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ESEEM of Disordered Systems in Frequency Domain: Analytical Formulae in the Case of Nuclear Spin 1/2 and Weak Hyperfine Interaction

A. G. Maryasov

Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk, Russian Federation

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Abstract. The analytical expressions for the spectral density of the dead time free electron spin echo envelope modulation (ESEEM) signal of disordered system are obtained for paramagnetic center with nuclear spin 1/2 and weak axially symmetric hyperfine interaction. The spectral density is given by the Fourier transformation of the ESE signal averaged over all orientations. The order of the two linear operations may be changed. Fourier transformation of the nonaveraged ESE signal supplies us with the sum of the Dirac δ-functions. Averaging of such a spectrum is rather trivial operation leading to the spectral densities in the final form.

1 Introduction

The method of electron spin echo (ESE) [1] is effectively used to analyze the structure of paramagnetic centers (PCs) and to study the local nuclear surrounding of unpaired electron of free radical. The spin echo signal provides information on hyperfine electron-nuclear interaction manifested in echo signal envelope modulation (ESEEM) [1–2]. Analyzing this phenomenon makes it possible to determine the magnetic resonance parameters of a system for drawing valid conclusions on its structure.

Note that so far there has been no analytical expression in the literature for ESEEM spectra in a frequency domain although the formulae describing the ESE signal modulation are simple enough. The analytical dependences for disordered systems in the time domain have been derived earlier [3]. The response is expressed in terms of the Fresnel integrals. With this report we are trying to compensate for a deficiency in the theory.

2 Primary ESE

Let us consider the simplest case of a radical with one nucleus with spin 1/2. Hyperfine interaction (hfi) is considered axially-symmetric (in this case, it can

be fully characterized by two parameters: a, isotropic hfi constant and $T_\perp$, anisotropic hfi tensor component, all parameters of spin-Hamiltonian are measured in hertz), and small as compared with the nuclear Zeeman frequency ν_I,

$$|a|,\ |T_\perp| \ll |\nu_I|. \tag{1}$$

The microwave (mw) pulses are supposed to excite the electron spin nonselectively as concerns the electron paramagnetic resonance (EPR) transitions.

We restrict ourselves to the consideration of the signals of primary and stimulated spin Echoes whose amplitudes are obtained in a given approximation with the help of eqs. (36) and (37) from chapter 2 in ref. 2. It is assumed that all conditions needed for the validity of these equations are met. Leaving the first nonvanishing corrections due to hfi in cosine arguments, we get

$$V(\tau) \approx 1 - \frac{T_{zx}^2 + T_{zy}^2}{2\nu_I^2}\left\{1 - \cos\left[2\pi\left(\nu_I + \frac{a + T_{zz}}{2}\right)\tau\right] - \cos\left[2\pi\left(\nu_I - \frac{a + T_{zz}}{2}\right)\tau\right]\right.$$
$$\left. + \frac{1}{2}\cos\left[2\pi\left(2\nu_I + \frac{T_{zx}^2 + T_{zy}^2}{4\nu_I}\right)\tau\right] + \frac{1}{2}\cos[2\pi(a + T_{zz})\tau]\right\}, \tag{2}$$

where τ is the interval between the mw pulses forming the ESE signal, T_{zq} are the components of anisotropic hfi tensor in the laboratory system of coordinates ($q = x, y, z$) with axis z directed along the external magnetic field. In our case of axial symmetry we get

$$T_{zx}^2 + T_{zy}^2 = 9T_\perp^2 X^2(1 - X^2),$$
$$T_{zz} = T_\perp(1 - 3X^2),$$
$$X = \cos\Theta, \tag{3}$$

where Θ is the angle between the directions of the axis of symmetry and the external magnetic field.

The relationship following from Eq. (2) may be useful, the relative modulation amplitude in the ordered system is two times larger than the shift of the peak near the second harmonic nuclear Zeeman frequency expressed in units of ν_I. Note also that Eq. (2) is independent of the ν_I sign. Thus, in a given approximation it is impossible to determine the sign of gyromagnetic ratio for the nucleus producing the modulation effect. Therefore, we assume below that $\nu_I > 0$ for definiteness.

To obtain a signal for the disordered system, Eq. (2) should be averaged over all possible orientations. In the case of axial symmetry this procedure is reduced to integration of Eq. (2) over X from 0 to 1. However, switching to the frequency domain gives the same information which is more convenient for interpretation, because the Fourier transformation of cosines in the right-hand side in Eq. (2)

gives the sum of Dirac δ-functions. This allows integration over orientations for the disordered system in the final form. In this case, the disordered system spectrum will have nonzero value at several segments of the frequency axis. Let us denote the oscillating part of the averaged ESE signal as $F(\tau)$,

$$F(\tau) = \int_0^1 \left(V(\tau) + \frac{9T_\perp^2 X^2 (1 - X^2)}{2\nu_I^2} - 1 \right) \mathrm{d}X = \left\langle V(\tau) \right\rangle + \frac{3T_\perp^2}{5\nu_I^2} - 1 . \tag{4}$$

Note that the relative modulation amplitude $\bar{k} = 3T_\perp^2/5\nu_I^2$. Applying the Fourier transformation to Eq. (4), we get

$$F(\nu) = c\frac{T_\perp^2}{\nu_I^2}(F_0 - F_{1+} - F_{1-} + F_2) . \tag{5}$$

In this case c is the numerical coefficient. The F values obey the equations

$$F_0(\nu) = \frac{1}{2}\int_0^1 \mathrm{d}X (X^2 - X^4)\{\delta[\nu - (a + T_{zz})] + \delta[\nu + (a + T_{zz})]\} , \tag{6}$$

$$F_{1\pm}(\nu) = \int_0^1 \mathrm{d}X (X^2 - X^4)\left\{ \delta\left[\nu - \left(\nu_I \pm \frac{a + T_{zz}}{2} \right) \right] + \delta\left[\nu + \left(\nu_I \pm \frac{a + T_{zz}}{2} \right) \right] \right\} , \tag{7}$$

$$F_2(\nu) = \frac{1}{2}\int_0^1 \mathrm{d}X (X^2 - X^4)\left\{ \delta\left[\nu - \left(2\nu_I + \frac{T_{zx}^2 + T_{zy}^2}{4\nu_I} \right) \right] + \delta\left(\nu + \left(2\nu_I + \frac{T_{zx}^2 + T_{zy}^2}{4\nu_I} \right) \right) \right] . \tag{8}$$

The spectrum is an even function of frequency. As follows from Eqs. (5)–(8), it consists of five groups of lines, namely, two singlets in the vicinity of frequencies $\pm 2\nu_I$, and three doublets centered about 0 and $\pm\nu_I$. In this case, the components of each doublet can overlap depending on the relationship between isotropic (a) and anisotropic ($T_\perp$) hfi components. The doublets centered about the nuclear Zeeman frequency ($\pm\nu_I$) display a spectral density of an opposite sign as compared with the other components. Their form coincides with the signal near zero frequency but they are two times narrower. With Eq. (3), for the axially-symmetric hfi tensor we get

$$F_0(\nu) = \frac{1}{4|T_\perp|}\left[\varphi\left(\frac{\nu + a}{T_\perp} \right) + \varphi\left(\frac{-\nu + a}{T_\perp} \right) \right] , \tag{9}$$

$$F_{1+}(\nu) + F_{1-}(\nu) = \frac{1}{|T_\perp|}\left[\varphi\left(\frac{2(\nu - \nu_I) + a}{T_\perp}\right) + \varphi\left(\frac{-2(\nu - \nu_I) + a}{T_\perp}\right)\right], \qquad (10)$$

$$F_2(\nu) = \begin{cases} \dfrac{\nu_I}{18\sqrt{2}T_\perp^2}\left[\sqrt{1+\sqrt{1-\widetilde{\nu}}} + \sqrt{1-\sqrt{1-\widetilde{\nu}}}\right]\sqrt{\dfrac{\widetilde{\nu}}{1-\widetilde{\nu}}} & \text{if } 0 \le \widetilde{\nu} \le 1, \\ 0 & \text{otherwise.} \end{cases} \qquad (11)$$

In this case, we introduce an auxiliary function

$$\varphi(z) = \begin{cases} \dfrac{2}{9\sqrt{3}}\sqrt{1+z}\left(1 - \dfrac{z}{2}\right) & \text{if } -1 \le z \le 2, \\ 0 & \text{otherwise,} \end{cases} \qquad (12)$$

and designation

$$\widetilde{\nu} = \frac{16\nu_I(\nu - 2\nu_I)}{9T_\perp^2}. \qquad (13)$$

For F_1 and F_2, we give expressions of spectral densities for positive values of frequency. These for negative frequencies can be determined from the relation $F(\nu) = F(-\nu)$.

Let us underline that the above relations do not take into account the dead time of the ESE spectrometer. Its influence on ESEEM is considered thoroughly in the book ref. 2 (see chapter 3, section II and chapter 6, section VIII, and references therein).

Note that in the spectroscopy of pulsed electron-electron double resonance (PELDOR) the ESE signal modulation is also observed for biradicals. It is caused by the dipole-dipole electron-electron interaction (for details, see ref. 4). In this case, in the frequency domain the so-called Pake doublet is observed whose components could be distorted when the biradical ESR spectrum is partially excited. To take this distortion of the Pake doublet into account, we have introduced in [5] the $\xi(X)$ function (called the formfactor) and obtained the analytical formula for its calculation as applied to the PELDOR method. Comparing Eqs. (4) and (6) of this report with eq. (19) in ref. 5 shows that in the case of ESEEM, $\xi(X) = X^2 - X^4$. Expressions for F_0 (to within constant multiplier) can be derived from eq. (21) in ref. 5 by substituting $J \to a$, $\omega_D \to T_\perp$, and $\omega_T \to \nu$ with the help of the above expression for the formfactor.

As compared with the PELDOR spectrum (modified Pake doublet), the components of the ESEEM spectrum doublets have no singularity points and are continuous functions of frequency. This is due to the fact that when the external magnetic field is oriented along the principal hfi tensor axes, the electron and nuclear spins are quantized along the external magnetic field and there are no forbidden transitions giving rise to the ESEEM effect. For ESEEM, the doublet spectrum in the frequency domain shows no singularities and discontinuities.

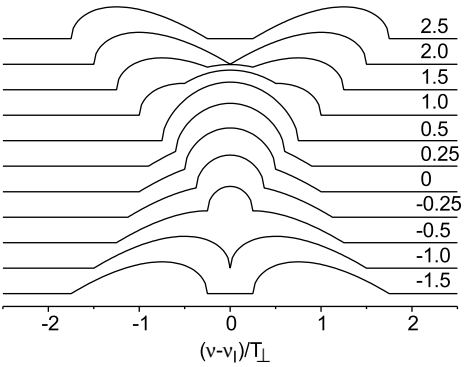

Fig. 1. Spectral density of the modulation doublet near nuclear Zeeman frequency (it is described by Eq. (10), see text). The value of $a/T_\perp$ ratio is indicated above each curve. Each component of the doublet has the maximum intensity at the frequency $\nu = \nu_I \pm a/2$.

The doublet lineshape depends on the relationship between isotropic and anisotropic hfi components, a and $T_\perp$. As follows from Eqs. (9) and (10), in a given case, only the sign of the $a/T_\perp$ ratio can be determined. Figure 1 shows the F_1 doublet centered about the ν_I frequency. In the absence of isotropic hfi ($a = 0$), its width at the center of height $\nu_{1/2}$ equals $T_\perp$ to within good accuracy, $\nu_{1/2} \cong 0.9656T_\perp$. The F_0 doublet has the same lineshape, it is two times wider and its amplitude is four times less $F_{1+}(\nu) + F_{1-}(\nu) = 8F_0(2\nu - \nu_I)$. We suggest to call them the "modulation doublets".

The spectrum of singlet F_2 depends on the only parameter $\widetilde{\nu}$, the reduced value of frequency. As follows from Eqs. (11) and (13), the line near the doubled nuclear Zeeman frequency has singularity of the inverse square root type at the frequency

$$\nu_s = 2\nu_I + \frac{9T_\perp^2}{16\nu_I}, \tag{14}$$

which can be also used to determine $T_\perp$ from the experimental data. It is noteworthy that the singularity has been located correctly earlier (see, e.g., [2], eq. (50) from chapter 6, and the original paper [6]). Figure 2 plots the spectral density of F_2 singlet vs. a reduced value of frequency.

The relative modulation amplitude and the relative singularity point shift from the doubled nuclear Zeeman frequency are related via the equation

$$\frac{\nu_s - 2\nu_I}{\bar{k}\nu_I} = \frac{15}{16}. \tag{15}$$

Equation (15) can be used to estimate the number of nuclei of the same type in the vicinity of an unpaired electron, because in a given approximation of weak

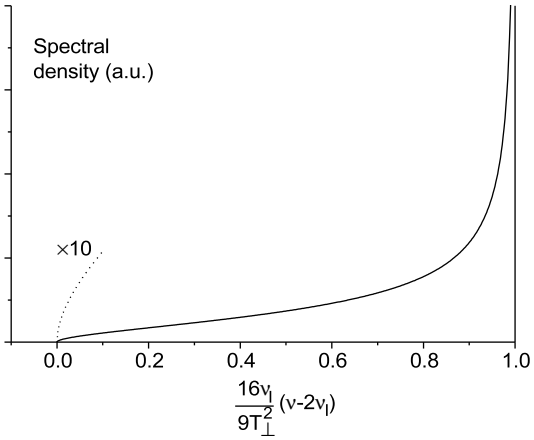

Fig. 2. Lineshape of the singlet near the doubled nuclear Zeeman frequency (see Eq. (13)). The spectrum has the singularity point at $\nu = 2\nu_I + 9T_\perp^2/16\nu_I$.

hfi the relative modulation amplitude will be proportional to the number of nuclei (according to the product rule [2]) and the shift of the line will be equal to the mean one for all nuclei creating the ESE signal modulation.

The above formulae can be readily generalized for higher spins in the absence of quadrupole interaction. To obtain ESE amplitude within the same accuracy $T_\perp^2/\nu_I^2$ one may use eq. (1) from chapter 7 in ref. 2 as a starting point instead of eq. (36) from chapter 6; this leads to simple multiplication of the modulation amplitude and the spectral density by the constant, e.g., $c \to 4I(I+1)c/3$ (this is eq. (25) from ref. 7, see also ref. 8 for details) in Eq. (5) of this paper. More general description may be based on results of ref. 9, presented also in chapter 2, section IV of ref. 2).

3 Stimulated ESE

In the case of the stimulated echo signal, of interest is the use of the two-dimensional (2-D) Fourier spectroscopy [10] by times τ between the first and second pulses (conjugated frequency ν_T) and T between the second and third pulses (conjugated frequency ν_T). In this case, we restrict ourselves to the analysis of the terms of the type $\cos(A\tau)\cos(BT)$. Contribution of this type to the stimulated echo signal in a given approximation obeys the expression readily derived by transforming eq. (37) (chapter 2) in ref. 2

$$V_{cc}(\tau,T) \approx -\frac{T_{zx}^2 + T_{zy}^2}{8\nu_I^2}\left\{\cos\left[2\pi\left(2\nu_I + \frac{T_{zx}^2 + T_{zy}^2}{4\nu_I}\right)\tau\right] + \cos[2\pi(a + T_{zz})\tau]\right\}$$

$$\times\left\{\cos\left[2\pi\left(\nu_I+\frac{a+T_{zz}}{2}\right)T\right]+\cos\left[2\pi\left(\nu_I-\frac{a+T_{zz}}{2}\right)T\right]\right\}. \tag{16}$$

Applying the cosine Fourier transformation with respect to times τ and T to Eq. (16), for the 2-D spectrum of disordered system we get

$$F(\nu_\tau,\nu_T)=c'\frac{T_\perp^2}{\nu_I^2}(F_{0+}+F_{0-}+F_{2+}+F_{2-}), \tag{17}$$

where c' is a constant,

$$F_{0\pm}(\nu_\tau,\nu_T)=\int_0^1 \mathrm{d}X(X^2-X^4)\{\delta[\nu_\tau-(a+T_{zz})]+\delta[\nu_\tau+(a+T_{zz})]\}$$
$$\times\delta\left[\nu_T-\left(\nu_I\pm\frac{a+T_{zz}}{2}\right)\right], \tag{18}$$

$$F_{2\pm}(\nu_\tau,\nu_T)=\int_0^1 \mathrm{d}X(X^2-X^4)\,\delta\left[\nu_\tau-\left(2\nu_I+\frac{T_{zx}^2+T_{zy}^2}{4\nu_I}\right)\right]$$
$$\times\delta\left[\nu_T-\left(\nu_I\pm\frac{a+T_{zz}}{2}\right)\right]. \tag{19}$$

Equation (18) and (19) contain the product of δ-functions which simplifies integration resulting in

$$F_{0\pm}(\nu_\tau,\nu_T)=\frac{1}{2\,|T_\perp|}\left[\varphi\left(\frac{\nu_\tau+a}{T_\perp}\right)\delta\left(\nu_T-\nu_I\pm\frac{\nu_\tau}{2}\right)\right.$$
$$\left.+\varphi\left(\frac{-\nu_\tau+a}{T_\perp}\right)\delta\left(\nu_T-\nu_I\mp\frac{\nu_\tau}{2}\right)\right], \tag{20}$$

$$F_{2\pm}(\nu_\tau,\nu_T)=\frac{1}{|T_\perp|}\varphi\left(2\frac{\mp(\nu_T-\nu_I)+a/2}{T_\perp}\right)$$
$$\times\delta\left(\nu_\tau-2\nu_I+\frac{[a+T_\perp\pm2(\nu_I-\nu_T)][a-2T_\perp\pm2(\nu_I-\nu_T)]}{4\nu_I}\right). \tag{21}$$

The frequencies of modulation in times τ and T depend on the paramagnetic center orientation which, in this case of axial symmetry, is determined by the only parameter, angle Θ between the axis of hfi tensor axial symmetry and the direction of external magnetic field (Eq. (3)). This functional dependence of frequencies leads to the fact that the 2-D spectral density at the ν_τ,ν_T-plane differs

from zero only in a few linear and curvilinear segments whose equations can be derived by equating the arguments of δ-function to zero in the right-hand sides in Eqs. (20) and (21). See also the definition of function φ given in Eq. (12). Note that integrating Eq. (17) over ν_τ, we get the modulation doublet in the vicinity of the nuclear Zeeman frequency as a function of ν_T. A similar integration over ν_T gives the modulation doublet near zero frequency and the singlet Eq. (11) near the doubled nuclear Zeeman frequency by coordinate ν_τ.

Let us note that the more important for experimentalists case of the 2-D HYSCORE spectra was the object of the in depth analysis (see, e.g., [11] and references therein). It will be considered in a separate paper.

Conclusions

Applying the Fourier transformation before the averaging of the ESE signal over all orientations we get the analytical expressions for the ESEEM spectral densities of disordered systems for the simplest case, i.e., nuclei with spin 1/2 and weak axially-symmetric hfi. It is shown for the primary ESE signal that the spectral densities near zero frequency and near nuclear Zeeman frequency are modulation doublets which are continuous functions of frequency. The spectral density near the doubled nuclear Zeeman frequency is the singlet having the singularity point of the inverse square root type. The 2-D spectral densities of the stimulated echo signal differ from zero in several linear and curvilinear segments, the analytical expressions for the spectral amplitudes along these segments are obtained.

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Author's address: Alexander G. Maryasov, Institute of Chemical Kinetics and Combustion, Rassian Academy of Sciences, Institutskaya 3, Novosibirsk 630090, Russian Federation