Non-Stationary Saturation of Inhomogeneously Broadened EPR Lines

Zura Kakushadze§†

§ Quantigic® Solutions LLC
680 E Main St #543, Stamford, CT 06901 2
† Free University of Tbilisi, Business School & School of Physics
240, David Agmashenebeli Alley, Tbilisi, 0159, Georgia

(September 3, 1990; in LaTeX form: January 17, 2020)3

Abstract

Non-stationary saturation of inhomogeneously broadened EPR lines is studied when cross-relaxation has the characteristics of spectral diffusion. A system of generalized kinetic equations is solved in quadratures in this approximation. The result is valid not only when the contribution of the spectral diffusion is negligible or dominant, but also in the intermediate case.
1 Introduction

Experimentally observed EPR (electron paramagnetic resonance) lines usually are broadened inhomogeneously [14] and are described by the inverse temperatures $\beta(\omega, t)$ and $\beta_d(t)$ of the spin packet (SP) with the frequency $\omega$ and the dipole reservoir (DR), respectively [4]. Saturation of such systems has been studied in detail in the stationary case ($t \to \infty$). In this note we study non-stationary saturation of inhomogeneously broadened EPR lines, whose dynamics is described by the following system of generalized kinetic equations [4], [15]:

$$\frac{\partial \beta(\omega, t)}{\partial t} = -\frac{\beta(\omega, t)}{T_{SL}} + \frac{\beta(\omega, t) - \beta_L}{T_{SL}} + \pi \omega^2 \varphi(\omega - \Omega) \left[ \beta(\omega, t) + \frac{\Omega - \omega}{\omega} \beta_d(t) \right] -$$

$$- \frac{1}{\omega} \int d\omega' g(\omega' - \omega_0) W_{CR}(\omega' - \omega) \times$$

$$\times \left[ \omega' \beta(\omega', t) - \omega \beta(\omega, t) + (\omega - \omega') \beta_d(t) \right] = 0 \quad (1)$$

$$\frac{\partial \beta_d(t)}{\partial t} = -\frac{\beta_d(t)}{T_{DL}} + \frac{1}{\omega_d^2} \int d\omega g(\omega - \omega_0) \omega (\omega - \Omega) \times$$

$$\times \left[ \partial \beta(\omega, t) + \beta(\omega, t) - \beta_L \right] = 0 \quad (2)$$

Here: $\partial$ denotes the time derivative; $\beta_L = \text{const}$ is the inverse temperature of the lattice; $\omega_1$ and $\Omega$ are the semi-amplitude and the frequency of the UHF (ultrahigh frequency) field; $\omega_0$ is the Zeeman frequency of the external constant magnetic field; $T_{SL}$ and $T_{DL}$ are the SP and DR spin-lattice relaxation times, respectively; $\omega_d$ is the DR energy “quantum”; $W_{CR}(\omega' - \omega)$ is the probability of cross-relaxation (CR); $\varphi(x)$ and $g(x)$ are the homogeneous and inhomogeneous line forms, respectively.

2 Notations and Approximations

Let $\Delta^*$, $\Delta_1$ and $\Delta_{CR}$ be the widths of the inhomogeneous line form, the hole burned therein, and the CR line form, respectively. Usually the following condition holds [7]:

$$\Delta_1 \ll \Delta^* \ll \omega_0, \Omega \quad (3)$$

That is, a narrow hole is burned in the inhomogeneously broadened line, which we assume hereinafter. We will also assume that$^5$

$$\Delta_{CR} \ll \Delta^* \quad (4)$$

With (3) and (4), the system (1) and (2) can be approximated as follows:

$^4$ For additional related literature, see, e.g., [5], [3], [6], and references therein.

$^5$ Non-stationary saturation of inhomogeneously broadened EPR lines under effective CR, where we have $\Delta_{CR} \gg \Delta^*$, was studied in [9].
\[
\int d\omega' \ f(\omega' - \omega) \left[ \gamma(\omega', p) - \gamma(\omega, p) \right] - \\
\quad - \left[ p + 1 + \pi \omega_d^2 T_{SL} \varphi(\omega - \Omega) \right] \gamma(\omega, p) = \pi \omega_d^2 T_{SL} \varphi(\omega - \Omega)
\]

(5)

\[
\left[ p + \frac{T_{SL}}{T_{DL}(p)} \right] \gamma_d(p) + \frac{(p + 1) \Omega}{\omega_d^2} \int d\omega \ g(\omega - \omega_0) \ (\omega - \Omega) \gamma(\omega, p) = 0
\]

(6)

Here

\[
f(x) = T_{SL} \ g(\Omega - \omega_0) \ W_{CR}(x)
\]

(7)

\[
T_{DL}^{-1}(p) = T_{DL}^{-1} + \frac{\pi \omega_1^2}{\omega_d^2} (p + 1) \ g(\Omega - \omega_0) \int dy \ \frac{\varphi(y) \ y^2}{p + 1 + \pi \omega_1^2 T_{SL} \varphi(y)} + \\
+ \frac{1}{2 \omega_d^2} \int dx \ W_{CR}(x) \ x^2 \int dy \ g^2(y)
\]

(8)

\[
\gamma(\omega, p) = \frac{\omega}{\Omega} \ p \int_0^\infty d\tau \exp(-p\tau) \left[ \beta(\omega, T_{SL} \ \tau)/\beta_L - 1 \right]
\]

(9)

\[
\gamma_d(p) = p \int_0^\infty d\tau \exp(-p\tau) \left[ \beta_d(T_{SL} \ \tau)/\beta_L - 1 \right]
\]

(10)

with the equilibrium initial conditions:

\[
\beta(\omega, 0) = \beta_d(0) = \beta_L
\]

(11)

The inverse temperatures are obtained from \( \gamma(\omega, p) \) and \( \gamma_d(p) \) (which are determined by solving (5) and (6))\(^6\) via the inverse Laplace transform.

The quantity

\[
\Delta' = \left[ \pi \varphi(0) \right]^{-1} \left[ 1 + \pi \omega_1^2 T_{SL} \varphi(0) \right]^{1/2}
\]

has the meaning of the frequency interval within which the SP is saturated by the UHF field. If

\[
\Delta' \ll \Delta_1
\]

(13)

then the width of the hole burned in the EPR line is determined by the CR and (5) can be further approximated as follows:

\[
\int d\omega' \ f(\omega' - \omega) \left[ \gamma(\omega', p) - \gamma(\omega, p) \right] - (p + 1) \ \gamma(\omega, p) = \\
\quad = \pi \omega_d^2 T_{SL} \varphi(\omega - \Omega) \left[ 1 + \gamma(\Omega, p) \right]
\]

(14)

\(^6\) Let us note that in (5) the subleading terms containing \( \gamma_d(p) \) are omitted; however, those terms do contribute nontrivially to (6) via (8). In the third term on the r.h.s. of (8) the denominator appearing in the integral in the second term thereof is approximated away due to the narrow width \( \Delta \) of the homogeneous line form \( \varphi(y) \) (see below). Also, in (6) another subleading term is neglected, to wit, that which would stem from the first term in (5) due to the aforementioned subleading contribution of \( \gamma_d(p) \) into (5), which contribution is omitted (see above). Furthermore, in (5) and (8) the function \( g(x) \) is treated as constant as its width \( \Delta^* \) is much larger than all other relevant quantities, including the characteristic spectral diffusion length in the frequency space (see below). However, in (6) the function \( g(x) \) is not treated as constant as the integral would vanish in this approximation due to the fact that \( \gamma(\omega, p) \) is a symmetric function of \( \omega - \Omega \) (see below).
Without delving into this case in detail, let us mention that this equation is integrable in quadratures.

In the diffusion approximation $\Delta_{CR} \ll \Delta_1$ [4], [5], the nonlocal equation (5) can be approximated by a local differential equation:

$$\Delta_d^2 \frac{\partial^2 \gamma(\omega, p)}{\partial \omega^2} - \left[p + 1 + \pi \omega_1^2 T_{SL} \varphi(\omega - \Omega)\right] \gamma(\omega, p) = \pi \omega_1^2 T_{SL} \varphi(\omega - \Omega) \quad (15)$$

where

$$\Delta_d^2 = \frac{1}{2} \int dx \ f(x) \ x^2 = \frac{\Delta_{CR}^2}{2} T_{SL} g(\Omega - \omega_0) \int dx \ W_{CR}(x) \quad (16)$$

Now, the order of magnitude of $\Delta_d$ has the meaning of the frequency distance to which spin excitations are propagated within the time $T_{SL}$ due to the CR, which in this case has the characteristics of the so-called spectral diffusion (SD).

In the works [4], [5], [1], [15], when studying the effect of the SD on the saturation in the stationary case, the additional condition (13) was assumed, i.e., it was assumed that $\Delta' \ll \Delta_d$. The results of the instant note (see the next section) hold for general $\Delta'$ and $\Delta_d$ (i.e., here we do not assume $\Delta' \ll \Delta_d$).

Further, usually the function $\varphi(x)$ is assumed to be a truncated Lorentz distribution [12]. For the reasons which will become clear below, we will assume that

$$\varphi(x) = (2\Delta)^{-1} \exp(-|x|/\Delta) \quad (17)$$

where $\Delta$ has the meaning of the SP width and for inhomogeneous broadening we have $\Delta \ll \Delta^*$. The above approximation is justified as the difference between the exponential form from the Lorentz distribution does not exceed 9% (while the maximum deviations of the Gaussian from the Lorentz distribution and the exponential form are approximately 23% and 22%, respectively).

### 3 Solving System of Equations

To determine the inverse temperatures, we must solve the following self-conjugate inhomogeneous boundary problem:

$$\frac{\partial^2 \phi(x)}{\partial x^2} - \left[p + 1 + \frac{\pi \omega_1^2}{2\Delta_d^2} T_{SL} \exp(-|x|/\Delta)\right] \phi(x) = h(x) \quad (18)$$

$$\lim_{x \to \pm \infty} \phi(x) = 0 \quad (19)$$

where the boundary conditions are dictated by the fact that the deviations from the equilibrium occur only in the $\Delta_1$-vicinity of the frequency $\Omega$. We have

$$\phi(x) = \int dy \ \Gamma(x, y) \ h(y) \quad (20)$$
where the Green’s function \( \Gamma(x, y) \) satisfies the following equation
\[
\frac{\partial^2 \Gamma(x, y)}{\partial x^2} - \left[ \frac{p + 1}{\Delta_d^2} + \frac{\pi \omega_1^2}{2 \Delta \Delta_d^2} T_{SL} \exp(-|x|/\Delta) \right] \Gamma(x, y) = \delta(x - y) \tag{21}
\]
and the boundary conditions
\[
\lim_{x \to \pm \infty} \Gamma(x, y) = 0 \tag{22}
\]
Also, the Green’s function is symmetric:
\[
\Gamma(x, y) = \Gamma(y, x) \tag{23}
\]
Via a direct substitution into (21), one can readily verify that
\[
\Gamma(x, 0) = -\Delta \left[ \lambda \, I'_\nu(\lambda) \right]^{-1} I_\nu(\lambda \exp(-|x|/2\Delta)) \tag{24}
\]
where \( I_\nu(z) \) is the modified Bessel function of the first kind [11] (also see [13]), the prime denotes a derivative w.r.t. the function argument, and
\[
\lambda = \omega_1 \sqrt{2 \pi T_{SL} \Delta/\Delta_d} \tag{25}
\]
\[
\nu = 2\Delta \sqrt{p + 1/\Delta_d} \tag{26}
\]
Using (20), (23) and (24) we can fix \( \phi(0) \). Then, for \( x \geq 0 \) we have the following boundary problem:
\[
\frac{\partial^2 \phi(x)}{\partial x^2} - \left[ \frac{p + 1}{\Delta_d^2} + \frac{\pi \omega_1^2}{2 \Delta \Delta_d^2} T_{SL} \exp(-|x|/\Delta) \right] \phi(x) = h(x) \tag{27}
\]
\[
\lim_{x \to \pm \infty} \phi(x) = 0 \tag{28}
\]
\[
\phi(0) \text{ is given} \tag{29}
\]
which can be solved using the fundamental system of solutions of the homogeneous equation (with \( h(x) = 0 \)):
\[
\phi_1(x) = I_\nu(\lambda \exp(-x/2\Delta)) \tag{30}
\]
\[
\phi_2(x) = I_{-\nu}(\lambda \exp(-x/2\Delta)) \tag{31}
\]
Omitting the derivation (which is based on standard techniques), the solution is given by (\( x \geq 0 \)):
\[
\phi(x) = \phi(0) \, \phi_1(x)/\phi_1(0) + \int_0^\infty dy \, \Gamma^*(x, y) \, h(y) \tag{32}
\]
where (the Heaviside function \( \theta(x > 0) = 1, \, \theta(0) = 1/2, \) and \( \theta(x < 0) = 0 \))
\[
\Gamma^*(x, y) = \frac{\pi \Delta}{\sin(\pi \nu)} \left\{ I_{-\nu}(\lambda) \, I_\nu \left( \lambda \exp \left( \frac{-x}{2\Delta} \right) \right) - I_\nu \left( \lambda \exp \left( \frac{-y}{2\Delta} \right) \right) - \theta(x - y) \, I_\nu \left( \lambda \exp \left( \frac{-x}{2\Delta} \right) \right) \, I_{-\nu} \left( \lambda \exp \left( \frac{-y}{2\Delta} \right) \right) \right\} + (x \leftrightarrow y) \tag{33}
\]
Further, for arbitrary $x$ we have
\[ \phi(x) = \phi(0) \phi_1(|x|)/\phi_1(0) + \int_0^\infty dy \, \Gamma^*(|x|, y) \left[ \theta(x) h(y) + \theta(-x) h(-y) \right] \] (34)

Therefore:
\[ \Gamma(x, y) = \theta(x y) \Gamma^*(|x|, |y|) - \Delta \left[ \lambda I_\nu(\lambda) I'_\nu(\lambda) \right]^{-1} I_\nu \left( \lambda \exp \left( \frac{|x|}{2\Delta} \right) \right) I_\nu \left( \lambda \exp \left( -\frac{|y|}{2\Delta} \right) \right) \] (35)

So, the solution of (15) is given by
\[ \gamma(\omega, p) = \pi \omega_1^2 T_{SL} \Delta_d^{-2} \int dy \, \Gamma(\omega - \Omega, y) \varphi(y) \] (36)

4 Limiting Cases

As mentioned above, (13) corresponds to the limit where the width of the hole is determined by the SD. This condition can be expressed as follows:
\[ \Delta \ll \Delta_d \] (37)
\[ \lambda \ll 1 \] (38)

which formally is equivalent to taking the limit $\Delta \to 0$. Using the representation of the function $I_\nu(z)$ via a power series [2], we have (up to subleading terms in $\Delta$)
\[ \Gamma(x, y) = \frac{\Delta_d}{2 \sqrt{p+1}} \left[ \frac{\mu}{\mu + \sqrt{p+1}} \exp \left( -\frac{\sqrt{p+1}}{\Delta_d} (|x| + |y|) \right) - \exp \left( -\frac{\sqrt{p+1}}{\Delta_d} |x - y| \right) \right] \] (39)

where
\[ \mu = \pi \omega_1^2 T_{SL}/2\Delta_d \] (40)

is the effective parameter of saturation. For $\gamma(\omega, p)$ and $\gamma_d(p)$ we have
\[ \gamma(\omega, p) = -\frac{\mu}{\mu + \sqrt{p+1}} \exp \left( -a \sqrt{p+1} \right) \] (41)
\[ \gamma_d(p) = 4\kappa \Omega \Delta_d g'(\Omega - \omega_0) \left[ \frac{1}{\sqrt{p+1}} - \frac{1}{\mu + \sqrt{p+1}} \right] \] (42)

and for the inverse temperatures we obtain (via the inverse Laplace transform):
\[ \frac{[\beta_L - \beta(\omega, t)]/\beta_L}{\beta_L} = \frac{\mu}{\omega} \left[ -\frac{\mu}{\mu^2 - 1} \exp \left( \mu a + (\mu^2 - 1)\tau \right) \text{erfc} \left( \frac{a}{2\sqrt{\tau}} + \mu \sqrt{\tau} \right) + \frac{\exp(-a)}{2(\mu + 1)} \text{erfc} \left( \frac{a}{2\sqrt{\tau}} - \sqrt{\tau} \right) + \frac{\exp(a)}{2(\mu - 1)} \times \text{erfc} \left( \frac{a}{2\sqrt{\tau}} + \sqrt{\tau} \right) \right] \] (43)
\[ \frac{[\beta_d(t) - \beta_d]/\beta_d}{\beta_d} = \frac{4\mu}{\mu^2 - 1} \kappa \Omega \Delta_d g'(\Omega - \omega_0) \times \left[ \mu \text{erf}(\sqrt{\tau}) - 1 + \exp \left( (\mu^2 - 1)\tau \right) \text{erfc}(\mu \sqrt{\tau}) \right] \] (44)
Here\(^7\)

\[
a = |\omega - \Omega|/\Delta_d \tag{45}
\]

\[
\tau = t/T_{SL} \tag{46}
\]

\[
\kappa = \left[ \frac{\int dy \, g^2(y)}{g(\Omega - \omega_0)} + \frac{T_{SL}}{T_{DL}} \frac{\omega_0^2}{\Delta_d^2} \right]^{-1} \tag{47}
\]

Next, let us consider the limiting case where the contribution of the SD to the saturation of the inhomogeneously broadened line is negligible. This corresponds to taking the limit \(\Delta_d \to 0\), which can be accomplished via the asymptotic formulas for the modified Bessel functions \((z, \nu \to \infty)\) [2] (also see [8]):

\[
I_{\nu}(z) \approx \exp \left( (z^2 + \nu^2)^{1/2} - \nu \text{ arsh}(\nu/z) \right) / \left[ \sqrt{2\pi} \ (z^2 + \nu^2)^{1/4} \right] \tag{48}
\]

\[
K_{\nu}(z) \approx \exp \left( \nu \text{ arsh}(\nu/z) - (z^2 + \nu^2)^{1/2} \right) / \left[ \sqrt{2\pi} \ (z^2 + \nu^2)^{1/4} \right] \tag{49}
\]

Here \(K_{\nu}(z)\) is the Macdonald function (the modified Bessel function of the second kind):

\[
I_{-\nu}(z) = I_{\nu}(z) + 2 \sin(\pi \nu) \ K_{\nu}(z)/\pi \tag{50}
\]

Taking into account the properties of the \(\delta\)-function

\[
\lim_{z \to +\infty} z \exp(-z|x|)/2 = \delta(x) \tag{51}
\]

\[
\delta(F(x)) = \delta(x - x_0)/|F'(x_0)| \tag{52}
\]

where \(F(x_0) = 0\), we get (up to subleading terms in \(\Delta_d\))

\[
\Gamma(x, y) = -\Delta_d^2 \left[ p + 1 + \pi \omega_0^2 \ T_{SL} \varphi(x) \right]^{-1} \delta(x - y) \tag{53}
\]

as it should be.

\section{Concluding Remarks}

The choice of the function \(\varphi(x)\) as the exponential line form is motivated by the fact that (15) in this case can be solved in quadratures via modified Bessel functions, which are well-studied. On the other hand, when \(\varphi(x)\) has the form of the (truncated) Lorentz distribution, the Green’s function \(\Gamma(x, y)\) cannot be expressed via elementary or known special functions.

\(^7\) Taking into account that \(T_{SL}/T_{DL} = 2\) or \(T_{SL}/T_{DL} = 3\) [15], typically \(\omega_d \ll \Delta_d\), and the first term in (47) is of order 1, as in [10] we can neglect the second term in (47). Also, the contribution of the second term in (8) into \(\kappa\) in (47) is negligible in the small \(\Delta\) limit. Finally, as in [10], in (43) we can approximate the overall multiplicative factor \(\Omega/\omega\) by 1.
References

[1] Atsarkin, V.A. and Demidov, V.V. (1979) Dipole-reservoir cooling and dynamic polarization of nuclei in saturation of inhomogeneous EPR line. Soviet Physics JETP 49(6): 1104-1108. [Zh. Eksp. Teor. Fiz. 76, 2185-2193 (June 1979).]

[2] Baitman, H. and Erdélyi, A. (1953) Higher Transcendental Functions, Vol. II. New York, NY: McGraw-Hill.

[3] Bendiashvili, N.S., Buishvili, L.L. and Zviadadze, M.D. (1970) Contribution to the Theory of Spin-Lattice Relaxation in Crystals with Paramagnetic Impurities. Soviet Physics JETP 31(2): 321-322. [Zh. Eksp. Teor. Fiz. 58, 597-600 (February, 1970).]

[4] Buishvili, L.L., Zviadadze, M.D. and Khutsishvili, G.R. (1968) Quantum-Statistical Theory of the Dynamical Polarization of Nuclei in the Case of Non-Uniform ESR Line Broadening. Soviet Physics JETP 27(3): 469-475. [Zh. Eksp. Teor. Fiz. 54, 876-890 (March, 1968).]

[5] Buishvili, L.L., Zviadadze, M.D. and Khutsishvili, G.R. (1969) Role of Spectral Diffusion and Dipole-Dipole Reservoir in the Saturation of an Inhomogeneously Broadened Line. Soviet Physics JETP 29(1): 159-163. [Zh. Eksp. Teor. Fiz. 56, 290-298 (January, 1969).]

[6] Buishvili, L.L., Zviadadze, M.D. and Khutsishvili, G.R. (1973) Strong Saturation of Inhomogeneously Broadened Lines. Soviet Physics JETP 36(5): 933-938. [Zh. Eksp. Teor. Fiz. 63, 1764-1775 (November, 1972).]

[7] Buishvili, L.L., Zviadadze, M.D. and Khutsishvili, G.R. (1982) Quasithermodynamic Theory of Magnetic Resonance. Tbilisi, Georgia (in Russian).

[8] Digital Library of Mathematical Functions (2020) Modified Bessel Functions: §10.41 Asymptotic Expansions for Large Order. Available online: https://dlmf.nist.gov/10.41.

[9] Kakushadze, Z. (1990) Non-Stationary Saturation of Inhomogeneously Broadened Spin Systems with Effective Cross-Relaxation. Bulletin of Georgian Academy of Sciences 139(2): 285-288 (in Russian). [An English translation is available online: https://arxiv.org/abs/2001.01362.]

[10] Kakushadze, Z. (1991) Non-Stationary Saturation of Inhomogeneously Broadened EPR Lines. Phys. Proc. Tbilisi State Univ. 306: 93-103 (in Russian).

[11] Kamke, E. (1977) Differentialgleichungen: Lösungsmethoden und Lösungen, I. Gewöhnliche Differentialgleichungen. Leipzig, Germany: B.G. Teubner (in German).
[12] Kittel, C. and Abrahams, E. (1953) Dipolar Broadening of Magnetic Resonance Lines in Magnetically Diluted Crystals. *Physical Review* 90(2): 238-239.

[13] Polyanin, A.D. and Zaitsev, V.F. (2003) *Handbook of exact solutions for ordinary differential equations*. (2nd ed.) Boca Raton, FL: Chapman & Hall/CRC.

[14] Portis, A.M. (1953) Electronic Structure of $F$ Centers: Saturation of the Electron Spin Resonance. *Physical Review* 91(5): 1071-1078.

[15] Zviadadze, M.D. (1984) *Doctor of Science Thesis*. Tbilisi, Georgia: Tbilisi State University (in Russian).