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# A Rigorous Procedure for Calculation of Pulsed EPR Signals with Relaxation

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# Abstract

A procedure is developed to calculate pulsed electron paramagnetic resonance (EPR) signals with relaxation rigorously. It can be carried out within a reasonable time on a PC using Fortran or Matlab, not requiring any sophisticated software. The flow chart for this kind of simulation is included. It is illustrated here numerically, as coded in Matlab, to calculate the twodimensional spin echo correlation spectroscopy (2D-SECSY) and two-dimensional electron-electron double-resonance (2D-ELDOR) signals for two cases: (i) a coupled electron-nuclear system with the electron spin (S=  $\frac{1}{2}$ ) and nuclear spin (I=  $\frac{1}{2}$ ) corresponding to the experimental results of Lee, Patyal and Freed [1] in a malonic acid single crystal, and (ii) 2D-ELDOR signal obtained for an electron-electron dipolar-coupled system of two nitroxide radicals in a malonic acid single crystal, with hyperfine interactions included, for a proposed experiment, intended for distance measurements, important for biological systems. The limits of applicability of the algorithm used here are discussed.

**Keywords:** Pulsed EPR, Two-dimensional spin-echo-correlation spectroscopy (2D-SECSY), Two-dimensional electron-electron double-resonance (2D-ELDOR), Stochastic Liouville equation (SLE), Electron-electron dipolar-coupled system, Distance measurements in biological systems.

# Introduction

Pulsed electron paramagnetic resonance (EPR) is a powerful technique that can be exploited to reveal the electronic and geometric structures in detail around paramagnetic centers, including nanoscale environments. It has a wide range of applications in biology, chemistry, physics and materials science [1-5]. It can distinguish weak interactions between electron spins, as well as those between electron and nuclear spins, not resolved by continuous wave (CW) EPR. A rigorous simulation of pulsed EPR spectra is necessary for a quantitative analysis to extract correctly information on electronic and geometric structure from pulsed EPR data.

This paper is devoted to the very important subject of pulsed EPR in the presence of relaxation. In most cases, relaxation processes are ignored because of high conceptual and computational complexity of a proper description of relaxation processes. This paper provides a comprehensive theoretical treatment including a detailed description of relaxation process.

There are availabletwo open-source packages that are implemented in Matlab, which are much moregeneral than the approach introduced in the present manuscript, namely SPINACH [6] and SPIDYAN [7]. The present procedure, on the other hand, offers an advantage in that within the framework of its applicability it can be carried out on a lap top within a short time using Matlab or Fortran, and does not require any costly software. From this point of view, it is felt that this work serves a useful purpose to practitioners of EPR pulse spectroscopy needing to treat relaxation rigorously in a simple manner.

In order to take into account relaxation rigorously, it is imperative to use Liouvillevon Neumann (LVN) equation, which is an exact quantum-mechanical equation of motion for the density matrix. The Stochastic Liouville Equation (SLE) is a stochastic version of the LVN equation. This equation is valid even for relatively slow random processes, and is therefore especially suitable for EPR, where the natural timescale is short so that the random processes are not usually fast on this time scale. There are three cases, where SLE is applicable:

(a) Time-independent SLE, which does not include any time-dependent Hamiltonians;

(b) Time-dependent SLE, which includes in addition to (a) a

relaxation term and a time-dependent, but not stochastically time dependent, Hamiltonian, e.g. a Hamiltonian representing the pulses. *This is the only case that will be treated in this paper*.

(c) The SLE includes time-independent and time-dependent, as well as stochastically time-dependent, Hamiltonians, but does not include relaxation. Here one uses the SLE when due to the time scale of the fluctuations of the Hamiltonians itself, it is impossible to explicitly define relaxation rates, e.g. as that proposed in Table IV and Appendix B of LPF[1].

It is noted here that SLE equation has been used to describe ESR and NMR properties of high spin quantum number systems (transition metal ions) including zero-field splitting interactions, see e.g. [8-9].

A numerical simulation technique for calculating electron spin and electron-nuclear spin-echo signals detected in pulsed EPR experiments has been exploited here, based on SLE including relaxation, as described by the case (b) above. The SLE is treated here as a matrix differential equation, by expanding the spin density matrix in a chosen basis set of functions, and the SLE is then transformed into a matrix differential equation in the expansion coefficients. The theoretical approach will here be numerically implemented; the applied algorithm and individual computational steps will be thoroughly discussed, and illustrated by examples.

The organization of this paper is as follows. The general procedure for coding SLE for pulsed EPR experiments is developed in the next Section. Thereafter, the details of calculation of 2-D (two dimensional) SECSY and 2-D ELDOR signals, including selection of coherent electron pathway, are given in the following Section. For illustration, simulations of pulsed EPR spectra for 2D-SECSY and 2D-ELDOR experiments are carried out in appendix A for the case discussed by Lee, Patyal and Freed[1] (hereafter LPF) in a malonic acid single crystal. In addition, the technique is illustrated by calculation of 2D-ELDOR signal for dipolar-coupled nitroxide radicals in malonic single crystal, which can be exploited to estimate distances between two nitroxide radicals in appendix B. The conclusions and future perspectives are presented in Sections carrying those titles.

# **Solution of SLE**

The evolution of the density matrix  $\rho$ , taking into account relaxation effects is expressed in Liouville space as follows [10-14].

$$\frac{d}{dt}\rho(t) = -i\left[\widehat{H},\rho(t)\right] - \widehat{\widehat{\Gamma}}(\rho(t) - \rho_0)$$
(1)

In Eq. (1),  $\hat{H} = \hat{H}_0 + \hat{H}_1$  is the Hamiltonian operator, where  $\hat{H}_0$ and  $\hat{H}_1$  are its time-independent and time-dependent parts, respectively;  $\hat{\Gamma}$  is the relaxation superoperator, and assumed to be time independent here. (Throughout the paper, the single and double carets "and "a" will be used to denote the operator and the superoperator, respectively.) In Eq. (1)  $\rho_0$  is the initial thermal equilibrium density matrix, governed by the Boltzmann distribution:

$$\rho_{0} = \frac{\left[\exp\left(-\hbar\widehat{H}/kT\right)\right]}{Tr\left[\exp\left(-\hbar\widehat{H}/kT\right)\right]} \propto S_{Z}$$
(2)

Equation (1) is an operator equation, which can be expressed as a matrix equation in a given set of operators,  $|i\rangle\langle j|$ ; i, j = 1, 2, ..., n where  $|i\rangle$  are the eigenvectors of  $\widehat{H}$ . The coefficients,  $\rho_{ij}$ ,  $\widehat{H}_{ij}$  in the expansion of the operators  $\rho$  and  $\widehat{H}$  in this basis, respectively, are then used to write the corresponding matrix equation.

The difference between the time-dependent density matrix and the equilibrium density matrix is denoted as  $\chi(t) \equiv \rho(t) - \rho_0$ . . In view of Eq. (2)  $\rho_0$  commutes with  $\widehat{H}$ . Then Eq. (1) can be expressed as follows:

$$\frac{d}{dt}\chi(t) = -i\left[\widehat{H},\chi(t)\right] - \widehat{\Gamma}\chi(t)$$
(3)

# Evolution of density matrix in the absence of pulse (free evolution)

Because SLE, as given by Eq.(3), is a matrix differential equation in a chosen basis, where the operators are represented as matrices,  $\chi(t)$  can be considered as a column in the basis space, as follows:

$$\frac{d}{dt}col(\chi(t)) = -col\left\{i\left[\widehat{H},\chi(t)\right] + \widehat{\Gamma}\chi(t)\right\}$$
(4)

Here col(X) denotes the columnization of the matrix X formed by stacking the columns of X into a single column vector. It is then a  $n^2 \times 1$  matrix.

Defining  $\hat{\hat{x}}$  as the column vector of dimension  $n^2 \times 1$ :

$$\widehat{\widehat{\chi}} \equiv col(\chi(t)) \tag{5}$$

The right side of Eq. (4) can be expressed using the property  $col(ABC) = (C^T \otimes A) col(B)$  [15] as follows:

$$col\left[\widehat{H},\chi\right] = \left(I_n \otimes \widehat{H} - \widehat{H}^T \otimes I_n\right) col(\chi)$$
(6)

where  $I_n$  is  $n \times n$  unit matrix, and  $\widehat{H}^T$  denotes the matrix transpose of  $\widehat{H}$ .

Define

$$\hat{\hat{L}} \equiv I_n \otimes \hat{H} - \hat{H}^T \otimes I_n \tag{7}$$

which is the Liouville superoperator matrix or Liouvillian with the dimension  $n^2 \times n^2$ 

As for the second term on the right-hand side of Eq.(4), it can be expressed in the matrix form as:

$$\hat{\tilde{R}}\hat{\chi} = col(\hat{\Gamma}\chi(t))$$
(8)

where the double-subscript matrix  $\hat{R}$  is derived from the 4-subscript matrix  $\hat{\hat{\Gamma}}$  as

$$\widehat{\widehat{R}}_{\alpha\times n+\beta,\alpha'\times n+\beta'} = \widehat{\widehat{\Gamma}}_{\alpha\beta\alpha'\beta'}$$
(9)

and  $\hat{\mathbf{R}}$  is the relaxation superoperator matrix in Liouville space, introduced phenomenologically.

Combining Eq.(4) for the SLE with (6) and (8), the SLE is expressed in matrix form as follows:

$$\frac{d}{dt}\hat{\hat{\chi}} = -i\hat{\hat{L}}\hat{\hat{\chi}} - \hat{\hat{R}}\hat{\hat{\chi}}$$
(10)

Defining now the generalized Liouville superoperator to include also the relaxation superoperator:

$$\widehat{\hat{L}}' \equiv i\widehat{\hat{L}} + \widehat{\hat{R}}$$
(11)

one can express Eq. (10) as follows:

$$\frac{d}{dt}\hat{\hat{\chi}} = -\hat{\hat{L}}\hat{\hat{\chi}}$$
(12)

The solution of Eq. (12) is

$$\widehat{\hat{\chi}}(t) = e^{-(t-t_0)\widehat{\mathcal{L}}}\widehat{\hat{\chi}}(t_0)$$
(13)

In Eq. (13)  $\hat{\chi}(t_0)$  is the density matrix at the beginning of the evolution.

# Evolution of density matrix under the action of a pulse

During the pulse the density matrix is changed due to the combined action of  $\widehat{H} = \widehat{H}_0 + \widehat{H}_1$ , where  $\widehat{H}_0$  is the static Hamiltonian, e.g. that given by Eq. (A.2) below, and the pulse,  $\widehat{H}_1$  is expressed as

$$\widehat{H}_{1}(t) = \widehat{\varepsilon}(t) = B_{1}\gamma_{e} \left(S_{x}\cos\phi + S_{y}\sin\phi\right) \mathbf{1}_{n} = \frac{\omega}{2} \left(e^{-i\phi}S_{+} + e^{i\phi}S_{-}\right) \mathbf{1}_{n} \quad (14)$$

where  $\hat{\boldsymbol{\varepsilon}}(t)$  is the irradiating microwave pulse with intensity,  $B_1 = \omega/\gamma_e$  and phase  $\phi$ . The tip angle  $\theta$  over time t during the pulse is  $\theta = \omega t = B_1 \gamma_e t$ .

Assuming  $|\widehat{H}_0 + \widehat{H}_1| \gg |\widehat{\Gamma}|$ , the SLE as given in Eq. (1) then reduces to



**Figure 1:** (Top) Pulse sequence for obtaining 2D-SECSY signal. The  $t_1$  time between the two pulses and  $t_2$  time from the echo are stepped. (Bottom) Coherence pathways used for calculating 2D-SECSY signal for an unpaired electron (S =  $\frac{1}{2}$ ) interacting with a single nucleus (I =  $\frac{1}{2}$ ). p is the coherence order, which represents transverse magnetization, corresponding to spins rotating in a plan perpendicular to the external field [19].

$$\frac{d}{dt}\rho(t) = -i\left[\widehat{H}_0 + \widehat{H}_1(t),\rho(t)\right]$$
(15)

Columnzing the  $n \times n$  matrix as a  $n^2 \times 1$  column vector, and following the same procedure that led to Eq. (6), one can express Eq. (15) as follows:

$$\frac{d\hat{\hat{\rho}}}{dt} = -\hat{\hat{P}}\hat{\hat{\rho}}$$
(16)

where the propagator, taking into account the static Hamiltonian and the pulse, is

$$\widehat{\widehat{P}} = \left[ I_n \otimes \left( \widehat{H}_0 + \widehat{H}_1(t) \right) - \left( \widehat{H}_0 + \widehat{H}_1(t) \right)^T \otimes I_n \right]$$
(17)

The solution of Eq. (16) is

$$\widehat{\widehat{\rho}}(t) = e^{-(t-t_0)\widehat{\widehat{\rho}}} \widehat{\widehat{\rho}}(t_0)$$
(18)

Here  $\hat{\hat{\rho}}(t_0)$  is the initial density matrix when the pulse is applied.

#### Simulation procedure

The algorithm procedure for calculation of pulse EPR signal is as follows. The time evolution of the density matrix includes evolution under the action of the static Hamiltonian,  $H_0$ , in the absence of pulses, and under the action of pulse, as illustrated in appendix A and B.

Calculation of the final density matrix,  $\rho_f$ , corresponding to the coherence pathways (Figures 1 and 2), uses Eqs. (13) and (18) for the evolution of the density matrix in the absence and presence of pulses, respectively. In particular, in the present case, the calculations are made for the pulse sequences shown in Figures 1 and 2 for the coherent pathway  $S_{c-}$ . In these cases, there are used two times,  $t_1$  and  $t_2$ , for time-domain signals, which are stepped in the experiment (Figures 1 and 2). The Fourier transform (FT) of the two-dimensional (2D) time domain signal  $S(t_1,t_2)$ , is the corresponding 2D-FT signal,  $S(\omega_1, \omega_2)$ .



**Figure 2:** (Top) Pulse sequence for obtaining 2D-ELDOR signal. The  $t_1$  time between the first two pulses and  $t_2$  time from the echo are stepped. Here  $T_m$  is the mixing time. (Bottom) Coherence pathways used for calculating 2D-ELDOR signal for an unpaired electron (S = ½) interacting with a single nucleus (I = ½). p is the coherence order, which represents transverse magnetization, corresponding to spins rotating in a plan perpendicular to the external field [19].

The 2D time-domain signal is calculated from  $\rho_f$  as follows:

$$S(t_1, t_2) = Tr(S_+ \rho_f) = Tr((S_x + iS_y)\rho_f)$$
(19)

#### **Coherence** pathways

A coherence pathway is the sequence of coherence orders that the magnetization evolves through during a pulse sequence. All experiments start with zero order coherence (z-magnetization) and should end with a coherence order of -1, which is by convention the one that is detected by the quadrature detector. Without quadrature detection the +1 coherences would be equally detectable, all higher orders are not correlated with observable magnetization.

The selection of the appropriate coherence pathways can be experimentally achieved by phase cycling, or by the use of pulsed field gradients [16-18]. The properties of the RF-pulses, e.g. flip angle, offset effects, inhomogeneity, require a weighting over the different coherence transfer pathways [9,19,20]. The coherence pathways  $S_{c-}$  and  $S_{c+}$  for obtaining 2D-SECSY and 2D-ELDOR signals, used commonly, are depicted in Figures 1 and 2, respectively. In this paper, the signal is calculated over the coherent pathways  $S_{c-}$  in accordance with that used by LPF [1].

Selection of coherent pathways by appropriate selection of the corresponding elements of the density matrix. For single electron-nuclear coupled system with electron spin S=1/2, nuclear spin I=1/2, the dimension of the coupled spin Hamiltonian is  $(2S_1 + 1) \times (2I_1 + 1) = 4$ , so that the density matrix in the electron-nuclear spin-coupled direct product space the total density matrix  $\rho = \rho_e \otimes \rho_n$ , where  $\rho_e$  and  $\rho_n$  are, respectively, the density matrices in the electronic and nuclear subspaces. In the following, the coherence order is defined as follows; herep is the coherence order, which represents transverse magnetization, corresponding to spins rotating in a plane perpendicular to the external field [21,22].

(i) For the pathway with coherence order p = 1, all matrix elements of the density matrix,  $\rho$ , are put equal to zero, except for those corresponding to  $\rho_e(1,2)$ .

(ii) For the pathway with coherence order p=0 all matrix elements of the density matrix, are put equal to zero, except for those corresponding to  $\rho_e(1,1)$  and  $\rho_e(2,2)$ .

(iii) For the pathway with coherence order p = -1, all matrix elements of the density matrix,  $\rho$ , are put equal to zero, except for those corresponding to  $\rho_e(2,1)$ .

# **Rotating frame**

The calculations are carried in the rotating frame during a pulse, wherein the spin is in resonance, so that the effective magnetic field  $B_{ef} = \left(B - \frac{\hbar\omega}{g\mu_B}\right)$  becomes zero. During static evolution, the field used here is the applied magnetic field using a static frame. This is valid when the calculations are carried out in the absence of a pulse, although one can also use the rotating frame in the

absence of a pulse, wherein  $B_{eff} = 0$ . Both choices are correct.

# Simulation of 2D-SECSY and 2D-ELDOR signals

The technique developed here is used to simulate two illustrative cases of 2D-SECSY and 2D-ELDOR signals obtained in an irradiated malonic acid single crystal [1]. These cases are: (i) An electron spin coupled to a nuclear spin. The calculated spectra are compared with the experimental results of LPF [1], and (ii) dipolar interaction between two nitroxide radicals [21,23]. The calculations in (ii) are intended for a suggested experiment enabling distance determination in biological samples.

An electron spin coupled to a nuclear spin: The sample used in LPF [1] was an irradiated malonic acid crystal [24], involving the case of an unpaired electron spin S=1/2, interacting with a single nucleus I=1/2, by hyperfine (HF) interaction, wherein the principal axes of the HF tensor  $\tilde{A}$  and those of the  $\tilde{g}$  matrix are coincident. More details of the procedure used by LPF including the Hamiltonian and basis vectors used are given in appendix A. In this experiment the various parameters are as follows: the external magnetic field  $B_0=3000.0$  Gauss; the  $\pi/2$  pulse is of duration ~5ns [1]; nuclear Zeeman frequency  $\omega_n=14.0$  MHz; the spin-Hamiltonian parameters:  $\tilde{g} = (g_{xx}, g_{yy}, g_{zz}) = (2.0026, 2.0035,$ 2.0033);  $\tilde{A} = (A_{xx}, A_{yy}, A_{zz}) = (-61.0$  MHz, -91.0 MHz, -29.0 MHz).

The input values used in the simulation of the time-domain signals, as described in appendix A.1 and A.2, are as follows [1]: Gaussian inhomogeneous broadening  $\Delta = 4$  MHz; electron spin-spin relaxation time,  $T_{2n} = 22$  µs; nuclear spin-spin relaxation time,  $T_{2e} = 0.900$  µs; inverse electron spin-spin relaxation time, ; inverse nuclear spin-spin relaxation time,  $W_e = 0.0167$ µs<sup>-1</sup>; inverse electron nuclear spin-spin relaxation time,  $W_x = 0.00617$ µs<sup>-1</sup>; inverse electron-nuclear spin-spin relaxation time,  $W_x = W_y$ ; inverse Heisenberg exchange relaxation time,  $\omega_{HE} = 0.0$ µs<sup>-1</sup>.

The 2D-SECSY time-domain signals were calculated, as shown in Figure 3, corresponding to the experiment of LPF [1] for: (i) three orientations of the external magnetic field  $(\theta, \phi) = (5^{\circ}, 0^{\circ})$ ,  $(30,0^{\circ})$ ,  $(50^{\circ}, 0^{\circ})$  in the zx-quadrant, so that the corresponding Euler angles are  $(\alpha, \beta, \gamma) = (0, -\theta, 0)$ ; (ii) two orientations  $(\theta, \phi) =$  $(5^{\circ}, 90^{\circ})$  and  $(45^{\circ}, 90^{\circ})$  in the zy-quadrant, which correspond to  $(\alpha, \beta, \gamma) = (0, \theta, 90^{\circ})$ . [The orientation of the external static field  $B_0$  is defined by the angles  $\theta$  and  $\phi$ , where  $\theta$  is the angle between  $B_0$  and the z axis, and  $\phi$  is the angle between the x axis and the projection of  $B_0$  on the xy plane.]

As for the 2D-ELDOR time-domain signals, they were calculated for the orientation  $(\theta,\phi) = (30^{\circ},0^{\circ})$  in the zx-quadrant, so that  $(\alpha,\beta,\gamma) = (0,-\theta,0)$  [1], with four mixing times  $T_{\rm m}$  (the fixed time interval between the second and third  $\pi/2$  pulses; see Figure 2): (a) 5 µs; (b) 20 µs; (c) 40 µs; (d) 60 µs.

One can compare the Fourier transform (FT) of the experimental data of LPF [1] with those simulated here for SECSY and ELDOR signals, as shown in Figures 3-5. It is found that for ELDOR signals the corresponding positions of the main frequency peaks, i.e. the nuclear modulation frequency  $\omega_a$  and  $\omega_b$ , are the same



**Figure 3:** Experimental Fourier transforms (LPF's Fig.8 [1]) (upper) and that simulated with relaxation taken into account (bottom) of 2D-SECSY spectra at  $(\theta, \phi)$  orientations of (a) (5°, 0°), (b) (30°, 0°), (c) (50°, 0°) in the zx-quadrant  $[(\alpha, \beta, \gamma) = (0, -\theta, 0)]$  [1]. The corresponding simulated time-domain figures are shown in the middle row. The relaxation constants  $T_2(ns)$  used for the various orientations are: (a) 800, (b) 812, (c) 687. A Gaussian inhomogeneous broadening width  $\Delta$ =4 MHz. Eq. (A.34) is used in the simulation of the 2D-FT signal for each orientation.



**Figure 4:** Experimental (LPF's Fig.9 [1]) (upper) and that simulated with relaxation taken into account (bottom) of the 2D-SECSY spectra at  $(\theta, \phi)$  orientations of (a) (5°, 90°), (b) (45°, 90°) in the zy-quadrant  $[(\alpha, \beta, \gamma) = (0, \theta, 90^{\circ})]$ , in the second and third column respectively [1]. The corresponding simulated time-domain figures are shown in the middle row. The relaxation constants  $T_2(ns)$  for the various orientations are (a) 1223, (b) 1068. A Gaussian inhomogeneous broadening width  $\Delta$ =4 MHz. Eq. (A.34) is used in the simulation of 2D-FT signal for each orientation.



**Figure 5:** Experimental FT (LPF Fig.11 [1]) (first column) and simulated time-domain with relaxation taken into account (second column) of the 2D-ELDOR spectra at  $(\theta, \phi)$  orientations of (30°, 0°) in the zx-quadrant  $[(\alpha, \beta, \gamma) = (0, -\theta, 0)]$ [1], with the mixing times  $T_m$ : (a) 5 µs; (b) 20 µs; (c) 40 µs; (d) 60 µs. The corresponding FT figures are shown in the last column. A Gaussian inhomogeneous broadening width  $\Delta$ =4 MHz. Eq. (A.34) is used in the simulation.

in all four cases shown in Figure 5. Their values are the same as those reported in LPF [1], i.e.  $\omega_{\alpha} \approx 7.0$  MHz and  $\omega_{\beta} \approx 32.0$  MHz. The shapes of the simulated spectra in the frequency domain as calculated here and those calculated by LPF[1] appear to be in good agreement with each other.

**Dipolar interaction between two nitroxide radicals:** For two nitroxide radicals coupled by the dipolar interaction in malonic acid crystal the time-domain 2D-SECSY and 2D-ELDOR signals were calculated for the pulse sequences  $S_{c^-}$  (Figure 1), neglecting the hyperfine and exchange interactions, otherwise the size of the matrix would have been prohibitively large in Liouville space [=(36x36)x(36x36)]. The value of the matrix  $\tilde{g} = (g_{xx}, g_{yy}, g_{zz}) = (2.0026, 2.0035, 2.0033)$  was used for each electron as those used by Misra et al. [21], and the value of the dipolar-interaction constant D=10 MHz was used (See Eq.(B.5) below for of the expression for D) [21]; the details are given in Appendix B.1. Figure 6 shows the simulated time-domain 2D-SECSY spectrum

at  $(\theta,\phi)$  orientations of  $(30^\circ, 0^\circ)$  in the zx-quadrant {the corresponding values for the Euler angles  $(\alpha,\beta,\gamma)$  are  $(0,-\theta,0)$  [1]}. In Figure 6, row F1 displays the FT of the slice of time domain along  $t_{2} = 0$ ; it clearly shows the dipolar peaks at  $\pm 10$  MHz, which correspond, as expected, to the value of  $\pm D = \pm 10$  MHz used in the present simulation. Figure 7 shows the simulated 2D-ELDOR time-domain spectrum and its FT, as calculated for the mixing time  $T_{\rm m} = 20 \,\mu s$  (Figure 2); row F1 displays the Fourier transform of the echo peak ( $t_2=0$  slice), which clearly shows the peaks at  $\pm D$  $= \pm 10$  MHz as expected. A Gaussian inhomogeneous broadening width  $\Delta = 4$  MHz, Eq. (A.34), is used in the simulation. It is noted from Figures 6 and 7 that inclusion of relaxation has significantly broadened the dipolar peaks, as expected. However, the spacings of Pake doublets, which are needed to estimate distances, remain unchanged. On the other hand, if constant-time experiments are to be done, then our calculation results without relaxation as shown in Figures 6 and 7 will be useful.



**Figure 6:** Simulated time-domain and its FT 2D-SECSY spectrum with and without relaxation for an electron-electron dipolar-coupled system at  $(\theta, \phi)$  orientations of (30°, 0°) in the zx-quadrant, so that  $[(\alpha, \beta, \gamma) = (0, -\theta, 0)]$  [1]. Figure F1 is the Fourier transform of the echo peak ( $t_2 = 0$  slice), which clearly shows the dipolar peaks at  $\pm 10$  MHz, the value of the dipolar coupling constant D used in the simulation, as expected. It is noted that inclusion of relaxation significantly broadens the Fourier peaks, as expected. A Gaussian inhomogeneous broadening width  $\Delta$ =4 MHz. Eq. (A.34) is used in the simulation.

# **Computing time**

The computation work is undertaken on a laptop with an x64based processor of Intel<sup>®</sup> Pentium<sup>®</sup> CPU B980 @2.4 GHz, an installed memory (RAM) 4.00 GB, an operation system of Windows 8.1, and a Matlab version 8.3.0.532 (R2014a). As for computational time, calculation of 2D-ELDOR pulsed signal takes ~10.56 seconds.

# **Concluding remarks**

This paper is devoted to the very important subject of pulsed EPR in the presence of relaxation, providing a comprehensive theoretical treatment including a detailed description of relaxation processes. The procedure of how to implement the theoretical approach numerically has been developed, and the applied algorithm and individual computational steps have been thoroughly discussed, and illustrated by examples. The salient features of the present work are as follows:

An algorithm for simulation of pulsed EPR signals taking into account relaxation rigorously by the use of SLE, based on solving the relevant matrix differential equation, has been developed. The corresponding flow chart (Figure 8) has been included. The Matlab source code can be obtained by requesting the authors.

The algorithm is illustrated here using MATLAB to calculate

2D-SECSY and 2D-ELDOR signals for two systems: (a) An electron-nuclear spin coupled system in a malonic acid crystal and compared with experimental results of LPF [1] and (b) an electron-electron dipolar-coupled system in a malonic acid crystal for a proposed experiment intended for distance measurements. These calculations can also be done using Fortran.

These relaxation calculations, based on solving SLE rigorously, have here been carried out on a commonly available lap top (see above) within a reasonable time, on the order of (~11seconds), without requiring any costly software.

# **Future Perspectives**

An application of this technique to consider relaxation as caused by fluctuation of spin-Hamiltonian parameters, an example of stochastically time-dependent Hamiltonian mentioned in the introduction [case (c)], as proposed in LPF [1], but not carried out there, is under investigation, and will be published in the not-too-distant future. As well, the calculation of a powder signal taking into account relaxation using this technique, extending the calculations of Misra *et al.* [19], which did not include relaxation, is currently in progress.

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**Figure 7:** Simulated 2D-ELDOR time-domain spectrum with and without consideration of relaxation for an electron-electron dipolar system at  $(\theta, \phi)$  orientations of (30°, 0°) in the zx-quadrant, so that  $[(\alpha, \beta, \gamma) = (0, -\theta, 0)]$  [1], with the mixing times  $T_m = 20 \ \mu s$ . Figure F1 is the Fourier transform of the echo peak ( $t_2 = 0$  slice), which clearly shows the dipolar peaks at  $\pm 10MHz$ , the value of the dipolar coupling constant D used in the simulation. It is noted that inclusion of relaxation significantly broadens the Fourier peaks as expected. A Gaussian inhomogeneous broadening width  $\Delta$ =4 MHz. Eq. (A.34) is used in the simulation.

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# Appendix A: An electron-nuclear coupled system in an irradiatedmalonic acid crystal.

These appendix describes the theoretical and experimental details of the calculation of pulsed EPR experiments as discussed by LPF [1], relevant to the simulations presented in this paper.

# A.1 Spin Hamiltonian and parameters

For the specific case of a single nucleus (I =  $\frac{1}{2}$ ) interacting with an unpaired electron (S =  $\frac{1}{2}$ )by the hyperfine (HF) interaction tensor, where the HF has the same principal axes as the g matrix, the total Hamiltonian can be expressed as the sum of static Hamiltonian and pule Hamiltonian [1]

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1 \tag{A.1}$$

where

$$\widehat{H_0} = CS_z - \omega_n I_z + AS_z I_z + \frac{1}{2}BS_z I_+ + \frac{1}{2}B^* S_z I_-$$
(A.2)

and the pulse Hamiltonian  $\widehat{H}_1 = \widehat{\varepsilon}(t)$  as in Eq.(14). In the  $|S_z I_z\rangle$  basis of a spin system with  $S_z = \pm 1/2$  and  $I_z = \pm 1/2$ , the explicit expression for  $\widehat{\varepsilon}(t)$ :

$$\hat{\varepsilon}(t) = B_1 \gamma_e \left( S_x \cos \phi + S_y \sin \phi \right) \mathbf{1}_n = \frac{\omega}{2} \left( e^{-i\phi} S_+ + e^{i\phi} S_- \right) \mathbf{1}_n \qquad (A.3)$$

is:

$$|1\rangle=|++\rangle |2\rangle=|+-\rangle |3|=|+\rangle |4|=|--\rangle$$

$$\begin{bmatrix} 0 & 0 & \frac{\omega}{2}e^{-\psi} & 0\\ 0 & 0 & 0 & \frac{\omega}{2}e^{-i\psi}\\ |3\rangle=|++\rangle \\ |4\rangle=|--\rangle \\ |4\rangle=|--\rangle \\ \begin{bmatrix} \frac{\omega}{2}e^{i\psi} & 0 & 0 & 0\\ 0 & \frac{\omega}{2}e^{\psi} & 0 & 0 \end{bmatrix}$$
(A.4)

The coefficients in Eq. (A.2) are expressed as follows [1]:

$$C = \frac{\beta_e B_0}{h} \left[ \bar{g} + F \frac{1}{2} (3\cos^2 \beta - 1) + F^{(2)} \sin^2 \beta \cos(2\gamma) \right]$$
(A.5)

$$A = -\gamma_e \left[ \overline{a} + D \frac{1}{2} (3\cos^2 \beta - 1) + D^{(2)} \sin^2 \beta \cos(2\gamma) \right]$$
(A.6)

$$B = -\gamma_e \left\{ D \frac{3}{4} \sin\beta \cos\beta - D^{(2)} \frac{1}{2} \sin\beta \left[ \cos\beta \cos(2\gamma) - i\sin(2\gamma) \right] \right\}$$
(A.7)

and

$$\overline{g} = \frac{1}{3} \left( g_{x} + g_{yy} + g_{z} \right) = \frac{g_{\parallel} + 2g_{\perp}}{3}$$
(A.8)

Here  $\overline{g}$  is the isotropic part of g-tensor,  $g_{\parallel}$ ,  $g_{\perp}$  are the components of the g-tensor in their principal axes systems.

$$\overline{a} = \frac{1}{3} \left( A_{xx} + A_{yy} + A_{zx} \right) = \frac{A_{\parallel} + 2A_{\perp}}{3}$$
(A.9)

where  $A_{\parallel}$ ,  $A_{\perp}$  are the components of hyperfine tensor in their principal axes systems;

$$F = \frac{2}{3} \left( g_{xx} - \frac{1}{2} \left( g_{xx} + g_{yy} \right) \right) = \frac{2}{3} \left( g_{\parallel} - g_{\perp} \right)$$
(A.10)

$$D = \frac{2}{3} \left( A_{xx} - \frac{1}{2} \left( A_{xx} + A_{yy} \right) \right) = \frac{2}{3} \left( A_{\parallel} - A_{\perp} \right)$$
(A.11)

$$F^{(2)} = \frac{1}{2} \left( g_{xx} - g_{yy} \right) \tag{A.12}$$

$$D^{(2)} = \frac{1}{2} \left( A_{xx} - A_{yy} \right) \tag{A.13}$$

Here  $\omega_n$  is the nuclear Larmor frequency,  $\Omega(\alpha, \beta, \gamma)$  are the Euler angles which describe the orientations of the principal axes of the g-matrix with respect to the static magnetic field.

### A.2 Relaxation matrix

The effect of spin relaxation is taken into account by the use of the phenomenological relaxation matrix based on Redfield theory [12] as outlined by LPF [1]:

$$\frac{d}{dt}\rho_{\alpha\alpha'}(t) = -i\omega_{\alpha\alpha'}\rho_{\alpha\alpha'} - \sum_{\beta\beta'}\widehat{\widehat{R}}_{\alpha\alpha'\beta\beta'}(\rho_{\beta\beta'} - \rho_{0\beta\beta'}) \qquad (A.14)$$

where

$$\boldsymbol{\omega}_{\alpha\beta} = \boldsymbol{E}_{\alpha} - \boldsymbol{E}_{\beta} \tag{A.15}$$

Here  $E_{\alpha}$ ,  $E_{\beta}$  are the eigenvalues of the static Hamiltonian,  $\hat{H}_{0}$ , for the electron-nuclear coupled system (S =  $\frac{1}{2}$ , I =  $\frac{1}{2}$ ) as given by Eq. (A.2).

In Eq. (A.14),  $\hat{R}_{\alpha\alpha'\beta\beta'}$  are relaxation matrix elements, where  $\alpha, \alpha', \beta, \beta'$  designate the eigenstates of the Hamiltonian  $\hat{H}_0$ . The following specific values for the matrix elements, as given by Freed [25-27], are used here:

$$\widehat{\widehat{R}}_{\alpha\beta,\alpha\beta} = \widehat{\widehat{R}}_{\beta\alpha,\beta\alpha} = -\left(\frac{1}{T_2}\right)_{\alpha\beta}$$
(A.16)

$$\widehat{\widehat{R}}_{\alpha\alpha,\beta\beta} = W_{\alpha\beta} \tag{A.17}$$

$$\widehat{\widehat{R}}_{\alpha\alpha}, _{\alpha\alpha} = -\sum_{\gamma \neq \alpha} W_{\alpha\gamma}$$
(A.18)

Otherwise

$$\widehat{\widehat{R}}_{\alpha\beta,\varsigma\eta} = \mathbf{0} \tag{A.19}$$

The relaxation pathways among the various eigenstates of the two electrons in the lattice, as defined in the  $H_a$  basis and described by

Freed [25], are shown in the figure below, where a and b indicate the nuclear sublevels of electronic magnetic quantum number  $M_s = 1/2$ , whereas c and d indicate the nuclear sublevels of  $M_s = -1/2$ .



Corresponding to the above diagram, it is assumed that [1]

$$W_{ab} = W_{ba} = W_{cd} = W_{dc} = W_n \tag{A.20}$$

$$W_{ac} = W_{ca} = W_{bd} = W_{db} = W_e \tag{A.21}$$

$$\boldsymbol{W}_{ad} = \boldsymbol{W}_{da} = \boldsymbol{W}_{y} \tag{A.22}$$

$$W_{bc} = W_{cb} = W_x \tag{A.23}$$

and

$$(T_2)_{ac} = (T_2)_{bd} = (T_2)_{ad} = (T_2)_{bc} = T_{2e}$$
 (A.24)

$$(T_2)_{ab} = (T_2)_{cd} = T_{2n}$$
 (A.25)

The non-zero elements of the relaxation matrix, corresponding to the above diagram, as obtained from Eqs. (A.16)-(A.19) are [1]:

$$\widehat{\widehat{R}}_{ab,ab} = \widehat{\widehat{R}}_{ba,ba} = \widehat{\widehat{R}}_{ad,ad} = \widehat{\widehat{R}}_{ab,ab} = -\frac{1}{T_{2n}}$$
(A.26)

$$\widehat{\widehat{R}}_{ac,ac} = \widehat{\widehat{R}}_{cac,ac} = \widehat{\widehat{R}}_{ad,ad} = \widehat{\widehat{R}}_{ad,da} = \widehat{\widehat{R}}_{bc,bc} = \widehat{\widehat{R}}_{cb,cb} = \widehat{\widehat{R}}_{bd,bd} = \widehat{\widehat{R}}_{db,ab} = -\frac{1}{T_{2e}} \quad (A.27)$$

$$\widehat{\widehat{R}}_{aa,aa} = \widehat{\widehat{R}}_{dd,di} = -W_e - W_n - W_y$$
(A.28)

$$\widehat{\widehat{R}}_{bb,bb} = \widehat{\widehat{R}}_{\infty,cc} = -W_e - W_n - W_x$$
(A.29)

$$\widehat{\widehat{R}}_{aa,bb} = \widehat{\widehat{R}}_{bb,aa} = \widehat{\widehat{R}}_{ac,dd} = \widehat{\widehat{R}}_{dd,ac} = W_n + \frac{\omega_{HE}}{4}$$
(A.30)

$$\widehat{\widehat{R}}_{aa,cc} = \widehat{\widehat{R}}_{bb,dl} = \widehat{\widehat{R}}_{cc,aa} = \widehat{\widehat{R}}_{dd,bb} = W_e + \frac{\omega_{HE}}{4}$$
(A.31)

$$\widehat{\widehat{R}}_{bb,\alpha} = \widehat{\widehat{R}}_{\alpha,bb} = W_x - \frac{\omega_{HE}}{4}$$
(A.32)

$$\widehat{\widehat{R}}_{aa,\rho c} = \widehat{\widehat{R}}_{dd,aa} = W_y - \frac{\omega_{HE}}{4}$$
(A.33)

; otherwise  $\widehat{\widehat{R}}_{\alpha\beta,\varsigma\eta} = 0$ . Here  $\omega_{H\!E} = 0\mu s^{-1}$  as used by LPF [1].

#### A.3 Gaussian inhomogeneous broadening effect

In accordance with LPF [1], the Gaussian inhomogeneous broadening effect, over and above the relaxation effect, in the

frequency-domain along  $\omega_2$  (=  $2\pi\nu$ ), corresponding to the step time  $t_2$ , as depicted in Figures 1 and 2, is taken into account by the following time-domain dependence:

$$f_b(t_2) = f(t_2) \frac{1}{\sqrt{2\pi}\Delta} \int_{-\infty}^{\infty} exp\left(-\frac{v^2}{2\Delta^2}\right) e^{-i2\pi v t_2} dv = f(t_2) e^{-2(\pi \Delta t_2)^2}$$
(A.34)

where  $f_b(t_2)$  is the Gaussian-broadened signal along  $t_2$  and  $\Delta$  is the Gaussian inhomogeneous broadening parameter expressed in frequency units.

Appendix B: Electron-electron dipolar interaction of coupled nitroxide radicals in a malonic acid crystal

## **B.1 Spin Hamiltonian and parameters**

For the specific case of the electron-electron dipolar interaction of two nitroxide radicals, each with electron spin S=1/2, nuclear spin I=1/2, the composite Hamiltonian can be expressed as [21,23]

$$\widehat{H}_0 = \widehat{H}_{01} + \widehat{H}_{02} + \widehat{H}_{12} \tag{B.1}$$

where

$$\widehat{H}_{0k} = S_{kz} \boldsymbol{g}_{k} \cdot \boldsymbol{B}_{0} - \gamma_{n} I_{kz} \boldsymbol{B}_{0} + S_{kz} \boldsymbol{A}_{k} \cdot \boldsymbol{I}_{k}; k = 1, 2$$
(B.2)

Ignoring the nuclear interaction, the various terms in Eq. (B.2) are:

$$\widehat{H}_{0k} = S_{kz} \boldsymbol{g}_k \cdot \boldsymbol{B}_0 \tag{B.3}$$

$$\widehat{H}_{12} = \widehat{H}_D + \widehat{H}_J = \frac{D}{2} \left( 3\cos^2\theta - 1 \right) \left( S_z^2 - \frac{1}{3} S^2 \right) + J \left( \frac{1}{2} - S_1 \cdot S_2 \right) \quad (B.4)$$

Here, in the direct-product space,  $\mathbf{S} = \mathbf{S}_1 \otimes \mathbf{I}_2 + \mathbf{I}_1 \otimes \mathbf{S}_2$ ,  $S_z = S_{z1} \otimes \mathbf{I}_2 + \mathbf{I}_1 \otimes \mathbf{S}_{z2}$ , *J* is the exchange-interaction constant between the two electrons,  $\theta$  is the angle between the dipolar axis and the static magnetic field  $\mathbf{B}_0$  and D is the dipolar-coupling constant:

$$D = \frac{3\gamma_e^2\hbar}{2r^3} = \frac{3}{2}d \tag{B.5}$$

In the present case, neglecting the nuclear part, the direct-product Hilbert space is  $S_1 \otimes S_2$ , with the dimension  $(2S_1+1) \times (2S_2+1)$ = 4. Then the dimensions of the superoperator  $\hat{H}_0$  in Liouville space are 16 × 16. [It is noted that if the nuclear space was taken into consideration the matrix dimensions are  $(16 \times 16) \times (16 \times 16)$ = 256×256, which would have been exorbitant for manipulation on a laptop.]

The results of calculation are shown in Figures 6 and 7 for

2D-SECSY and 2S-ELDOR cases. More details are given in the captions to these figures.

#### **B.2 Relaxation matrix**

For consideration of relaxation for this illustrative case, only the relaxation of each electron with the lattice is taken into account. Otherwise, if the nuclear relaxations are taken into account, the Liouville space becomes of much larger dimension (256 x 256), which becomes unmanageable as explained above. One can add the nuclear relaxation to this phenomenologically in the same way as carried out in LPF [1]. As a consequence, for each electron the same relaxation matrix applies as that discussed in Appendix A.2.

Then, the relaxation matrix for the two electrons, with the subscripts i=1,2 designating the two electrons, is:

$$\widehat{\widehat{R}}_{1} = \begin{bmatrix} \widehat{\widehat{R}}_{aa,aa} & \widehat{\widehat{R}}_{ab,ab} \\ \widehat{\widehat{R}}_{ba,ba} & \widehat{\widehat{R}}_{bb,bb} \end{bmatrix} = \begin{bmatrix} -W_{e} & \frac{1}{T_{2}} \\ \frac{1}{T_{2}} & -W_{e} \end{bmatrix}$$
(B.6)

The relaxation matrix for the electron-electron spin coupled dipolar system is then expressed as:

$$\widehat{\widehat{R}} = \widehat{\widehat{R}}_1 \otimes I_2 + I_1 \otimes \widehat{\widehat{R}}_2$$
(B.7)

Eq. (B.7)  $I_1$  and  $I_2$  are 2x2 unit matrices for electrons 1 and 2, respectively.

# B.3 Pulse-propagator superoperator for the dipolar-coupled system

For the two-electron dipolar-coupled system, the pulse propagator is expressed as

 $\hat{\varepsilon}(t) = B_{1}\gamma_{e} \left( S_{1x} \cos \phi + S_{1y} \sin \phi + S_{2x} \cos \phi + S_{2y} \sin \phi \right) = \frac{\omega}{2} \left( e^{-i\phi} S_{1+} + e^{i\phi} S_{1-} + e^{-i\phi} S_{2+} + e^{i\phi} S_{2-} \right)$ 

In the  $|S_{z1}S_{z2}\rangle$  basis of a dipolar system with electron magnetic quantum numbers  $M_1 = \pm 1/2$  and  $M_2 = \pm 1/2$ , the explicit expression for  $\hat{\epsilon}(t)$  is as follows:

$$\begin{bmatrix} \hat{\boldsymbol{\varepsilon}} \end{bmatrix} = \begin{bmatrix} \hat{\boldsymbol{\varepsilon}} \end{bmatrix} \otimes I_2 + I_1 \otimes \begin{bmatrix} \hat{\boldsymbol{\varepsilon}} \end{bmatrix}_2$$
(B.8)

|1>=+++> |2>=++-> |3=+++> |4=+++->



Figure 8: Describes the various steps in simulation.

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