Module V, Lecture 06: Simulation of ESR spectra

One of the key differences between NMR and EPR is that the latter is still dominated by continuous-wave experiments where a fixed microwave frequency is applied to the sample, and the magnetic field is swept linearly through the range specified by the user.

Simulation of field-swept ESR experiments

All interaction Hamiltonians have been discussed in the previous lectures of this course. For the purposes of this lecture, the spin Hamiltonian must be partitioned into three parts:

$$\hat{H}(t) = B_0\hat{H}_Z + \hat{H}_{MW}\cos(\omega_{MW}t) + \hat{H}_{INT} \tag{1}$$

where the first term is the Zeeman Hamiltonian (the operator is normalised to 1 Tesla), the second term is the microwave irradiation at the frequency ω_{MW} and the last term contains the remaining interactions. In the absence of microwave irradiation, the system has stationary states $|n\rangle$ with the energies E_n defined by the standard eigenvalue relation:

$$\left[B_0\hat{H}_Z + \hat{H}_{INT}\right]|n\rangle = E_n|n\rangle \tag{2}$$

The differences between these energies

$$\omega_{nk} = E_n - E_k \tag{3}$$

are the potential transition frequencies under weak perturbations. Here and below all energies are measured in the angular frequency units. Once the eigenvalues and eigenvectors of the Hamiltonian matrix are computed (a standard procedure available *e.g.* in *Matlab*), EPR line intensities at the frequency ω_{MW} may be computed using the well-known perturbation theory expression:

$$A_{nk} = \frac{1}{4\hbar^2}\left|\langle k|\hat{H}_{MW}|n\rangle\right|^2\Gamma(\omega_{MW} - \omega_{nk}) \tag{4}$$

where $\Gamma(\omega_{MW} - \omega_{nk})$ is the line shape function, usually a peak-shaped curve of some kind. In the most basic implementation of an ESR simulation code, the following stages are therefore involved:

1. For a given value of B_0, build the primary Hamiltonian matrix $\hat{H}_0 = B_0\hat{H}_Z + \hat{H}_{INT}$.
2. Compute eigenvalues and eigenvectors of $\hat{H}_0$.
3. For each pair of eigenvectors, compute the transition moment $\left|\langle k|\hat{H}_{MW}|n\rangle\right|^2$.
4. Compute the total spectral absorption at the current value of B_0 as

$$A(B_0) = \frac{g_{nk}}{4\hbar^2}\sum_{nk}\left|\langle k|\hat{H}_{MW}|n\rangle\right|^2\Gamma(\omega_{MW} - \omega_{nk}) \tag{5}$$

where g_{nk} accounts for degeneracies, Boltzmann populations and other more technical factors. The perturbation theory with respect to $\hat{H}_{MW}$ is usually safe to use, but this method is computationally very inefficient: a matrix diagonalization (a very expensive procedure) is required at each value of the magnetic field, followed by an even more expensive double sum in Equation (5).

More sophisticated methods attempt to first locate the "resonance fields" – the values of the applied magnetic field at which the energy difference between pairs of levels matches the frequency of the applied microwave irradiation:

$$\omega_{nk}\left(B_0\right)=\omega_{\mathrm{MW}}\qquad\forall n,k \tag{6}$$

These methods involve the following stages (roughly the flowchart of *EasySpin*):

1. Primary Hamiltonian eigenvalues and their derivatives are computed as a function of the applied magnetic field. As per the Hellmann-Feynman theorem, the derivative of the Hamiltonian eigenvalues with respect to the applied magnetic field is

$$\frac{\partial E_n}{\partial B_0}=\left\langle n\left|\frac{\partial\hat{H}}{\partial B_0}\right|n\right\rangle=\left\langle n\left|\hat{H}_Z\right|n\right\rangle \tag{7}$$

   Initially, a rough grid of B_0 values is chosen. This grid is refined by adaptive binary subdivision until sufficiently good sampling is obtained, and interpolated with a cubic spline.

2. Roots of Equation (6) are obtained numerically (Newton-Raphson method or similar) for each segment of the cubic spline. The eigenvectors at the corresponding field are obtained by interpolating the eigenvectors at the spline knots with the same cubic spline.

3. Transition moments are computed as $\left|\left\langle k\left|\hat{H}_{\mathrm{MW}}\right|n\right\rangle\right|^2$ between the energy levels responsible for the resonance condition.

4. Each transition is associated with a bell-shaped curve (the type is system-dependent) with the maximum located at the resonance field, integral proportional to the transition moment and the width assigned using one of the relaxation theories available (see Module III).

An important point is that all of the above methods require Hamiltonian diagonalization. Consequently, they are not applicable to systems with more than about 15 spins because the steeply growing matrix dimension makes diagonalization impractical.

Powder averaging

One of the thorniest problems in magnetic resonance of orientationally disordered systems (powders, glasses, *etc.*) is the requirement to average the simulation over all possible orientations of the system. For time domain simulations, nothing significantly better than a numerical integral over a grid of all possible orientations has ever been proposed. The key reason is that, while the spin interaction Hamiltonian can only contain low-rank Wigner *D*-functions of orientation parameters Ω

$$\hat{H}_{\mathrm{INT}}\left(\Omega\right)=\hat{H}_{\mathrm{ISO}}+\sum_{k,m=-2}^{2}\hat{H}_{km}\mathfrak{D}_{km}^{(2)}\left(\Omega\right) \tag{8}$$

its matrix exponential contains Wigner *D*-functions of all even spherical ranks:

$$\exp\left[-i\hat{H}_{\mathrm{INT}}\left(\Omega\right)t\right]=\sum_{l=0}^{\infty}\sum_{k,m=-l}^{l}\hat{C}_{km}^{(l)}\left(t\right)\mathfrak{D}_{km}^{(l)}\left(\Omega\right) \tag{9}$$

In many cases, this generates very spiky orientation dependences in the observables that require a very fine grid (thousands of points) to integrate accurately. Attempts to obtain analytical expressions for the operator coefficients $\hat{C}_{km}^{(l)}$ in front of the Wigner function in Equation (9) lead to calculations that are even harder than brute force integration.

For time domain simulations, the spherical averaging problem remains unsolved. Field swept simulations using the formalism outlined in the previous section have an elegant shortcut (invented by Stefan Stoll). The intermediate quantities in the field swept formalism – individual resonance line frequencies $\omega_{\text{res}}(\Omega)$, and their intensities $A(\Omega)$ are both integrable functions of low spherical rank. Therefore, the powder integral over these parameters

$$\begin{gathered} S(\omega)=\int A(\Omega)\delta\left[\omega-\omega_{\text{res}}(\Omega)\right]dV_{\Omega}= \\ =\frac{d}{d\omega}\int A(\Omega)h\left[\omega-\omega_{\text{res}}(\Omega)\right]dV_{\Omega}=\frac{d}{d\omega}\int\limits_{\omega_{\text{res}}(\Omega)\leq\omega}A(\Omega)\,dV_{\Omega} \end{gathered} \tag{10}$$

is numerically straightforward using spline-interpolated adaptive grids. In Equation (10), $\delta(\omega)$ is the delta-function (used to represent the spectral line before any convolution with the shape function is taken) and $h(\omega)$ is the Heaviside step function whose derivative is equal to the delta-function.

Transition screening

The final expression for the EPR spectrum in Equation (5) involves a very expensive double sum over the energy levels, which has quartic scaling with the Hamiltonian dimension and therefore dominates the simulation time (all other stages have at most cubic scaling). Any *a priori* considerations about reducing the computational effort at that stage are valuable, in particular:

1. Energy difference screening: large values of $\omega_{\text{MW}}-\omega_{nk}$ typically translate into small values of the lineshape function $\Gamma(\omega_{\text{MW}}-\omega_{nk})$. The corresponding terms may therefore be dropped from the sum without computing the transition moment. Most of the potential transitions do, in fact, belong to this category.

2. Quantum number screening: in high-field ESR and ENDOR spectroscopy, only the transitions corresponding to a single-spin flip have a realistic chance of being visible. All other transitions may be dropped from consideration.

3. Field-of-view screening: allowed transitions falling far outside the field sweep window need not be included into the simulation.

The number of terms in Equation (5) that survive the above procedures is typically orders of magnitude smaller than the number of terms in the original sum.