spectra. A powder consists of a uniform random orientational distribution of a large number of paramagnetic centres. The powder spectrum is nothing but the sum of the spectra arising from the single centres. For speedy computation, it is necessary to compute as few orientations as possible from a uniform distribution of orientations on the unit sphere. For this purpose, EasySpin uses a novel highly homogeneous triangular arrangement with octahedral symmetry (see illustration). Other programs use simple theta/phi grids (SIM), spiral arrangements (EPR-NMR) or triangular grids with D_{4h} symmetry (XSophe). For each orientation, the single-crystal spectrum is computed. Each single-crystal spectrum is multiplied by a weighting factor which is proportional to the solid angle covered by the neighborhood of the orientation (the borders of these so-called Voronoi cells are shown in the illustration below). EasySpin is the first program to include exact weighting factors for this summation.

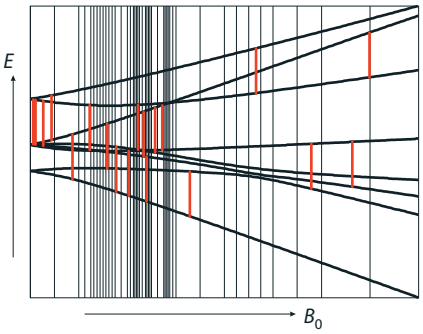


145 orientations over a hemisphere with their neighborhoods

Resonance fields

For field-swept EPR spectra, resonance fields can be computed either analytically or numerically. Analytical solutions are limited in scope and exist only for small systems with one dominant interaction (e.g. the electron Zeeman interaction). Nowadays, practically all programs use entirely numerical procedures. First, state energies and vectors at one or more values of the external magnetic field are computed by numerically diagonalizing the spin Hamiltonians in their full matrix representations. These matrix diagonalizations form the most time-consuming step of the entire simulation procedure.

Second, the state energies and vectors are used to compute the resonance fields. This is the point where numerical programs differ from each other. XSophe implements a linear field segmentation scheme with second-order perturbational corrections, SIM iterates using cubic polynomials, and EPR-NMR uses a Newton-Raphson approach. EasySpin obtains the resonance fields by interpolation from an adaptively modelled cubic spline representation of the energy level diagram. This new method is accurate and very robust and needs less Hamiltonian diagonalizations than the other methods. In a complicated situation with many anticrossings (see illustration), the method needs at most three diagonalizations per resonance field (illustration: 19 resonance fields, 45 diagonalizations).

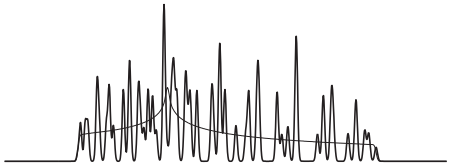


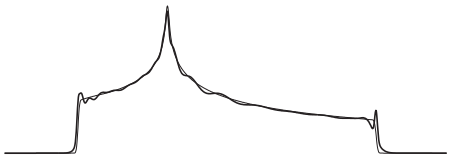
Interpolation

The high cost of computing resonance fields can be avoided by the application of much faster interpolative procedures. Once resonance fields are known for two similar spin Hamiltonians, differing slightly e.g. in the orientation of the spin system with respect to the external magnetic field, the resonance fields of spin Hamiltonians lying in between can be computed interpolatively with only small error. Both cubic and linear interpolation can be used, depending on whether resonance fields or intensities are computed. EasySpin makes extensive use of these interpolation techniques.

Gradient smoothing

Another feature of EasySpin's spectrum simulation algorithm that enhances performance is the use of gradient smoothing. Before combining the computed single orientation spectra into a total powder spectrum, an additional broadening is added to the intrinsic line widths in order to reduce computational noise, i.e. to bridge the gaps between the various peaks in the computed spectrum (see illustration). In technical terms, this additional smoothing linewidth is proportional to the magnitude of the gradient of the resonance field with respect to the orientation of the magnetic field in the molecular frame. The concept was first developed in a rudimentary form by Høgni Weihe for his program SIM and was later independently implemented in a more general form in both EasySpin and XSophe (where it is called "mosaic misorientation model").


55 orientations, no gradient smoothing


55 orientations, with gradient smoothing

EasySpin simulation example

EasySpin's functions do not have a graphical user interface, they can only be accessed from the Matlab command line. Nevertheless, they are straightforward to use. Matlab features a full-fledged programming language, so that many specialized EPR problems can be treated by programming new functions based upon EasySpin's toolbox.

All the algorithmical improvements described above make EasySpin's cw EPR spectrum simulation function `pepper()` general and very efficient. The following lines are the input necessary to simulate a powder spectrum of a Cu^{2+} complex at X band:

```
Sys = struct('S',1/2,'I',3/2,'gn',1.484);
Sys.g = [2 2 2.2]; Sys.A = [50 50 300];
Par = struct('Range',[270,360],'mwFreq',9.5);
[B,Spectrum] = pepper(Sys,Par);
plot(B,Spectrum)
```

`pepper()` can treat parallel detection, temperature effects, higher order harmonics, systems with more than one electron, interaction matrices with arbitrary orientations and strains in *g*, *A* and *D*.

Other functions provide smaller building blocks for the user. To compute only the resonance fields of an $S = 1$ system with significant zero-field splitting, use

```
Sys = struct('S',1,'g',2,'D',[-1 -1 2]*3e3);
Par = struct('mwFreq',10);
Ori = [0;pi/5]; % [phi; theta]
ResFields = eigfields(Sys,Par,Ori)
```

which returns the fields in units of mT

```
ResFields = [40.9060 238.4059 44.1146]
```

ENDOR and Pulse EPR

Powder ENDOR spectra are much easier to simulate than cw EPR spectra. In addition, ENDOR spectra are commonly measured selecting very few orientations and therefore yielding single-crystal like spectra even for powders. However, the situation gets more complicated if ENDOR spectra are not taken at the edges of complicated EPR spectral line shape. In this case, a full treatment of the orientation selection is crucial. EasySpin offers an ENDOR simulation routine with an accurate orientation selection procedure. Its usage is very similar to that of `pepper()`.

A short word about pulse EPR simulations is in order. Generally applicable software is not yet available, due to the absence of a theoretically general and experimentally verified computational procedure. Current attempts are limited to special experiments and $S = 1/2$ systems with small g anisotropy and small hyperfine couplings and include tryscore (for HYSCORE, by Daniella Goldfarb, Weizmann Institute of Science) and a program by Zoltan Mádi (ETH Zurich). Bruker BioSpin is working on an XSophe version with basic pulse EPR functionality. EasySpin is to include pulse EPR features in its next release.

More functionality

Since Matlab's programming language is based on matrices, it is straightforward to compute spin operators and their functions. For example, the matrix representation of a 90° pulse on an $S = I = 1/2$ system can be computed by the two lines

```
Sy = sop([1/2 1/2],'ye');
Pulse = expm(i*pi/2*Sy)
```

In addition to the usual cartesian spin operators, EasySpin provides a full set of Stevens operators for $S > 1$.

Among other features, EasySpin includes a function to compute the effect of field modulation in a cw EPR experiment (pseudomodulation), a time evolution function for density matrices, a database of nuclear g values, many relevant physical constants, various line shape functions, apodization functions, tools to handle rotation matrices and Euler angles, etc.

Spectral fitting

The development and application of numerical optimization algorithms for fitting spin Hamiltonian parameters to experimental spectra is still in its infancy, mainly due to the usually exceptionally bad behavior of the error function. For powder spectra, current methods work well only when the starting guesses of the parameters are very close to the correct ones or when experimental spectra at different microwave frequencies are available. Thus, numerical fitting is mainly a tool for final refinement of spin Hamiltonian parameters. Some of the programs mentioned in the introduction have built-in spectral fitting capabilities. Matlab offers a variety of fully customizable optimization algorithms, which can be used together with EasySpin's simulation functions to write fitting programs even for multiple spectra and other complex situations.

Further reading

Stoll St.: Spectral Simulations in Solid-State EPR. Ph.D. thesis, ETH Zurich 2003.

Griffin M., Muys A., Noble C., Wang D., Eldershaw C., Gates K.E., Burrage K., Hanson G.R.: XSophe, a Computer Simulation Software Suite for the Analysis of Electron Paramagnetic Resonance Spectra. Mol. Phys. Rep. **26**, 60–84 (1999)

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