

Addendum B: ESR Spectrum of TEMPO

This addendum provides additional material to Sections 3.3.1 to 3.3.3 of Essentials of Dynamic Nuclear Polarization, Spindrift Publications, 2016—to be denoted henceforward shortly as *EofDNP*. It presents a more precise determination of the ESR spectrum of TEMPO dissolved in a glass of butanol.

As in *EofDNP* we determine the ESR spectrum in two steps. In the first step we calculate the spectrum of just the electron spin $S = \frac{1}{2}$ and the spin $I = 1$ of the ^{14}N nucleus in the nitroxide (NO^\bullet) group. In the second step we add the remaining interactions of the electron spin by convoluting this spectrum with a Gaussian.

In Section 3.3.2 of *EofDNP* we introduced two approximations in the first step. Except for A_{zz} we skipped all components of the hyperfine coupling between the electron spin $S = \frac{1}{2}$ and the spin $I = 1$ of the ^{14}N nucleus. Furthermore we skipped the Zeeman interaction of this nuclear spin. The more precise determination presented here does not invoke these two approximations and determines the ESR spectrum from the exact eigenstates and energy levels of the Hamiltonian describing the electron spin and the spin of the ^{14}N nucleus.

1. Principles of Calculating the Spectrum

The calculation of the exact ESR spectrum starts with the Hamiltonian

$$\mathcal{H} = -\hbar\mathbf{B}_0 \cdot \boldsymbol{\gamma} \cdot \mathbf{S} - \hbar\gamma\mathbf{B}_0 \cdot \mathbf{I} + \hbar\mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \quad (1)$$

describing the electron spin $S = \frac{1}{2}$ and the spin $I = 1$ of the ^{14}N nucleus. Here the first term is the Zeeman interaction of the electron spin with the externally applied static magnetic field \mathbf{B}_0 , the second term the Zeeman interaction of the nuclear spin with \mathbf{B}_0 and the last term the hyperfine interaction between the electron spin and the nuclear spin. In these terms \hbar is Planck's constant, $\boldsymbol{\gamma}$ the gyromagnetic ratio tensor of the electron spin, γ the gyromagnetic ratio of the ^{14}N spin and \mathbf{A} the hyperfine tensor. In TEMPO the principal axes of the gyromagnetic ratio tensor and the hyperfine tensor coincide. On these axes their components are

$$\boldsymbol{\gamma} = \begin{pmatrix} \gamma_{xx} & 0 & 0 \\ 0 & \gamma_{yy} & 0 \\ 0 & 0 & \gamma_{zz} \end{pmatrix} \quad (2)$$

and

$$\mathbf{A} = \begin{pmatrix} A_{xx} & 0 & 0 \\ 0 & A_{yy} & 0 \\ 0 & 0 & A_{zz} \end{pmatrix}. \quad (3)$$

We determine the ESR spectrum using first order perturbation theory. We choose the Hamiltonian (1) as the zero order term in the perturbation expansion and calculate its eigenstates and energy levels. Next we add a first order term

$$\mathcal{H}_m = -2\hbar\mathbf{B}_1 \cdot \boldsymbol{\gamma} \cdot \mathbf{S} \cos \omega_m t \quad (4)$$

representing a microwave field $2\mathbf{B}_1 \cos \omega_m t$ with an amplitude $2|\mathbf{B}_1|$ and a frequency ω_m perpendicular to \mathbf{B}_0 . The ESR spectrum then follows from the transitions that this first order term induces between the eigenstates of the Hamiltonian (1).

As a first step we determine matrix representations \mathcal{M}_0 of the Hamiltonian (1) and \mathcal{M}_m of and \mathcal{H}_m on a basis of eigenstates

$$\begin{array}{c} |m_S, m_I\rangle \\ \hline |+\frac{1}{2}; +1\rangle \\ |+\frac{1}{2}, 0\rangle \\ |+\frac{1}{2}, -1\rangle \\ |-\frac{1}{2}, +1\rangle \\ |-\frac{1}{2}, 0\rangle \\ |-\frac{1}{2}, -1\rangle \end{array} \quad (5)$$

of the Z-components S_Z and I_Z of the electron spin and the ^{14}N spin. Next, we determine the unitary operator \mathcal{U}^\dagger and its hermitian conjugate \mathcal{U} diagonalizing \mathcal{M}_0 . Then the diagonal elements $\hbar\omega_m$ of

$$\mathcal{U}^\dagger \cdot \mathcal{M}_0 \cdot \mathcal{U} = \mathcal{E}, \quad (6)$$

are the energy levels, and the columns of \mathcal{U} are the eigenvectors of \mathcal{M}_0 . In the following step we transform the matrix representation \mathcal{M}_m of \mathcal{H}_m with the unitary operator \mathcal{U}^\dagger :

$$\mathcal{U}^\dagger \cdot \mathcal{M}_m \cdot \mathcal{U} = \mathcal{M}'_m \quad (7)$$

The non-diagonal elements $(\mathcal{M}'_m)_{nm}$ of this matrix cause transitions between energy levels $\hbar\omega_{nn}$ and $\hbar\omega_{mm}$ at a rate proportional to

$$|(\mathcal{M}'_m)_{nm}|^2 \delta(\omega_m - |\omega_{nn} - \omega_{mm}|) \quad (8)$$

The ESR spectrum is then obtained by plotting the squares of all non-diagonal matrix elements $|(\mathcal{M}'_m)_{nm}|^2$ as a function of the energy differences $|\omega_{nn} - \omega_{mm}|$.

From this point onward we follow the same procedure as in Section 3.3.1 of *EofDNP*. We extend the treatment to TEMPO dissolved in a glass, so the TEMPO molecules are oriented randomly, or, inversely, the magnetic field is oriented randomly with respect to principal axes. We introduce spherical coordinates

$$\mathbf{B}_0 = \begin{pmatrix} B_{0X} \\ B_{0Y} \\ B_{0Z} \end{pmatrix} = B_0 \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix}. \quad (9)$$

The probability that the magnetic field is oriented in direction (θ, ϕ) is proportional to the solid angle

$$d\Omega = d \cos \theta d\phi \quad (10)$$

We can therefore extend the ESR spectrum to TEMPO dissolved in a glass by integrating the spectra obtained in the previous step over ϕ and $\cos \theta$.

We finish the determination of the ESR spectrum adding the hyperfine and super-hyperfine interaction with the other nuclear spins in the sample. As in Section 3.3.3 of *EofDNP* we assume that these two interactions lead to Gaussian broadening

$$g_{SI}(\omega) = \frac{1}{\sqrt{2\pi\Delta_A^2}} \exp\left(-\frac{\omega^2}{2\Delta_A^2}\right) \quad (11)$$

of the spectrum. The full ESR spectrum is then the convolution

$$g(\omega) = \int_{-\infty}^{\infty} d\omega' g_0(\omega') g_{SI}(\omega - \omega') \quad (12)$$

of the spectrum $g_0(\omega)$ calculated above and the Gaussian broadening $g_{SI}(\omega)$.

2. Matrix Representations

We continue with some details of the procedure outlined above. In this section we consider the matrix representation of the Hamiltonian (1) on a basis of eigenstates (5) of S_Z and I_Z . To shorten the notation we define the frequency vector with components

$$\begin{pmatrix} \omega_{0S}^X \\ \omega_{0S}^Y \\ \omega_{0S}^Z \end{pmatrix} = - \begin{pmatrix} \gamma_{XX} B_{0X} \\ \gamma_{YY} B_{0Y} \\ \gamma_{ZZ} B_{0Z} \end{pmatrix} = - \begin{pmatrix} \gamma_{XX} B_0 \sin \theta \cos \phi \\ \gamma_{YY} B_0 \sin \theta \sin \phi \\ \gamma_{ZZ} B_0 \cos \theta \end{pmatrix} \quad (13)$$

and write

$$\begin{aligned} \omega_{0S}^{\pm} &= \omega_{0S}^X \pm i\omega_{0S}^Y, \\ \omega_{0I}^{\pm} &= \gamma_I (B_{0X} \pm iB_{0Y}), \\ \omega_{0I}^Z &= \gamma_I B_{0Z}. \end{aligned} \quad (14)$$

Then, on a basis of eigenstates (5) the electron Zeeman energy is represented by

$$\frac{1}{2} \hbar \begin{pmatrix} \omega_{0S}^Z & 0 & 0 & \omega_{0S}^- & 0 & 0 \\ 0 & \omega_{0S}^Z & 0 & 0 & \omega_{0S}^- & 0 \\ 0 & 0 & \omega_{0S}^Z & 0 & 0 & \omega_{0S}^- \\ \omega_{0S}^+ & 0 & 0 & -\omega_{0S}^Z & 0 & 0 \\ 0 & \omega_{0S}^+ & 0 & 0 & -\omega_{0S}^Z & 0 \\ 0 & 0 & \omega_{0S}^+ & 0 & 0 & -\omega_{0S}^Z \end{pmatrix} \quad (15)$$

and the nuclear Zeeman energy by

$$\frac{1}{2} \hbar \begin{pmatrix} -2\omega_{0I}^Z & \omega_{0I}^- \sqrt{2} & 0 & 0 & 0 & 0 \\ \omega_{0I}^+ \sqrt{2} & 0 & \omega_{0I}^- \sqrt{2} & 0 & 0 & 0 \\ 0 & \omega_{0I}^+ \sqrt{2} & 2\omega_{0I}^Z & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\omega_{0I}^Z & \omega_{0I}^- \sqrt{2} & 0 \\ 0 & 0 & 0 & \omega_{0I}^+ \sqrt{2} & 0 & \omega_{0I}^- \sqrt{2} \\ 0 & 0 & 0 & 0 & \omega_{0I}^+ \sqrt{2} & 2\omega_{0I}^Z \end{pmatrix}. \quad (16)$$

To obtain the matrix representation of the hyperfine interaction, we introduce step operators

$$\begin{aligned} S_{\pm} &= S_x \pm iS_y, \\ I_{\pm} &= I_x \pm iI_y \end{aligned} \quad (17)$$

and introduce the short notation

$$\begin{aligned} A_{++} &= A_{XX} + A_{YY}, \\ A_{--} &= A_{XX} - A_{YY}, \end{aligned} \quad (18)$$

allowing us to rewrite it as

$$\begin{aligned} \hbar \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} &= \hbar (I_x A_{XX} S_x + I_y A_{YY} S_y + I_z A_{ZZ} S_z) \\ &= \hbar \left(\frac{1}{4} (I_+ S_+ + I_- S_-) A_{--} + \frac{1}{4} (I_+ S_- - I_- S_+) A_{++} + I_z A_{ZZ} S_z \right) \end{aligned} \quad (19)$$

Thus we find for the matrix representation of the hyperfine interaction;

$$\frac{1}{4} \hbar \begin{pmatrix} 2A_{ZZ} & 0 & 0 & 0 & A_{--}\sqrt{2} & 0 \\ 0 & 0 & 0 & A_{++}\sqrt{2} & 0 & A_{--}\sqrt{2} \\ 0 & 0 & -2A_{ZZ} & 0 & A_{++}\sqrt{2} & 0 \\ 0 & A_{++}\sqrt{2} & 0 & -2A_{ZZ} & 0 & 0 \\ A_{--}\sqrt{2} & 0 & A_{++}\sqrt{2} & 0 & 0 & 0 \\ 0 & A_{--}\sqrt{2} & 0 & 0 & 0 & 2A_{ZZ} \end{pmatrix}. \quad (20)$$

We finish this section with the matrix representation of the interaction (4) of the electron spin with the microwave field. Just as for the static magnetic field \mathbf{B}_0 we introduce a frequency vector

$$\begin{pmatrix} \omega_{1S}^x \\ \omega_{1S}^y \\ \omega_{1S}^z \end{pmatrix} = - \begin{pmatrix} \gamma_{XX} B_{1X} \\ \gamma_{YY} B_{1Y} \\ \gamma_{ZZ} B_{1Z} \end{pmatrix} = - \begin{pmatrix} \gamma_{XX} B_1 \sin \theta \cos \phi \\ \gamma_{YY} B_1 \sin \theta \sin \phi \\ \gamma_{ZZ} B_1 \cos \theta \end{pmatrix} \quad (21)$$

and shorten our notation, writing

$$\omega_{1S}^{\pm} = \omega_{1S}^x \pm i\omega_{1S}^y. \quad (22)$$

Then, on a basis of eigenstates (5) of S_z and I_z the interaction of the electron spin with the microwave field is represented by

$$2\hbar \begin{pmatrix} \omega_{1S}^z & 0 & 0 & \omega_{1S}^- & 0 & 0 \\ 0 & \omega_{1S}^z & 0 & 0 & \omega_{1S}^- & 0 \\ 0 & 0 & \omega_{1S}^z & 0 & 0 & \omega_{1S}^- \\ \omega_{1S}^+ & 0 & 0 & -\omega_{1S}^z & 0 & 0 \\ 0 & \omega_{1S}^+ & 0 & 0 & -\omega_{1S}^z & 0 \\ 0 & 0 & \omega_{1S}^+ & 0 & 0 & -\omega_{1S}^z \end{pmatrix} \cos \omega_m t. \quad (23)$$

The sum of (15), (16) and (20) is the matrix \mathcal{M}_0 that we wish to diagonalize in the procedure described above, and (23) is the matrix \mathcal{M}_m that we wish to transform with the unitary operator \mathcal{U}^\dagger , in order to determine the ESR spectrum.

3. Numerical Methods

We use numerical methods to determine the eigenvalues of the matrix \mathcal{M}_0 and the unitary operators \mathcal{U}^\dagger and \mathcal{U} diagonalizing it. The matrices involved are complex, and the first step consists of transforming the problem to real arithmetic. We follow the method described in [1] and notice that complex numbers $a + ib$ obey the same multiplication rules as real asymmetric 2×2 matrices

$$\begin{pmatrix} a & -b \\ b & a \end{pmatrix} \quad (24)$$

As a result a Hermitian $n \times n$ matrix $\mathcal{A} = \mathbf{A} + i\mathbf{B}$ transforms in the same way as a real symmetric $2n \times 2n$ matrix

$$\begin{pmatrix} \mathbf{A} & -\mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \quad (25)$$

To show this we first transform $\mathcal{A} = \mathbf{A} + i\mathbf{B}$ with the unitary matrix $\mathcal{U}^\dagger = \mathbf{U} - i\mathbf{V}$:

$$\mathcal{U}^\dagger \cdot \mathcal{A} \cdot \mathcal{U} = (\mathbf{U} - i\mathbf{V})(\mathbf{A} + i\mathbf{B})(\mathbf{U} + i\mathbf{V}) = (\mathbf{C} + i\mathbf{D}) = \mathcal{C}, \quad (26)$$

where

$$\begin{aligned} \mathbf{C} &= \mathbf{U}\mathbf{A}\mathbf{U} - \mathbf{U}\mathbf{B}\mathbf{V} + \mathbf{V}\mathbf{B}\mathbf{U} + \mathbf{V}\mathbf{A}\mathbf{V} \\ \mathbf{D} &= \mathbf{U}\mathbf{B}\mathbf{U} + \mathbf{U}\mathbf{A}\mathbf{V} - \mathbf{V}\mathbf{A}\mathbf{U} + \mathbf{V}\mathbf{B}\mathbf{V}. \end{aligned} \quad (27)$$

Next we write $\mathcal{A} = \mathbf{A} + i\mathbf{B}$ as a $2n \times 2n$ matrix (25), $\mathcal{U}^\dagger = \mathbf{U} - i\mathbf{V}$ as a $2n \times 2n$

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & \mathbf{A} \end{pmatrix} \quad (28)$$

and perform the transformation again. We find:

$$\begin{pmatrix} \mathbf{U} & \mathbf{V} \\ -\mathbf{V} & \mathbf{U} \end{pmatrix} \begin{pmatrix} \mathbf{A} & -\mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{U} & -\mathbf{V} \\ \mathbf{V} & \mathbf{U} \end{pmatrix} = \begin{pmatrix} \mathbf{C} & -\mathbf{D} \\ \mathbf{D} & \mathbf{C} \end{pmatrix}. \quad (29)$$

This observation enables us to proceed as follows. We write the 6×6 Hermitian matrix representation of \mathcal{H}_0 as a 12×12 real matrix in the shape (25). Next we use Jacobi transformations to determine the real orthogonal 12×12 matrix which diagonalizes this real 12×12 matrix. This provides the eigenvalues of \mathcal{H}_0 needed to insert in (8). Next we also write the 6×6 Hermitian matrix representation (23) of \mathcal{H}_m as a 12×12 real matrix in the shape (25) and transform it using (29). From the result we finally determine the squares of the transition matrix elements needed to insert in (8).

4. Example Result

Figure 1 presents a result of the procedure described above. The calculation is performed for an externally applied magnetic field $B_0 = 3.4$ T. For the components of the

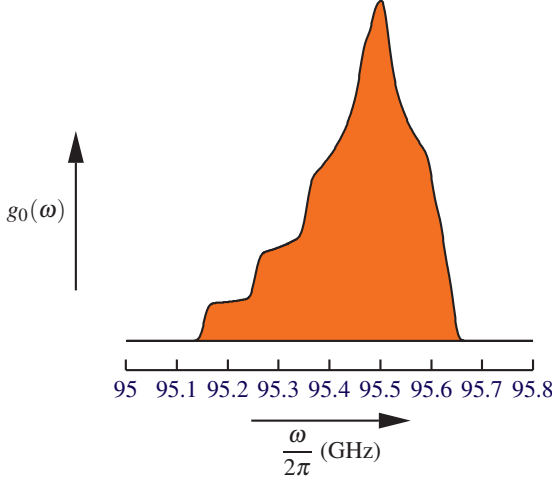


Figure 1: Theoretical ESR spectrum for TEMPO dissolved in a glass of butanol. The static magnetic field is set at 3.4 T. The dotted curve presents the spectrum before convolution with Gaussian broadening by hyperfine and super-hyperfine interaction. The drawn curve shows the spectrum after convolution with Gaussian broadening.

gyromagnetic ratio tensor and the hyperfine tensor we use the values given in [2] for TEMPO in butanol:

$$\begin{aligned}
 \gamma_{XX} &= -2\pi \times 28.124 \cdot 10^9 \text{ s}^{-1} \text{ T}^{-1}, \\
 \gamma_{YY} &= -2\pi \times 28.084 \cdot 10^9 \text{ s}^{-1} \text{ T}^{-1}, \\
 \gamma_{ZZ} &= -2\pi \times 28.016 \cdot 10^9 \text{ s}^{-1} \text{ T}^{-1}
 \end{aligned}
 \tag{30}$$

and

$$\begin{aligned}
 A_{XX} &= 2\pi \times 20.5 \cdot 10^6 \text{ s}^{-1}, \\
 A_{YY} &= 2\pi \times 17.7 \cdot 10^6 \text{ s}^{-1}, \\
 A_{ZZ} &= 2\pi \times 100.9 \cdot 10^6 \text{ s}^{-1}.
 \end{aligned}
 \tag{31}$$

Furthermore we insert the value $\gamma_I = +2\pi \times 3.0777 \cdot 10^6 \text{ s}^{-1} \text{ T}^{-1}$ for the gyromagnetic ratio of ^{14}N —as calculated from [3]. Finally we estimate the second moment of the Gaussian broadening to be the same as in Section 3.3.3 of *EofDNP*:

$$\Delta_A^2 = 0.2 \cdot 10^{16} \text{ s}^{-2}.
 \tag{32}$$

Figure 1 shows the result of this procedure for a static magnetic set at 3.4 T. For comparison with experiment, Figure 2 reproduces Figure 3.12 from *EofDNP*. It represents the the ESR spectrum $g(\omega)$ as a function of $\omega/2\pi$ for OH-TEMPO dissolved in frozen water. The curve is obtained by integrating the experimental results for the derivative of $g(\omega)$ presented in [4]. The magnetic field is 3.4 T. Except that the experimental spectrum is somewhat further smoothed, the two ESR spectra appear to be the same.

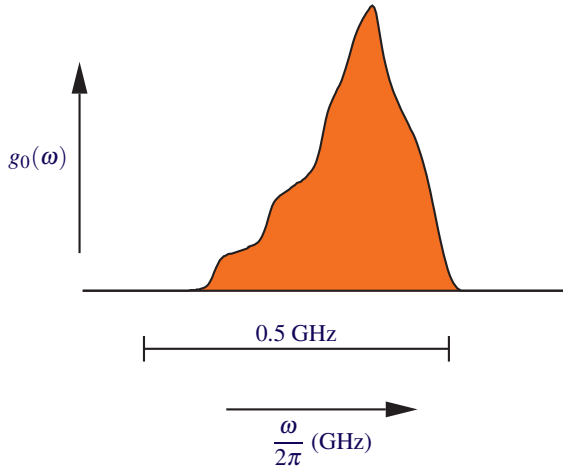


Figure 2: The ESR spectrum $g(\omega)$ as a function of $\omega/2\pi$ for OH-TEMPO dissolved in frozen water. The curve is obtained by integrating the experimental results for the derivative of $g(\omega)$ presented in [4]. The magnetic field is 3.4 T.

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