Module IV, Lecture 01: Spin Dynamics in Solid State DNP Experiments

A solid state DNP system typically comprises a number of electrons (usually located on specially added stable radicals) and nuclei scattered randomly through the volume of a glassy sample, placed into a high magnetic field and exposed to microwave irradiation from an external source. Because of the randomness in system geometry, no DNP simulation performed so far in the literature lays any claim to a quantitative match with the experiment. For a given system geometry such simulations can be done.

The treatment below might seem too general for most practical purposes – it includes every interaction the spin system could potentially have – but such is the perspective of software developers: we do not actually know which systems are simulated by the users and under which case-specific assumptions.

Laboratory frame spin Hamiltonian

The spin Hamiltonian for a system with an arbitrary number of electrons and nuclei under microwave irradiation has the following general form:

$$\hat{H} = \hat{H}_{\mathrm{Z}} + \hat{H}_{\mathrm{NN}} + \hat{H}_{\mathrm{EN}} + \hat{H}_{\mathrm{EE}} + \hat{H}_{\mathrm{MW}} \tag{1}$$

The Zeeman interaction Hamiltonian $\hat{H}_{\mathrm{Z}}$ has contributions from electrons and nuclei:

$$\hat{H}_{\mathrm{Z}} = \sum_k \vec{B}_0 \cdot \mathbf{A}_{\mathrm{E}}^{(k)} \cdot \hat{\vec{E}}^{(k)} + \sum_k \vec{B}_0 \cdot \mathbf{A}_{\mathrm{N}}^{(k)} \cdot \hat{\vec{N}}^{(k)} \tag{2}$$

where $\vec{B}_0 = \begin{pmatrix} 0 & 0 & B_0 \end{pmatrix}$ is the applied magnetic field, $\mathbf{A}_{\mathrm{E}}^{(k)}$ are electron Zeeman interaction tensors and $\mathbf{A}_{\mathrm{N}}^{(k)}$ are nuclear Zeeman interaction tensors. Both types of tensors are, in general, anisotropic and are easy to calculate or extract from the experimental data. Inter-nuclear interaction Hamiltonian contains scalar and point dipolar contributions:

$$\hat{H}_{\mathrm{NN}} = \sum_{j<k} J_{\mathrm{NN}}^{(j,k)} \left(\hat{\vec{N}}_j \cdot \hat{\vec{N}}_k \right) - \frac{\mu_0}{4\pi} \sum_{j<k} \frac{\gamma_{\mathrm{N}}^{(j)} \gamma_{\mathrm{N}}^{(k)}}{r_{jk}^5} \left(3(\hat{\vec{N}}_j \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \hat{\vec{N}}_k) - r_{jk}^2 (\hat{\vec{N}}_j \cdot \hat{\vec{N}}_k) \right) \tag{3}$$

where both indices run over nuclei, $J_{\mathrm{NN}}^{(j,k)}$ are inter-nuclear *J*-couplings (rather hard to calculate, but usually available from experimental data, angular frequency units assumed), $\gamma_{\mathrm{N}}^{(j)}$ are nuclear magnetogyric ratios and $\vec{r}_{jk}$ are inter-nuclear distance vectors, which may be extracted from energy minimum molecular geometry. In the spherical tensor form:

$$\hat{H}_{\mathrm{NN}} = \sum_{j<k} \sum_{lm} d_{jklm}^{(\mathrm{NN})} \hat{T}_m^{(l)} (j,k) \tag{4}$$

The electron-nuclear Hamiltonian contains isotropic and anisotropic hyperfine interactions:

$$\hat{H}_{\mathrm{EN}} = \sum_{j,k} \hat{\vec{E}}_j \cdot \mathbf{A}_{\mathrm{EN}}^{(j,k)} \cdot \hat{\vec{N}}_k = \sum_{j,k} \sum_{lm} d_{jklm}^{(\mathrm{EN})} \hat{T}_m^{(l)} (j,k) \tag{5}$$

where j index runs over electrons, k index runs over nuclei and $\mathbf{A}_{\mathrm{EN}}^{(j,k)}$ are electron-nuclear hyperfine interaction tensors. They are easy to predict and do not have the point dipole form because electrons are delocalized. Inter-electron interaction Hamiltonian contains exchange and dipolar contributions:

$$\hat{H}_{\mathrm{EE}} = \sum_{j<k} J_{\mathrm{EE}}^{(j,k)} \left(\hat{\vec{E}}_j \cdot \hat{\vec{E}}_k \right) - \frac{\mu_0}{4\pi} \sum_{j<k} \frac{\gamma_{\mathrm{E}}^{(j)} \gamma_{\mathrm{E}}^{(k)}}{r_{jk}^5} \left(3(\hat{\vec{E}}_j \cdot \vec{r}_{jk})(\vec{r}_{jk} \cdot \hat{\vec{E}}_k) - r_{jk}^2 (\hat{\vec{E}}_j \cdot \hat{\vec{E}}_k) \right) \tag{6}$$

where both indices run over electrons, the electron magnetogyric ratios $\gamma_{\mathrm{E}}^{(j)}$ may be different for different electrons and orientation due to the difference in their *g*-factors. Exchange interactions $J_{\mathrm{EE}}^{(j,k)}$ are in practice unpredictable theoretically because they effectively include the non-point dipolar effects and other contributions – they must be determined experimentally. In the spherical tensor form:

$$\hat{H}_{\mathrm{EE}}=\sum_{j<k}\sum_{lm}d_{jklm}^{(\mathrm{EE})}\hat{T}_{m}^{(l)}\left(j,k\right) \tag{7}$$

Finally, the microwave term at the frequency ω_{MW} is assumed to generate an oscillating magnetic field on the X axis of the laboratory frame of reference:

$$\hat{H}_{\mathrm{MW}}=\cos\left(\omega_{\mathrm{MW}}t\right)\sum_{k}a_{\mathrm{MW}}^{(k)}\hat{E}_{\mathrm{X}}^{(k)}=\frac{e^{-i\omega_{\mathrm{MW}}t}+e^{i\omega_{\mathrm{MW}}t}}{4}\sum_{k}a_{\mathrm{MW}}^{(k)}\left(\hat{E}_{+}^{(k)}+\hat{E}_{-}^{(k)}\right),\qquad a_{\mathrm{MW}}^{(k)}=B_{1}\left[\mathbf{A}_{\mathrm{E}}^{(k)}\right]_{\mathrm{XX}} \tag{8}$$

The amplitudes of the microwave terms at different electrons are, in general, different because the electrons might in general have different g-tensors and would therefore respond differently to the magnetic component of the applied microwave field $\vec{B}_{1}=\begin{pmatrix}B_{1} & 0 & 0\end{pmatrix}$. In practice, the spherical tensor expansions and matrix representations of all Hamiltonian terms are calculated automatically at each spin system orientation by *Spinach* kernel from the coordinate and coupling data provided by the user.

General DNP simulation formalism

If the purpose is to simulate high-field DNP without significant approximations, the most convenient rotating frame is the one that removes all time dependence from the Hamiltonian – this is accomplished by the electron rotating frame transformation with respect to the microwave frequency, that is, using $\omega_{\mathrm{MW}}\sum_{k}\hat{E}_{\mathrm{Z}}^{(k)}$ operator and keeping only zero order terms in the average Hamiltonian theory with respect to the period of the rotating frame. As a result, the Zeeman Hamiltonian becomes:

$$\hat{H}_{\mathrm{Z}}'=\sum_{k}\left(\omega_{\mathrm{E}}^{(k)}-\omega_{\mathrm{MW}}\right)\hat{E}_{\mathrm{Z}}^{(k)}+\sum_{m}\vec{B}_{0}\cdot\mathbf{A}_{\mathrm{N}}^{(m)}\cdot\hat{\vec{N}}^{(m)},\qquad\omega_{\mathrm{E}}^{(k)}=B_{0}\left[\mathbf{A}_{\mathrm{E}}^{(k)}\right]_{\mathrm{ZZ}} \tag{9}$$

and the time dependence disappears from the microwave irradiation term:

$$\begin{gathered}\hat{H}_{\mathrm{MW}}'=\frac{e^{-i\omega_{\mathrm{MW}}t}+e^{i\omega_{\mathrm{MW}}t}}{4}\sum_{k}a_{\mathrm{MW}}^{(k)}\left(e^{i\omega_{\mathrm{MW}}t}\hat{E}_{+}^{(k)}+e^{-i\omega_{\mathrm{MW}}t}\hat{E}_{-}^{(k)}\right)=\\=\frac{1}{4}\sum_{k}a_{\mathrm{MW}}^{(k)}\left(\hat{E}_{+}^{(k)}+e^{-2i\omega_{\mathrm{MW}}t}\hat{E}_{-}^{(k)}+e^{2i\omega_{\mathrm{MW}}t}\hat{E}_{+}^{(k)}+\hat{E}_{-}^{(k)}\right)\approx\frac{1}{4}\sum_{k}a_{\mathrm{MW}}^{(k)}\left(\hat{E}_{+}^{(k)}+\hat{E}_{-}^{(k)}\right)\end{gathered} \tag{10}$$

The inter-nuclear part given in Equations (3) and (4) remains unchanged because it commutes with electron operators. In the electron-nuclear part of the Hamiltonian only weak and pseudosecular terms survive ($\hat{E}_{\mathrm{Z}}\hat{N}_{\mathrm{Z}}$ and $\hat{E}_{\mathrm{Z}}\hat{N}_{\pm}$) and in the inter-electron part only the secular terms ($\hat{E}_{\mathrm{Z}}^{(m)}\hat{E}_{\mathrm{Z}}^{(k)}$ and $\hat{E}_{\pm}^{(m)}\hat{E}_{\mp}^{(k)}$) remain. The relaxation superoperator (whatever the model) should similarly be stripped of all terms that oscillate under the electron rotating frame transformation.

Simple forward time propagation under the resulting Liouvillian:

$$\hat{\hat{L}}=\hat{\hat{H}}_{\mathrm{Z}}'+\hat{\hat{H}}_{\mathrm{NN}}'+\hat{\hat{H}}_{\mathrm{EN}}'+\hat{\hat{H}}_{\mathrm{MW}}'+i\hat{\hat{R}}_{\mathrm{TH}} \tag{11}$$

where double hat signifies a commutation superoperator, primes indicate microwave frequency rotating frame and $\hat{\hat{R}}_{\mathrm{TH}}$ is thermalized (*i.e.* modified in such a way as to drive the system to the correct thermal equilibrium), gives the time dependence of the longitudinal magnetization on the *m*-th nucleus:

$$N_{\mathrm{Z}}^{(m)}(t) = < \hat{N}_{\mathrm{Z}}^{(m)} \mid \exp(-i\hat{\hat{L}}t) \mid \hat{\rho}_{\mathrm{eq}} > \tag{12}$$

and thus the time dependence of the DNP effect. In practical calculations an average over spin system orientations and distance distributions is usually needed.

If steady-state magnetization is required, a single sparse backslash operation suffices:

$$\begin{gathered} 0 = -i\hat{\hat{H}}\hat{\rho}_{\infty} + \hat{\hat{R}}\left(\hat{\rho}_{\infty} - \hat{\rho}_{\mathrm{eq}}\right) \quad \Rightarrow \quad \hat{\rho}_{\infty} = \left(-i\hat{\hat{H}} + \hat{\hat{R}}\right)^{-1}\hat{\hat{R}}\hat{\rho}_{\mathrm{eq}} \\ N_{\mathrm{Z}}^{(m)}(\infty) = < \hat{N}_{\mathrm{Z}}^{(m)} \mid \hat{\rho}_{\infty} > \end{gathered} \tag{13}$$

Unlike Equation (11), the relaxation superoperator in this expression should not be thermalized.

The implementation of the method described in this section is called "exact" in the *Spinach* library. Its greatest advantage is generality – all kinds of solid-state DNP simulations may be performed, including those that do not fall into the standard solid effect / cross effect classification and those involving nuclei of several different types. A purely computational downside is the fact that the norm of the resulting Liouvillian is of the order of nuclear Zeeman interaction (hundreds of MHz). To obtain a trajectory that lasts (typically) a few seconds either an expensive long-range propagator is required, or a few billion time steps. Neither is particularly difficult on modern hardware – example simulations included with *Spinach* accomplish this for over 20 spins in Liouville space.

Solid Effect DNP

We will now make three significant assumptions: that the system has only one electron (and therefore all inter-electron couplings vanish), that all nuclei in the system have the same Zeeman frequency ω_{N} and that the microwave frequency is equal to either the electron-nuclear double-quantum frequency $\omega_{\mathrm{E}} + \omega_{\mathrm{N}}$ or to the electron-nuclear zero-quantum frequency $\omega_{\mathrm{E}} - \omega_{\mathrm{N}}$. The Zeeman Hamiltonian in Equation (2) then becomes:

$$\hat{H}_{\mathrm{Z}} = \omega_{\mathrm{E}}\hat{E}_{\mathrm{Z}} + \omega_{\mathrm{N}}\sum_{m}\hat{N}_{\mathrm{Z}}^{(m)} \tag{14}$$

If we perform a rotating frame transformation with respect to this Hamiltonian, it formally disappears from the rotating frame description. The inter-nuclear interaction term acquires some frequencies:

$$\hat{H}'_{\mathrm{NN}} = \sum_{j<k}\sum_{m=-2}^{2} d_{jkm} e^{im\omega_{\mathrm{N}}t}\hat{T}_{m}^{(2)}(j,k) \tag{15}$$

and the microwave irradiation Hamiltonian transforms into:

$$\begin{gathered} \hat{H}'_{\mathrm{MW}} = \frac{a_{\mathrm{MW}}}{4}\left(e^{-i\omega_{\mathrm{MW}}t} + e^{i\omega_{\mathrm{MW}}t}\right)\left(e^{i\omega_{\mathrm{E}}t}\hat{E}_{+} + e^{-i\omega_{\mathrm{E}}t}\hat{E}_{-}\right) = \\ = \frac{a_{\mathrm{MW}}}{4}\left(e^{i[\omega_{\mathrm{E}}-\omega_{\mathrm{MW}}]t}\hat{E}_{+} + e^{-i[\omega_{\mathrm{E}}+\omega_{\mathrm{MW}}]t}\hat{E}_{-} + e^{i[\omega_{\mathrm{E}}+\omega_{\mathrm{MW}}]t}\hat{E}_{+} + e^{-i[\omega_{\mathrm{E}}-\omega_{\mathrm{MW}}]t}\hat{E}_{-}\right) \end{gathered} \tag{16}$$

By our assumption, the microwave frequency is close to the electron frequency, meaning that $\omega_{\mathrm{E}} + \omega_{\mathrm{MW}}$ is much larger than $\omega_{\mathrm{E}} - \omega_{\mathrm{MW}}$ and may be ignored:

$$\hat{H}'_{\mathrm{MW}} = \frac{a_{\mathrm{MW}}}{4}\left(e^{i\Delta t}\hat{E}_{+} + e^{-i\Delta t}\hat{E}_{-}\right), \qquad \Delta = \omega_{\mathrm{E}} - \omega_{\mathrm{MW}} = \pm\omega_{\mathrm{N}} \tag{17}$$

The electron-nuclear coupling term also acquires some frequencies:

$$\hat{H}''_{\mathrm{EN}}=\sum_k\left(-\frac{d_{ek,1}e^{i\omega_{\mathrm{N}}t}}{2}\hat{E}_{\mathrm{Z}}\hat{N}_{+}^{(k)}+\frac{d_{ek,-1}e^{-i\omega_{\mathrm{N}}t}}{2}\hat{E}_{\mathrm{Z}}\hat{N}_{-}^{(k)}+\sqrt{\frac{2}{3}}d_{ek,0}\hat{E}_{\mathrm{Z}}\hat{N}_{\mathrm{Z}}^{(k)}\right)\tag{18}$$

After collecting the terms in the rotating frame Hamiltonian and grouping them according to their frequency, we get (assuming $\Delta=+\omega_{\mathrm{N}}$):

$$\begin{aligned}
\hat{H}_{++}&=\frac{1}{2}\sum_{j<k}d_{jk,2}\hat{N}_{+}^{(j)}\hat{N}_{+}^{(k)}\\
\hat{H}_{+}&=-\frac{1}{2}\sum_k d_{ek,1}\hat{E}_{\mathrm{Z}}\hat{N}_{+}^{(k)}-\frac{1}{2}\sum_{j<k}d_{jk,1}\left(\hat{N}_{\mathrm{Z}}^{(j)}\hat{N}_{+}^{(k)}+\hat{N}_{+}^{(j)}\hat{N}_{\mathrm{Z}}^{(k)}\right)+\frac{a_{\mathrm{MW}}}{4}\hat{E}_{+}\\
\hat{H}_{0}&=\sqrt{\frac{2}{3}}\sum_k d_{ek,0}\hat{E}_{\mathrm{Z}}\hat{N}_{\mathrm{Z}}^{(k)}+\sqrt{\frac{2}{3}}\sum_{j<k}d_{jk,0}\left(\hat{N}_{\mathrm{Z}}^{(j)}\hat{N}_{\mathrm{Z}}^{(k)}-\frac{1}{4}\left(\hat{N}_{+}^{(j)}\hat{N}_{-}^{(k)}+\hat{N}_{-}^{(j)}\hat{N}_{+}^{(k)}\right)\right)\\
\hat{H}_{-}&=\frac{1}{2}\sum_k d_{ek,-1}\hat{E}_{\mathrm{Z}}\hat{N}_{-}^{(k)}+\frac{1}{2}\sum_{j<k}d_{jk,-1}\left(\hat{N}_{\mathrm{Z}}^{(j)}\hat{N}_{-}^{(k)}+\hat{N}_{-}^{(j)}\hat{N}_{\mathrm{Z}}^{(k)}\right)+\frac{a_{\mathrm{MW}}}{4}\hat{E}_{-}\\
\hat{H}_{--}&=\frac{1}{2}\sum_{j<k}d_{jk,-2}\hat{N}_{-}^{(j)}\hat{N}_{-}^{(k)}
\end{aligned}\tag{19}$$

These terms are generated automatically in Spinach from user-supplied electron and nuclear coordinates. Our final Liouvillian is:

$$\hat{\hat{H}}(t)=e^{-2i\omega_{\mathrm{N}}t}\hat{\hat{H}}_{--}+e^{-i\omega_{\mathrm{N}}t}\hat{\hat{H}}_{-}+\hat{\hat{H}}_{0}+e^{i\omega_{\mathrm{N}}t}\hat{\hat{H}}_{+}+e^{2i\omega_{\mathrm{N}}t}\hat{\hat{H}}_{++}+i\hat{\hat{R}}\tag{20}$$

We are now all set to apply the average Hamiltonian theory by cumulant averaging over the nuclear Zeeman oscillation period. Simply using the Waugh's average Hamiltonian theory for the commutation superoperators (and packing $i\hat{\hat{R}}$ into $\hat{\hat{H}}_0$ for convenience), we get:

$$\begin{aligned}
\hat{\hat{H}}^{(0)}&=\frac{\omega_{\mathrm{N}}}{2\pi}\int_0^{2\pi/\omega_{\mathrm{N}}}\hat{\hat{H}}(t)\,dt=\hat{\hat{H}}_0\\
\hat{\hat{H}}^{(1)}&=-\frac{i}{2}\frac{\omega_{\mathrm{N}}}{2\pi}\int_0^{2\pi/\omega_{\mathrm{N}}}dt_2\int_0^{t_2}dt_1\left[\hat{\hat{H}}(t_2),\hat{\hat{H}}(t_1)\right]\\
\hat{\hat{H}}^{(2)}&=-\frac{1}{6}\frac{\omega_{\mathrm{N}}}{2\pi}\int_0^{2\pi/\omega_{\mathrm{N}}}dt_3\int_0^{t_3}dt_2\int_0^{t_2}dt_1\left(\left[\hat{\hat{H}}(t_3),\left[\hat{\hat{H}}(t_2),\hat{\hat{H}}(t_1)\right]\right]+\left[\left[\hat{\hat{H}}(t_3),\hat{\hat{H}}(t_2)\right],\hat{\hat{H}}(t_1)\right]\right)
\end{aligned}\tag{21}$$

and so on – after some extra non-commutative patterns are defined, Mathematica crunches these expressions in seconds. Second-order averaging is generally sufficient in practical calculations.

The result is an average Hamiltonian with eigenvalues determined by the amplitudes of electron-nuclear interactions (kHz to MHz) rather than nuclear Zeeman frequencies (around GHz) meaning that much longer time steps can be taken at the propagation stage. The downside is a loss of generality and a significant potential for breakdown in the various approximations.