Influence of frequency exchange rate on free induction decay after saturation

A. I. Burshtein and A. A. Zharikov
Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, U.S.S.R.

V. S. Malinovsky
Novosibirsk State University, 630090 Novosibirsk, U.S.S.R.
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The free induction decay (FID) and light-echo kinetics are calculated under the assumption that a two-level system frequency is a purely discontinuous noncorrelated Markovian process, and its statistical distribution is a bi-Lorentzian contour. The latter assumption is primarily mathematical, but useful. The model allows one to obtain an exact solution of the FID problem, which recovers the results obtained earlier with perturbation theory (the fast modulation limit) as well as the result concerning the slow modulation limit. It is shown that only in the latter case does the field dependence of the FID rate found by De Voe and Brewer [Phys. Rev. Lett. **50**, 1269 (1983)] have a self-consistent explanation.

I. INTRODUCTION

An interaction of a radiation field with a two-level system (TLS) is usually described by Bloch equations,[1,2] if the line broadening is considered as homogeneous. However, the line, which is reasonably considered as homogeneous in a weak field, is not homogeneous in a strong one. This became clear in the experiments by De Voe and Brewer,[3] who studied the field dependence of the free-induction-decay (FID) rate after switching off the saturating field. As a sample, they used crystalline LaF_3:Pr^{3+}, in which the Pr^{3+} ion has a very wide inhomogeneous spectrum $\Phi(\omega_0)$, determined by the dispersion of the crystalline local electric fields. In addition, the frequency of the studied resonance transition $^3H_4$-$^1D_2$ depends on the orientation of the magnetic momenta of fluorine nuclei surrounding the ion. Because of this it is also dispersed within the limits of a narrow packet of frequencies, but this broadening can be inhomogeneous as well as homogeneous. It depends on how fast the resonance frequency migrates in the packet due to mutual reorientation of fluorine nuclei. In any case, magnetic inhomogeneity results in an additional broadening mechanism, enlarging the rate of phase relaxation compared with its spontaneous value $(1/T_2)$. De Voe and Brewer's experiment proves, though, that the corresponding increase of the FID rate, observed in weak fields, is suppressed in strong ones.[3] This conclusion is quite contrary to that following from the Bloch theory. Considering the magnetic broadening to be homogeneous, it does not take into account the origin of phase relaxation and therefore ignores the influence of the field on its rate, in principle.

This paradox has stimulated numerous attempts to substitute the Bloch phenomenological description of phase relaxation by a more adequate one, which is able to explain the experiment. Assuming a homogeneous character of magnetic broadening, most authors employed nonmodel perturbation theory (PT) in the random detuning of a frequency in a packet $\varepsilon(t)$. It can be developed when the distribution over detunings $\phi(\varepsilon)$ has a finite second moment $d=\langle\varepsilon^2\rangle$. Besides, frequency modulation rate $1/\tau_0$ must be great, so that the packet actually transforms into the homogeneous line with the width $\Gamma=d\tau_0$. In the pioneering works[4-6] different versions of such theories were considered.

Most of them employ the Markovian version of PT, which may be called a "Lorentzian" approximation. In its framework the line is considered as not only homogeneous, but even of Lorentzian form, and the corresponding phase relaxation is rigorously exponential. In reality, at $t<\tau_0$ the relaxation is nonexponential, and line wings for $\omega_0 \gg 1/\tau_0$ vanish as ω_0^{-4}, but not quadratically. Therefore, the Lorentzian approximation is acceptable, if the width of a hole in the spectrum $\Phi(\omega_0)$, appearing because of its stationary saturation, is less than $1/\tau_0$. Verification of this statement *post factum* proves its invalidity.[7]

But non-Markovian perturbation theory[4] is not better either, even though it is free of the Lorentzian approximation. The agreement of any PT with experiment can be gained only for the parameter $\Gamma\tau_0$ in the range 0.7–1.1, which is not at all small, as it must be because of the applicability conditions of PT. According to some sources its real value is even greater ($\sim$11.5, of Ref. 8). This means that magnetic modulation is not fast enough, and the corresponding packet can even be inhomogeneously broadened.

In order to eliminate perturbation-theory restrictions, one should only suppose that the frequency fluctuation process $\varepsilon(t)$ is a purely discontinuous Markovian noise; i.e., ε changes instantly at successive moments of time over a Poisson distribution separated by intervals at an average equal to τ_0. Throughout the intervals it is conserved, and the next value ε depends only on the former. The averaged response of the TLS to such a perturbation can be calculated by sudden modulation theory.[9] Usually, though, for the sake of simplicity, a particular case of such a perturbation is considered, known as the uncorrelated process.[10,11] In this process a new value ε does not even depend on the former one, but appears with equilibrium probability $\phi(\varepsilon)$. Due to that fact, the FID signal can be calculated analytically as a whole.[7] But the general solution done in quadratures is too cumbersome. It is rather difficult to find from it the field dependence of the FID rate, when $\phi(\varepsilon)$ is considered to be the Gaussian contour.

To solve this problem, we shall address here the model of the "bi-Lorentzian" contour. This contour has a finite second moment. Therefore, perturbation theory can be applied to it, as well as to the Gaussian contour. But an exact solution for the bi-Lorentzian contour is simpler than for the Gaussian one and it is easier to compare it with the results of the perturbation theory. However, the Lorentzian contour is just a particular case of the bi-Lorentzian one. The first one qualitatively differs from the Gaussian one by the absence of the second moment. In this case there is no alternative to the exact solution, as the perturbation theory is unapplicable to the contours of this kind.

From a physical point of view, the choice of either the Gaussian or the Lorentzian static contour is determined only by the spatial packing of magnetic nuclei surrounding an ion. It is well known that the dipole-dipole interaction with the nuclei yield the Gaussian inhomogeneous contour, the packing being regular, and the Lorentzian contour if it is chaoticlike in diluted systems.[12] But it is note quite correct to compare the Gaussian contour with the Lorentzian one, because the former narrows with quickly increasing modulation, while the latter remains unchanged.[13,14]

Our model contour occupies an intermediate position, possessing some features of both of them. For the superfast modulation the perturbation theory is valid, and for the slow one qualitatively different results were obtained. In the latter case, the FID rate in zero field essentially differs from the echo decay rate, though they coincide in the perturbation-theory limits. Besides, the FID nonmonotonically depends on the modulation rate. Therefore, there always exists an explanation of the effect which is an alternative to PT.

II. FID SIGNAL CALCULATION METHOD

Let us consider the TLS interaction with monochromatic wave $\mathscr{E}=E_0\exp(i\omega t)$. The latter induces transitions between the TLS levels, whose frequency

$$\frac{E_2(t)-E_1(t)}{\hbar}=\omega_0+\varepsilon(t) \tag{2.1}$$

is a stationary random process: its mean value ω_0 and detuning distributions $\phi(\varepsilon)$ are conserved with respect to time. In the coordinate system rotating with the field, the density matrix of the TLS,

$$\hat{\rho}=\begin{bmatrix}\rho_{11} & \rho_{12}\\ \rho_{21} & \rho_{22}\end{bmatrix},$$

satisfies the Liouville kinetic equation of the form

$$\dot{X}=-[\hat{L}_0+i\xi(t)\hat{L}_1]X+\hat{\Lambda}, \tag{2.2}$$

where

$$X=\begin{bmatrix}\sigma_{12}\\ \sigma_{21}\\ n\end{bmatrix},\quad \hat{L}_0=\begin{bmatrix}\dfrac{1}{\tilde{T}_2}-iz & 0 & \dfrac{-iW}{2}\\ 0 & \dfrac{1}{\tilde{T}_2}+iz & \dfrac{iW}{2}\\ -iW & iW & \dfrac{1}{\tilde{T}_1}\end{bmatrix}, \tag{2.3a}$$

$$\hat{L}_1=\begin{bmatrix}-1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0\end{bmatrix},\quad \hat{\Lambda}=\begin{bmatrix}0\\ 0\\ \dfrac{n_0}{\tilde{T}_1}\end{bmatrix}. \tag{2.3b}$$

Time is chosen in units of τ_0, $z=(\omega_0-\omega)\tau_0$ is the frequency detuning in units of τ_0^{-1}, $\xi(t)=\varepsilon(t)\tau_0$, $W=\chi\tau_0$, $n=\rho_{22}-\rho_{11}$ is the difference between level populations $(E_2>E_1)$, $\sigma_{12}=\sigma_{21}^*=\rho_{12}\exp(-i\omega t)$, T_1 and T_2 are the time of the longitudinal and transversal relaxation, and $\tilde{T}_1=T_1/\tau_0$, $\tilde{T}_2=T_2/\tau_0$.

After switching off the field ($W=0$), free induction decay is determined by the following expression:

$$\bar{\sigma}_{12}(t)=\langle \sigma_{12}^s\exp\{izt+i\int_0^t\xi(t')dt'-t/\tilde{T}_2\}\rangle . \tag{2.4}$$

Angular brackets denote the averaging of its right-hand side over random realizations of the process $\xi(t)$. The initial polarization σ_{12}^s created by saturating field is a stationary solution of Eq. (2.2). To determine the FID signal, it is necessary not only to find $\bar{\sigma}_{12}(t)$, but to average it over the broad inhomogeneous distribution of frequencies $\Phi(z)=\Phi(\omega)/\tau_0$. Taking into account that the distribution dispersion is much greater than that saturation region, we shall consider $\Phi(z)=\Phi_0=\text{const}$. Then the signal form is determined by the following expression:[2]

$$R(t)=\Phi_0\text{Im}\int\bar{\sigma}_{12}(t)dz . \tag{2.5}$$

Usually when calculating $R(t)$, the correlation of the TLS frequency fluctuations (before and after switching off the field) is neglected. This makes possible the decoupling procedure in the formula (2.4), averaging separately σ_{12}^s and the exponent. The decoupled formula essentially becomes simpler,

$$\bar{\sigma}_{12}(t)=\bar{\sigma}_{12}^sK(t)\exp[(iz-1/\tilde{T}_2)t] , \tag{2.6}$$

where $K(t)=\langle\exp[i\int_0^t\xi(t')dt']\rangle$ is the correlation function of the frequency modulation. So, in the simplest case, the problem reduces to the calculation of $K(t)$ and of the mean stationary value $\langle\sigma_{12}^s\rangle=\bar{\sigma}_{12}^s$. It is for this purpose that the perturbation theory in frequency fluctuations is applied, in the hope that

$$q^2=\langle\varepsilon^2\rangle\tau_0^2\ll 1 . \tag{2.7}$$

To have the possibility for a comparison, we first calculate $R(t)$, exploiting PT. Then, addressing the exact solution of the problem, we improve the criterion (2.7) and show that it is broken when PT is fitted to the experiment.

III. NON-MARKOVIAN PERTURBATION THEORY

It is known that in the framework of perturbation theory[9]

$$K(t)=\exp(-q^2 t) \; . \tag{3.1}$$

So, one should just calculate $\bar{\sigma}_{12}^s$ using the same theory.

Proceeding in Eq. (2.2) to the Liouville representation of interaction,

$$X(t)=\exp(-\hat{L}_0 t)\tilde{X}(t) \; , \tag{3.2}$$

the following equation is easily obtained in the second order of PT in $\xi(t)$:

$$\langle \dot{\tilde{X}}(t)\rangle = -\int_0^t r(t-t')e^{\hat{L}_0 t}\hat{L}_1 e^{-\hat{L}_0(t-t')}\hat{L}_1 e^{-\hat{L}_0 t'} \times \langle \tilde{X}(t')\rangle dt' + e^{\hat{L}_0 t}\hat{\Lambda} \; , \tag{3.3}$$

where $r(t-t')=\langle \xi(t)\xi(t')\rangle = q^2\exp(-t)$ is the noise correlation function. In this equation a usual decoupling procedure is used,[9] which leads to the separate averaging of the perturbation and the response to it. If the initial variables are employed again, and their average value is defined as $\bar{X}=\exp(-\hat{L}_0 t)\langle \tilde{X}\rangle$, then the final integrodifferential equation of non-Markovian perturbation theory is derived:

$$\dot{\bar{X}}(t)=-\hat{L}_0\bar{X}(t)-\int_0^t r(t-t')\hat{L}_1 e^{-\hat{L}_0(t-t')}\hat{L}_1\bar{X}(t')dt' + \hat{\Lambda} \; . \tag{3.4}$$

Applying the Laplace transformation to this equation, we have

$$\bar{X}(p)=\int_0^\infty e^{-pt}\bar{X}(t)dt = \frac{1}{p+\hat{L}_0+\hat{A}(p)}\left[\bar{X}(0)+\frac{1}{p}\hat{\Lambda}\right] , \tag{3.5}$$

$$\hat{A}(p)=\int_0^\infty r(\tau)\hat{L}_1 e^{-\hat{L}_0\tau}\hat{L}_1 e^{-p\tau}d\tau \; . \tag{3.6}$$

In addition to the non-Markovian approximation, the Markovian approximation of perturbation theory exists, when the operator $\hat{A}(p)$ is assumed[5,6]

$$\hat{A}=\int_0^\infty r(\tau)\hat{L}_1 e^{-\hat{L}_0\tau}\hat{L}_1 e^{\hat{L}_0\tau}d\tau \; . \tag{3.7}$$

This approximation is suitable for the description of a long-time behavior of the system $t \gg 1$ in the absence of pumping. The application to the nonstationary regime, however, is invalid.[7] The stationary solution should be found as follows:

$$\bar{X}^s=\lim_{p\to 0} p\bar{X}(p)=\frac{1}{\hat{L}_0+\hat{A}(0)}\hat{\Lambda} \; , \tag{3.8}$$

where $\hat{A}(0)$ is determined from expression (3.6),

$$\hat{A}(0)=q^2\hat{L}_1\frac{1}{1+\hat{L}_0}\hat{L}_1 \; . \tag{3.9}$$

Using (2.3) in (3.8) and (3.9) we find the mean stationary value of the nondiagonal element of the density matrix:

$$\bar{\sigma}_{12}^s=\frac{n_0 W}{2}\,\frac{-z^3+z^2\dfrac{i}{\tilde{T}_2}+z(q^2-\kappa^2)+i(\kappa^2/\tilde{T}_2+q^2 t_2)}{z^4+Bz^2+C} \; , \tag{3.10}$$

$$B=\kappa^2+W^2\tilde{T}_1/\tilde{T}_2+1/\tilde{T}^2-2q^2 \; , \tag{3.11a}$$

$$C=(\kappa/\tilde{T}_2+q^2 t_2/\kappa)(\kappa/\tilde{T}_2+q^2\kappa/t_2+W^2\kappa\tilde{T}_1) \; , \tag{3.11b}$$

$$\kappa^2=t_2^2(1+W^2/t_1 t_2), \quad t_{1,2}=1+1/\tilde{T}_{1,2} \; . \tag{3.11c}$$

Substituting (3.1) and the value $\bar{\sigma}_{12}^s$ into (2.6) and performing integration over z in the expression (2.5), we obtain for the FID the following expression:

$$R(t)=\frac{n_0 W}{2}\pi\Phi_0\exp\left[-\left[q^2+\frac{1}{\tilde{T}_2}\right]t\right] \times[A_1\tilde{K}_1(t)+A_2\tilde{K}_2(t)] \; , \tag{3.12}$$

where

$$A_1=\left[\sqrt{C}\left[\frac{1}{\tilde{T}_2}-2z_3\right]+\kappa^2/\tilde{T}_2+q^2 t_2\right]\Big/(2z_3\sqrt{C}) \; , \tag{3.13a}$$

$$A_2=[\kappa^2-q^2-\sqrt{C}+2z_3/\tilde{T}_2-B]/(2z_3\sqrt{C}) \; , \tag{3.13b}$$

$$\tilde{K}_1(t)=\begin{cases}[z_1\exp(-z_1 t)-z_2\exp(-z_2 t)]/(z_1-z_2) & \text{for } 4C\le B^2\\ \exp(-z_3 t)[\cos(z_4 t)+(z_3/z_4)\sin(z_4 t)] & \text{for } 4C\ge B^2 \; ,\end{cases} \tag{3.14}$$

$$\tilde{K}_2(t)=\begin{cases}[\sqrt{C}/(z_1-z_2)][\exp(-z_1 t)-\exp(-z_2 t)] & \text{for } 4C\le B^2\\ -(\sqrt{C}/\sqrt{2}z_4)\exp(-z_3 t)\sin(z_4 t) & \text{for } 4C\ge B^2 \; ,\end{cases} \tag{3.15}$$

$$z_{1,2}=\frac{1}{\sqrt{2}}[B\pm(B^2-4C)^{1/2}]^{1/2} \; , \quad z_{3,4}=\tfrac{1}{2}(2\sqrt{C}\pm B)^{1/2} \; . \tag{3.16}$$

The character of the decay depends on the sign of $\tilde{D}=B^2-4C$. We have either a two-exponential FID with rates z_1 and z_2 for $\tilde{D}>0$ or the decay with rate z_3 in the presence of oscillations at frequency z_4 for $\tilde{D}<0$. Assuming $\tilde{D}=0$, it is easy to find the position of the boundary between the two-exponential and the oscillatory behavior:

$$\frac{(\kappa^2-1/\tilde{T}_2^2-W^2\tilde{T}_1/\tilde{T}_2)^2}{4(t_2+1/\tilde{T}_2)(\kappa^2/t_2+W^2\tilde{T}_1+1/\tilde{T}_2)}=q^2 \; .$$

Taking into account that $\tilde{T}_1, \tilde{T}_2 \gg 1$, we hence obtain the boundary values of interaction strength for settled q^2. The FID signal is two-exponential for $W \le 1/2(q^2\tilde{T}_1)^{1/2}$ and for $W \ge 4(q^2\tilde{T}_1)^{1/2}$, and in the intermediate interval it is oscillatory

$$\frac{1}{2(q^2\tilde{T}_1)^{1/2}} \le W \le 4(q^2\tilde{T}_1)^{1/2} .$$

IV. UNCORRELATED MARKOVIAN FREQUENCY MODULATION

Let us consider the TLS frequency modulation by a stationary Markovian purely discontinuous process. In this case, the averaging in (2.4) may be represented as follows:[7,11]

$$\bar{\sigma}_{12}(t) = \int d\xi \exp\left[izt - \frac{t}{\tilde{T}_2}\right] K(\xi,t)\sigma_{12}^s(\xi) , \qquad (4.1)$$

where $\sigma_{12}^s(\xi)$ and $K(\xi,t)$ are "marginal" or conditional average values, whose argument ξ coincides. For the Laplace representation $\bar{\sigma}_{12}(p)$ from (4.1) we have

$$\bar{\sigma}_{12}(p) = \int_0^\infty \bar{\sigma}_{12}(t)\exp(-pt)dt = \int d\xi K(\xi,p)\sigma_{12}^s(\xi) , \qquad (4.2)$$

$$K(\xi,p) = \int_0^\infty K(\xi,t)\exp\left[-\left[p + \frac{1}{\tilde{T}_2} - iz\right]t\right]dt . \qquad (4.3)$$

According to Ref. 9 for the marginal function of the frequency modulation $K(\xi,t)$, we have

$$\dot{K}(\xi,t) = i\xi K(\xi,t) - [K(\xi,t) - \bar{K}(t)] , \qquad (4.4)$$

where $\bar{K}(t) = \int K(\xi,t)\phi(\xi)d\xi$, and $\phi(\xi) = \phi(\varepsilon)/\tau_0$. With the help of this equation, it is easy to derive the Laplace representation $K(\xi,p)$ and, substituting it into (4.2), obtain

$$\bar{\sigma}_{12}(p) = \frac{\displaystyle\int \frac{\sigma_{12}^s(\xi)}{p + t_2 - i(z+\xi)}d\xi}{\displaystyle 1 - \int \frac{\phi(\xi)}{p + t_2 - i(z+\xi)}d\xi} . \qquad (4.5)$$

For the stationary value $\sigma_{12}^s(\xi)$ to be derived, let us employ the kinetic equation for the density matrix, derived in the framework of the sudden modulation theory:[12]

$$\dot{\rho}(\xi,t) = -i[\hat{H}(\xi,t),\rho(\xi,t)] - \hat{R}\rho(\xi,t) - \left[\rho(\xi,t) - \int f(\xi,\xi')\rho(\xi',t)d\xi'\right] , \qquad (4.6)$$

where $\hat{H}(\xi,t)$ is the Hamiltonian of the TLS interaction with radiation field, $\hat{R}$ takes into account the lateral relaxation of components $\hat{\rho}$, $f(\xi,\xi')$ is the probability density of the appearance of frequency ξ after ξ'. If the process is uncorrelated, then $f(\xi,\xi') = \phi(\xi)$, and the system (4.6) may be rewritten as

$$\dot{X}(\xi,t) = -(\hat{L} + i\xi\hat{L}_1)X(\xi,t) + \phi(\xi)(\bar{X} + \hat{\Lambda}) , \qquad (4.7)$$

where $\hat{L} = \hat{L}_0 + 1$, the designations are the same as in (2.3). Assuming $\dot{X}(\xi,t) = 0$, we find

$$X_s(\xi) = \phi(\xi)\hat{\mathcal{L}}(\xi)(\bar{X}_s + \hat{\Lambda}) , \qquad (4.8)$$

where

$$\hat{\mathcal{L}}(\xi) = (\hat{L} + i\xi\hat{L}_1)^{-1} = \frac{1}{D}\begin{vmatrix} t_1[t_2 + i(z+\xi)] + \frac{W^2}{2} & \frac{W^2}{2} & \frac{iW}{2}[t_2 + i(z+\xi)] \\ \frac{W^2}{2} & t_1[t_2 - i(z+\xi)] + \frac{W^2}{2} & -\frac{iW}{2}[t_2 - i(z+\xi)] \\ iW[t_2 + i(z+\xi)] & -iW[t_2 - i(z+\xi)] & t_2^2 + (z+\xi)^2 \end{vmatrix} \qquad (4.9)$$

and

$$D = t_1[\kappa^2 + (z+\xi)^2], \quad \kappa^2 = t_2^2[1 + W^2/t_1t_2] .$$

Averaging (4.8), for mean stationary elements of the density matrix we have

$$\bar{X}_s = \hat{\bar{\mathcal{L}}}(1 - \hat{\bar{\mathcal{L}}})^{-1}\hat{\Lambda} , \qquad (4.10)$$

where $\hat{\bar{\mathcal{L}}} = \int \mathcal{L}(\xi)\phi(\xi)d\xi$. Using (4.10) in (4.8), one can derive the following relation between stationary marginal and stationary mean values:

$$X_s(\xi) = \phi(\xi)\hat{\mathcal{L}}(\xi)\hat{\bar{\mathcal{L}}}^{-1}\bar{X}_s . \qquad (4.11)$$

Employing expression (4.9) in (4.11), one can easily obtain

$$\sigma_{12}^s(\xi) = \frac{\phi(\xi)\left[[\kappa^2 I_0 + I_1(z+\xi)]\bar{\sigma}_{12}^s + it_2[I_0(z+\xi) - I_1]\dfrac{\bar{u}_s + i(\kappa^2/t_2)\bar{v}_s}{2}\right]}{D(\kappa^2 I_0^2 + I_1^2)} \qquad (4.12)$$

with designations $\sigma_{12}=(u+iv)/2$, $I_0=\int d\xi\,\phi(\xi)/D$, $I_1=\int d\xi\,\phi(\xi)(z+\xi)/D$. For the averaged stationary value $\bar{\sigma}^s_{12}$ from (4.10), we derive

$$\bar{\sigma}^s_{12}=\frac{n_0W}{2}\frac{-t_1I_1+it_1(t_2I_0-|A|)}{1+(I_0t_2-|A|)(W^2\tilde{T}_1-t_1)-I_0t_1\kappa^2/t_2}\,, \tag{4.13}$$

where $|A|=t_1(\kappa^2I_0^2+I_1^2)$.

Formulas (4.5), (4.12), and (4.13) are derived for an arbitrary equilibrium distribution $\phi(\xi)$. This general solution is valid for any strength of field and for any frequency modulation rate. But to derive the evident form of the FID signal we have now to make the distribution $\phi(\xi)=\phi(\varepsilon)/\tau_0$ more concrete.

V. BI-LORENTZIAN EQUILIBRIUM DISTRIBUTION

We suggest the "bi-Lorentzian" distribution of the present form

$$\phi(\xi)=\frac{ab(b+a)}{\pi}\frac{1}{(\xi^2+a^2)(\xi^2+b^2)}\,, \tag{5.1}$$

where $a=a_0\tau_0$ and $b=b_0\tau_0$ are its dimensionless widths. The second moment of this distribution $q^2=\int\xi^2\phi(\xi)d\xi=ab$, and its wings decay as $1/\xi^4$. Using the exact calculation and the calculation in PT, we shall be able to determine the applicability limits of the latter.

Besides, such the equilibrium distribution allows one to proceed in the limit $b\to\infty$ to the Lorentzian static distribution

$$\phi(\xi)=\frac{1}{\pi}\frac{a}{\xi^2+a^2}\,, \tag{5.2}$$

to which the perturbation theory cannot be applied at all.

For the equilibrium distribution (5.1), I_0 and I_1 in (4.12) may be easily calculated and for the Laplace representation $\bar{\sigma}_{12}(p)$ defined in (4.5), and we have

$$\bar{\sigma}_{12}(p)=K(p)\bar{\sigma}^s_{12}-K'(p)\bar{\beta}^s-K'(p)\frac{1}{p+t_2+\kappa}\bar{\alpha}^s\,. \tag{5.3}$$

Here

$$K(p)=\frac{p-iz-(p_1+p_2-1/\tilde{T}_2)}{(p-iz-p_1+1/\tilde{T}_2)(p-iz-p_2+1/\tilde{T}_2)}\,, \tag{5.4a}$$

$$K'(p)=\frac{-p_1p_2}{(p-iz-p_1+1/\tilde{T}_2)(p-iz-p_2+1/\tilde{T}_2)}\,, \tag{5.4b}$$

where

$$p_{1,2}=-\tfrac{1}{2}\{1+a+b\pm[(1+a+b)^2-4ab]^{1/2}\}\,. \tag{5.5}$$

At the same time (4.13) yields

$$\bar{\sigma}^s_{12}=\frac{n_0W}{2}\frac{-z^3+iz^2/\tilde{T}_2-z[(\kappa+a+b)^2-ab]+i(\kappa+a+b)\left[\dfrac{\kappa+a+b}{\tilde{T}_2}+\dfrac{abt_2}{\kappa}\right]}{z^4+B_1z^2+C_1}\,, \tag{5.6a}$$

$$\bar{\beta}^s=\frac{n_0W}{2}\frac{iz^2+z[1/\tilde{T}_2+t_2(\kappa+a+b)/\kappa]-i\dfrac{\kappa}{t_2}\left[\dfrac{\kappa+a+b}{\tilde{T}_2}+\dfrac{abt_2}{\kappa}\right]}{z^4+B_1z^2+C_1}\,, \tag{5.6b}$$

$$\bar{\alpha}^s=\frac{n_0W}{2}(a+b)\left[1-\frac{t_2}{\kappa}\right]\frac{iz^2-z(\kappa+a+b+\kappa/t_2\tilde{T}_2)-i\dfrac{\kappa}{t_2}\left[\dfrac{\kappa+a+b}{\tilde{T}_2}+\dfrac{abt_2}{\kappa}\right]}{z^4+B_1z^2+C_1}\,, \tag{5.6c}$$

where

$$B_1=(\kappa+a+b)^2+1/\tilde{T}_2^2+W^2\tilde{T}_1/\tilde{T}_2-2ab\,, \tag{5.6d}$$

$$C_1=\left[\frac{\kappa+a+b}{\tilde{T}_2}+\frac{abt_2}{\kappa}\right]\left[\frac{\kappa+a+b}{\tilde{T}_2}+\frac{ab\kappa}{t_2}+W^2\tilde{T}_1(\kappa+a+b)\right]. \tag{5.6e}$$

Performing the reverse Laplace transform, from (5.3 we derive

$$\bar{\sigma}_{12}(t)=\exp[-(1/\tilde{T}_2-iz)t][K(t)\bar{\sigma}^s_{12}-\dot{K}(t)\bar{\beta}^s]-\int_0^t L(z,\tau)\exp[-(t_2+\kappa)(t-\tau)]d\tau\,, \tag{5.7a}$$

$$L(z,\tau)=\exp[-(1/\tilde{T}_2-iz)\tau]\dot{K}(\tau)\bar{\alpha}^s\,, \tag{5.7b}$$

$$K(t)=\frac{1}{p_1-p_2}[p_1\exp(p_2t)-p_2\exp(p_1t)]\,, \tag{5.8a}$$

$$\dot{K}(t)=\frac{p_1p_2}{p_1-p_2}[\exp(p_2t)-\exp(p_1t)]\,. \tag{5.8b}$$

It is the first term of (5.7a) that exactly reproduces (2.6). The remainder take into account frequency fluctuation correlation before and after switching off the saturating field. Averaging (5.7) in (2.5), we derive the final expression for the FID signal:

$$R(t)=\frac{n_0 W}{2D_0}\pi\Phi_0\left[\exp(-t/\tilde{T}_2)\{K(t)[R_1K_1(t)+R_2K_2(t)]+\dot{K}(t)[R_3K_1(t)+R_4K_2(t)]\}+\int_0^t L(\tau)\exp[-(t_2+\kappa)(t-\tau)]d\tau\right], \quad (5.9)$$

where

$$L(\tau)=\exp(-\tau/\tilde{T}_2)\dot{K}(\tau)[R_5K_1(\tau)-R_6K_2(\tau)], \quad (5.10)$$

$$R_1=(\kappa+a+b)\left[\frac{\kappa+a+b}{\tilde{T}_2}+\frac{abt_2}{\kappa}\right]+\sqrt{C_1}[1/\tilde{T}_2-(2\sqrt{C_1}+B_1)^{1/2}], \quad (5.11a)$$

$$R_2=(\kappa+a+b)^2-ab+\sqrt{c_1}+(2\sqrt{C_1}+B_1)^{1/2}[1/\tilde{T}_2-(2\sqrt{C_1}+B_1)^{1/2}], \quad (5.11b)$$

$$R_3=\frac{\kappa}{t_2}\left[\frac{\kappa+a+b}{\tilde{T}_2}+\frac{abt_2}{\kappa}\right]-\sqrt{C_1}, \quad (5.11c)$$

$$R_4=\frac{1}{\tilde{T}_2}+\frac{t_2}{\kappa}(\kappa+a+b)-(2\sqrt{C_1}+B_1)^{1/2}, \quad (5.11d)$$

$$R_5=(a+b)\left[1-\frac{t_2}{\kappa}\right]\left[ab+\frac{\kappa}{t_2}\frac{\kappa+a+b}{\tilde{T}_2}-\sqrt{C_1}\right], \quad (5.11e)$$

$$R_6=(a+b)\left[1-\frac{t_2}{\kappa}\right]\left[\kappa+a+b+\frac{\kappa}{t_2}\frac{1}{\tilde{T}_2}+(2\sqrt{C_1}+B_1)^{1/2}\right], \quad (5.11f)$$

$$D_0=\sqrt{C_1}(2\sqrt{C_1}+B_1)^{1/2}, \quad (5.12)$$

$$K_1(t)=\mathrm{Re}\left[\frac{1}{z_1-z_2}[z_1\exp(iz_2t)-z_2\exp(iz_1t)]\right], \quad (5.13a)$$

$$K_2(t)=\mathrm{Im}\left[\frac{z_1z_2}{z_1-z_2}[\exp(iz_1t)-\exp(iz_2t)]\right], \quad (5.13b)$$

$$z_1=\begin{cases}\frac{i}{\sqrt{2}}[B_1+(B_1^2-4C_1)^{1/2}]^{1/2} & \text{for } B_1^2\ge 4C_1\\ \frac{1}{2}[-(2\sqrt{C_1}-B_1)^{1/2}+i(2\sqrt{C_1}+B_1)^{1/2}] & \text{for } B_1^2\le 4C_1,\end{cases} \quad (5.14)$$

$$z_2=\begin{cases}\frac{i}{\sqrt{2}}[B_1-(B_1^2-4C_1)^{1/2}]^{1/2} & \text{for } B_1^2\ge 4C_1\\ \frac{1}{2}[(2\sqrt{C_1}-B_1)^{1/2}+i(2\sqrt{C_1}+B_1)^{1/2}] & \text{for } B_1^2\le 4C_1.\end{cases} \quad (5.15)$$

From the general expression (5.9), the perturbation-theory result can be readily gained, the parameters a and b vanishing. For $K(t)$ in this case formula (3.1) is valid, and the value $\bar{\sigma}_{12}^s$ as defined in (5.6a) transits into (3.10). As a result, with (5.9) only the first term of the sum in curly brackets is conserved, and the final formula for the FID signal transits into (3.12).

In fact, for the exact result to be reduced to the particular case of perturbation theory, the unequalities

$$a,b \ll 1 \quad (5.16)$$

must be valid. The most rigid of these criteria is both necessary and sufficient. If, e.g., $b>a$, then it is the requirement that $b \ll 1$ that determines an applicability region of perturbation theory, and not at all the unequality $ab \ll 1$, which is identical to the conventional condition (2.7). The necessity to strengthen the applicability criterion is connected with the presence of two different widths in the bi-Lorentzian spectrum. The situation is quite the same when the noise is characterized not by the one correlation time only, but by two different correlation times.[10] The difference between the criteria (2.7) and (5.16) disappears only when $a=b$.

For the Lorentzian equilibrium distribution (5.2) the exact solution can be readily obtained, performing in the general expressions (5.9)–(5.15) the limiting transition $b\to\infty$:

$$R(t)=R_0\exp[-(1/\tilde{T}_2+a+F)t]\left[1+\frac{\Pi(1-\exp[-(1+\kappa-a-F)t])}{1+\kappa-a-F}\right], \quad (5.17)$$

where

$$R_0=\frac{n_0W}{2F}\pi\Phi_0\left[\frac{1}{\tilde{T}_2}+\frac{at_2}{\kappa}-F\right], \tag{5.17a}$$

$$F^2=\left[\frac{1}{\tilde{T}_2}+\frac{at_2}{\kappa}\right]\left[\frac{1}{\tilde{T}_2}+\frac{a\kappa}{t_2}+W^2\tilde{T}_1\right], \tag{5.17b}$$

$$\Pi=\frac{a(F+a+\kappa/t_2\tilde{T}_2)(F+1/\tilde{T}_2+at_2/\kappa)}{(1/\tilde{T}_2+at_2/\kappa)(1+\kappa/t_2)(a+\kappa t_1\tilde{T}_1)} . \tag{5.17c}$$

The correction term in (5.17) takes into account the correlation of the system motion before and after switching off the field. Solution (5.17) shows that free induction signal, generally speaking, is described by the sum of two exponents with different weight multipliers. The case of equal rates is specific, or degenerate, i.e.,

$$1+\kappa=a+F . \tag{5.18}$$

In this case one can easily derive from (5.17)

$$R(t)=R_0(1+\Pi t)\exp[-(1/\tilde{T}_2+a+F)t] . \tag{5.19}$$

A simple analysis makes it clear that for characteristic times of decay $(1/\tilde{T}_2+a+F)^{-1}$ the correlation correction $\Pi/(1/\tilde{T}_2+a+F)$ is less than 1 for any value of parameter. The same is true for the situation under the curve determined by Eq. (5.18), i.e., for any $1+\kappa\gg a+F$. The correction term in (5.17) decays in this region faster than the main one and, besides, its amplitude $\Pi/(1+\kappa-a-F)$ is small, Neglecting it, we have

$$R(t)\approx R_0\exp[-(1/\tilde{T}_2+a+F)t] . \tag{5.20}$$

Above the curve determined by Eq. (5.18), i.e., for $1+\kappa\ll a+F$, the time scale is separated into two regions by the point $t=t_b$. In each of these regions the solution may be approximately considered to be monoexponential

$$R(t)=\begin{cases} R_0\exp[-(1/\tilde{T}_2+a+F)t], & t\ll t_b \quad (5.21a)\\ \dfrac{R_0\Pi}{F+a-1-\kappa}\exp[-(1/\tilde{T}_2+1+\kappa)t] , & t\gg t_b . \quad (5.21b)\end{cases}$$

The value t_b is determined from the condition

$$t_b=\frac{1}{F+a-1-\kappa}\ln\left[1+\frac{(F+a-1-\kappa)(a+\kappa\tilde{T}_1)(\kappa+1)(1/\tilde{T}_2+a/\kappa)}{a(a+F+\kappa/\tilde{T}_2)(a/\kappa+F+1/\tilde{T}_2)}\right], \tag{5.22}$$

for which the correction term in (5.17) is compared with unity. If $t_b^{-1}\ll a+F$, then the correction term is negligible, too, and the solution has the form (5.21a), coinciding with (5.20). In the opposite case, there is no essential relaxation in the interval $t<t_b$, and practically it develops according to the law (5.21b). The boundary between these situations is determined by the curve described by the equation $t_b^{-1}=a+F$. Using (5.22) in it, we derive

$$\frac{a}{\tilde{T}_1}=\kappa\left[\frac{(e-1^2)W^2}{(\kappa+1)^2}+\frac{2(e-1)}{\kappa+1}-1\right]^{-1}\approx\kappa . \tag{5.23}$$

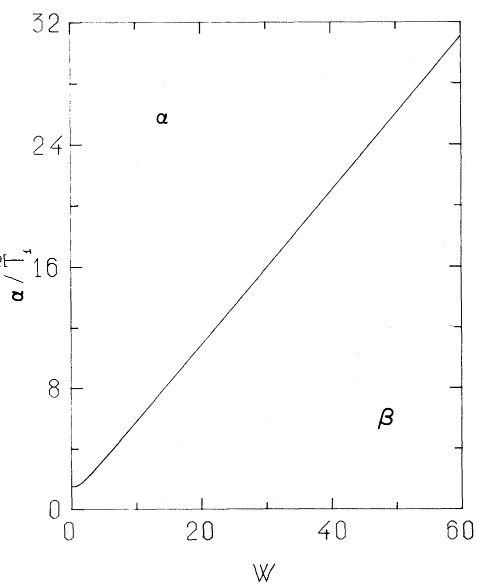


FIG. 1. Regions of the exponential decay: α, the decay rate is equal to $1+\kappa$; β, the decay rate is equal to $a+F$.

Figure 1 shows the separation of the considered cases on the plane $(a/\tilde{T}_1, W)$. Above the curve (5.23), shown in the figure, the decay rate is in general determined by the value $1+\kappa$, and below by the value $a+F$. In the upper region the system reaction may be considered as quasistatic, and in the region below, as averaged by motion. But this separation at $W=0$ does not coincide with echo-theory separation of fast and slow modulation (by the unequalities $a\gtrless 1$).[14] Instead, the criterion $a\gtrless\tilde{T}_1$ appears, in which $\tilde{T}_1$ arises as a parameter characterizing the system saturation before switching off the field.

VI. INTEGRAL RATE OF THE FREE INDUCTION DECAY

The above consideration shows that free induction relaxation may be consideration as an exponential process only approximately and far away from the boundary separating quasistatic and fast modulation. In reality, it is to some extent nonexponential, as Fig. 2 related to close quasistatics shows. This makes it difficult to compare the theory with the experiment in which only the decay time without the necessary analysis of the FID kinetics, is found. We have to decide what this value should be compared with. We suppose that the most suitable is

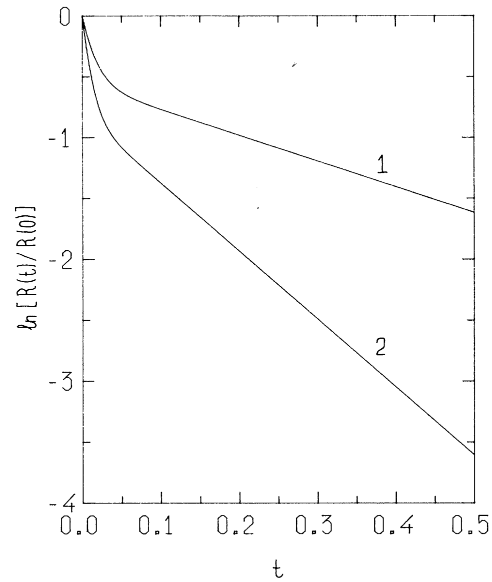


FIG. 2. Time dependence of the FID signals: $1-\chi\tau_0=0.45$, $2-\chi\tau_0=4.5$; and $a_0\tau_0=30$, $T_1/\tau_0=22.55$.

the mean decay time $\tau_0\int_0^\infty R(t)dt/R(0)$ or its reverse value γ, which we call the integral rate of the FID. In order to calculate it, we have not restricted ourselves to the analysis of the poles only, as is usually done,[4] but have performed the whole calculation, both in the exact theory and in perturbation theory.

It is quite clear that γ is expressed versus the derived solutions as follows:

$$\gamma\tau_0=\frac{R(0)}{\int_0^\infty R(t)dt}=\frac{\pi \lim_{z\to\infty} z\,\mathrm{Re}\bar{\sigma}_{12}^s+\int dz\,\mathrm{Im}\bar{\sigma}_{12}^s}{\mathrm{Im}\int dz\,\bar{\sigma}_{12}(p=0)}\ . \tag{6.1}$$

Using expressions (5.3) and (5.4) we have

$$\begin{aligned}\gamma\tau_0=R_1\{&\sqrt{C_1}[R_1+(p_1+p_2-1/\tilde{T}_2)R_2+p_1p_2R_4\\&-p_1p_2R_6/(t_2+\kappa)]F_1+\sqrt{C_1}R_2F_2\\&+[R_1(p_1+p_2-1/\tilde{T}_2)+p_1p_2R_3\\&+p_1p_2R_5/(t_2+\kappa)]F_3\}^{-1}\ ,\end{aligned} \tag{6.2}$$

where

$$F_1=\frac{(2\sqrt{C_1}+B_1)^{1/2}+\beta}{F_0}\ , \tag{6.3a}$$

$$F_2=\frac{\alpha-\sqrt{C_1}}{F_0}\ , \tag{6.3b}$$

$$F_3=-\frac{\alpha+\beta(2\sqrt{C_1}+B_1)^{1/2}+B_1+\sqrt{C_1}}{F_0}\ , \tag{6.3c}$$

$$\alpha=(t_2+a+b)/\tilde{T}_2+ab,\quad \beta=t_2+a+b+1/\tilde{T}_2\ , \tag{6.3d}$$

$$\begin{aligned}F_0=&\alpha(\alpha+B_1)+\beta(2\sqrt{C_1}+B_1)^{1/2}(\alpha+\sqrt{C_1})\\&+\sqrt{C_1}(\beta^2+\sqrt{C_1})\ .\end{aligned} \tag{6.3e}$$

Substituting the result of perturbation theory (3.12) to (6.1) we derive

$$\gamma_{\mathrm{PT}}\tau_0=\frac{A_1[(q^2+1/\tilde{T}_2)^2+2z_3(q^2+1/\tilde{T}_2)+\sqrt{C}\,]}{A_1(q^2+1/\tilde{T}_2+2z_3)-A_2\sqrt{C}} \tag{6.4}$$

[the parameters are defined in (3.12)–(3.16), and $q^2=ab$].

Before making a comparison of (6.2) and (6.4) with the experiment, let us compare them with each other in the vanishing field ($W\to 0$). In this case, from (6.2) we have

$$\begin{aligned}\gamma(0)\tau_0=&2d\beta\left[ab\left[\frac{t_2+a+b}{t_1t_2}+\tilde{T}_1\right]+\tilde{T}_1\beta(t_2+a+b)\right]\\&\times\left\{ab\alpha\left[2\left[\frac{t_2+a+b}{t_1t_2}+\tilde{T}_1\right]+\beta\frac{a+b}{t_1t_2^2}\right]+\beta^2(t_2+a+b)\left[\frac{ab}{t_1t_2}+\tilde{T}_1(t_2+a+b)\right]\right\}^{-1}\ .\end{aligned} \tag{6.5}$$

The perturbation-theory result derived from (6.4) is somewhat simpler:

$$\gamma_{\mathrm{PT}}^{(0)}=\frac{2}{\tau_0}\left[\frac{1}{\tilde{T}_2}+ab\right]=2\left[\frac{1}{T_2}+a_0b_0\tau_0\right]\ . \tag{6.6}$$

In PT applicability limits the packet is a homogeneous line, narrowed up to the value $\Gamma=a_0b_0\tau_0$. The phase relaxation rate in (6.6) increases by this very value. If $\gamma(0)/2$ is considered, counting it from $1/T_2$, it is the additional broadening, determined by magnetic inhomogeneity. In the perturbation theory it is essentially narrower then the initial width of bi-Lorentzian center a_0, because in PT applicability limits,

$$a_0\le b_0\ll 1/\tau_0\ . \tag{6.7}$$

In Fig. 3 one can see that when $a_0\ll b_0$ this region is somewhat narrower, and outside it the exact solution qualitatively differs from that in the perturbation theory. It reproduces that which is obtained from a purely Lorentzian static spectrum. The additional broadening is

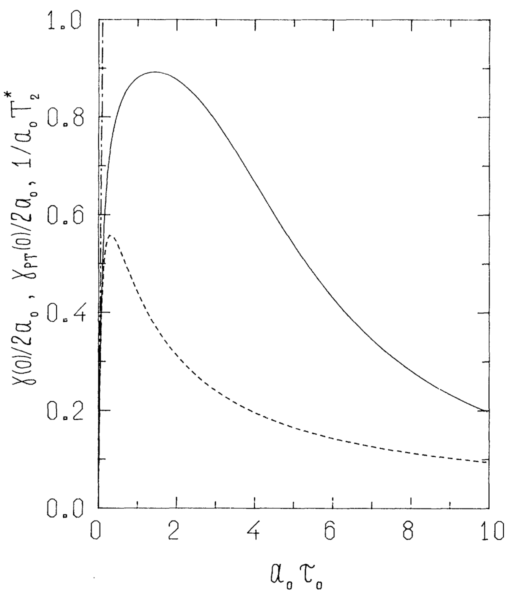


FIG. 3. FID rate at $\chi \to 0$: ——, $\gamma(0)/2a_0$, Eq. (6.5); —·—·—·, $\gamma_{\rm PT}(0)/2a_0$, Eq. (6.6); and echo rate: — — —, $1/a_0 T_2^*$, Eq. (6.10) as a function of the frequency modulation rate τ_0^{-1}; $a_0 T_1 = 100$, $b_0 = 10a_0$.

nearly equal a_0 at moderately fast modulation, but during the transition to the quasistatic region ($a \gg \tilde{T}_1$) it decreases as $1/\tau_0$. The latter value is the width of the subpacket in the inhomogeneously broadened packet.

This behavior of the FID rate during the transition from very fast modulation to very slow is worthy of comparison with the rate of the echo signal decay $1/T_2^*$. It is the more appropriate, as most papers consider the difference $\gamma(0) - 1/T_2^*$, providing T_2^* is measured.[3] As in perturbation theory $1/T_2^* = 1/T_2 + a_0 b_0 \tau_0$, this difference is just twice less than (6.6) in the limits determined by the inequality (6.7). With the modulation being slower, the relation $\gamma(0) = 2/T_2^*$ is no longer valid. To make it clear, we have calculated the echo signal of the bi-Lorentzian contour with the formula suggested in Ref. 13:

$$V(t) = \left[1 + 2\int_0^{t/2} |K(t')|^2 \exp(2t')\,dt' \right] \exp(-t_2 t) \,. \tag{6.8}$$

Using for $K(t)$ its value (5.8a), we hence derive

$$V(t) = \left\{ 1 - \frac{1}{(p_1 - p_2)^2} \left\{ \frac{(p_1+p_2+1)(p_1^2+p_2^2) - p_1 p_2 (p_1+p_2)}{p_1 p_2 + p_1 + p_2 + 1} - \frac{4p_1p_2}{p_1+p_2+2} - \frac{p_1^2}{p_2+1}\exp[(p_2+1)t] + \frac{4p_1p_2}{p_1+p_2+2}\exp\left[\left(\frac{p_1+p_2}{2} + 1 \right) t \right] - \frac{p_2^2}{p_1+1}\exp[(p_1+1)t] \right\} \right\} \exp(-t_2 t) \,. \tag{6.9}$$

Taking T_2^* for the mean integral time, we find

$$\frac{\tau_0}{T_2^*} = \left[\int_0^\infty V(t)\,dt \right]^{-1} = \frac{t_2 \alpha\beta (p_1-p_2)^2}{\alpha\beta(p_1-p_2)^2 + \beta\left[\frac{1}{\tilde{T}_2} - p_1 - p_2 \right](p_1^2+p_2^2) + \beta p_1 p_2 (p_1+p_2) - 4\alpha p_1 p_2} \,. \tag{6.10}$$

As Fig. 3 shows, $\gamma(0)/2$ coincides with $1/T_2^*$ only in perturbation-theory limits ($b_0\tau_0 \ll 1$) and in very deep quasistatic regions: for $a_0 \tau_0^2 \gg T_1$. In the intermediate region they differ rather essentially, and this can cause an error, if they are still identified.

The case $a = b$ is of special interest, as it imitates the monoparametrical contour, similar to the Gaussian contour in this sense, but of a different shape. Perturbation-theory limits shift in this case to the point $a_0\tau_0 = 1$, but still there is a large interval between it and the quasistatic region, where the decay times of the echo and the FID signal are essentially different (Fig. 4). This difference is especially clear, if by varying $a_0\tau_0$ we keep τ_0 invariant, as in Fig. 5. It reaches its maximum at $a_0\tau_0 \sim \sqrt{T_1/\tau_0}$. Therefore, the results of the FID signal extrapolation to zero fields may coincide with the echo data, either at very small or at very great $a_0\tau_0$.

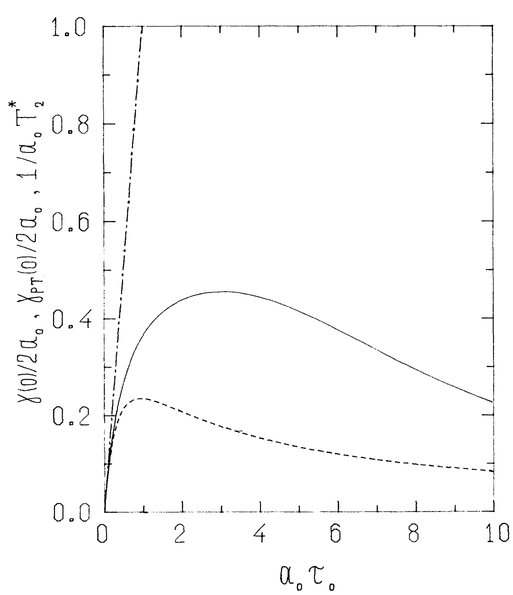
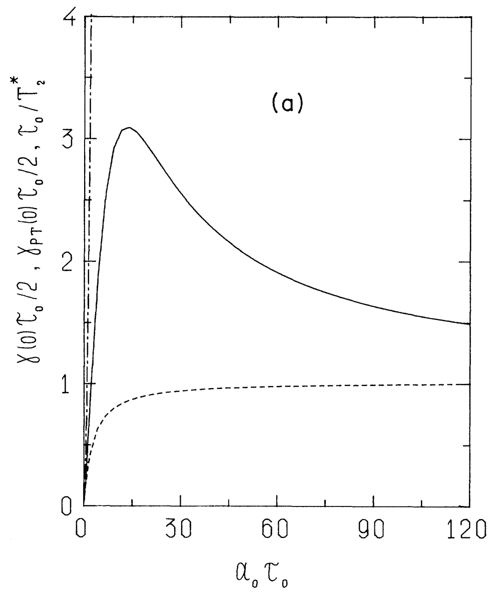


FIG. 4. The same as in Fig. 3, but with $b_0 = a_0$.

VII. DISCUSSION

Until now, the results of the experiments by De Voe and Brewer have been interpreted only in the framework of perturbation theory. Figure 5(a) shows that in the bi-Lorentzian model of contour it is valid only to $q = a_0\tau_0 = b_0\tau_0 < 0.3$. In the same limits the half-rate of the FID in the zero fields $\gamma(0)/2$ coincides with the reverse echo integral time $1/T_2^*$. On this basis most workers have used the echo data to complete curve $\gamma(\chi)$ by a zero point, which is inaccessible in the FID experiments. But one should avoid this; since the perturbation theory is inapplicable, the equality $\gamma(0)/2 = 1/T_2^*$ breaks down, and both experiments should be considered separately.



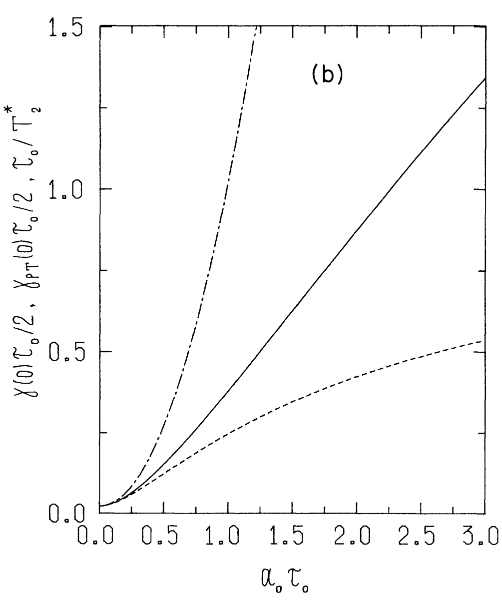


FIG. 5. (a) FID rate at $\chi \to 0$: ——, $\gamma(0)\tau_0/2$, Eq. (6.5); —·—·—·, $\gamma_{PT}(0)\tau_0/2$, Eq. (6.6); and echo rate: — — —, τ_0/T_2^*, Eq. (6.10) as a function of $q = a_0\tau_0$; $T_1/\tau_0 = 22.55$, $a_0 = b_0$; $q \leq 120$. (b) The same as in (a), but with $q \leq 3$.

Extrapolation of the $\gamma(\chi)$ data to the zero fields puts some reasonable limits on the choice of $\gamma(0)$ based only on the results of FID experiments. In the case shown in Fig. 6, we have chosen $\gamma(0)/2\pi = 15$ kHz. So the problem is if the dependence $\gamma(x)$, supplied with a zero point is described by the above-developed theory and for exactly what value of q. The choice of q for given $\gamma(0)$ makes the model quite viable, and both its parameters (a_0 and τ_0) can be uniquely found from Figs. 4 and 5 correspondingly. According to Fig. 4, at $q \to 0$ and at $q \to \infty$ the value a_0 diverges. But this value as a width of the static packet originated by dipole-dipole magnetic interaction cannot be infinitely great. Therefore we have to restrict ourselves with moderate values of q.

Using perturbation theory the authors of Ref. 5 varied q in the interval of 0.7–1.1 and the authors of Ref. 4 assumed it to be equal to 0.6. Both groups reported satisfactory agreement of the so-calculated $\gamma(\chi)$ dependence with the experimental one. But this agreement is illusive. As the limits of perturbation theory turned out to be broken, the dependence $\gamma(\chi)$ calculated with it essentially deviated from the correct one. If $q = 0.7$, as above, then the derivation of the exactly calculated curve from the experimental one becomes very essential with the increase of χ (Fig. 6). To eliminate them, it is necessary to enlarge q even more, finally breaking the limits of perturbation theory. Only at $q = 2.3$, which corresponds to $\tau_0 = 22$ μs and $a_0/2\pi = 16.6$ kHz can one gain satisfactory agreement of the exact theory with the experiment (Fig. 6).

The problem of the correspondence between the FID and echo data, especially outside perturbation-theory limits is of principal importance. At the moderate, but greater than 1, values of q the echo kinetics is much more nonexponential than the FID signal (Fig. 7). Because of this reason the integral decay time of T_2^* may be more than twice as large as the parameter of the long-time

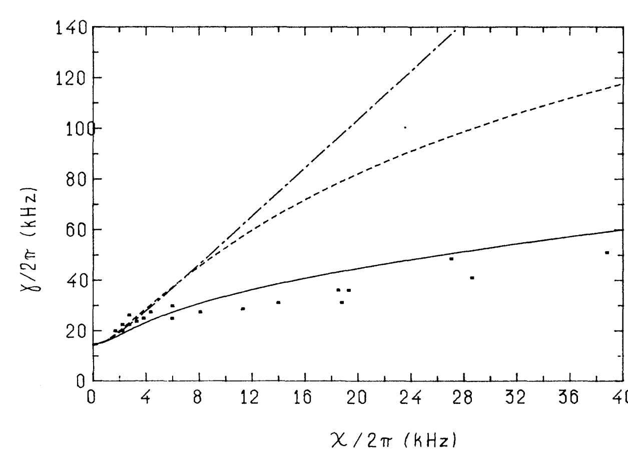


FIG. 6. Field dependence of the FID rate. —·—·—·, Bloch theory; — — —, exact theory [Eq. (6.2)] $q = 0.7$, $\tau_0 = 5$ μs, $a_0/2\pi = b_0/2\pi = 22.3$ kHz; ——, exact theory $q = 2.3$, $\tau_0 = 22$ μs, $a_0/2\pi = b_0/2\pi = 16.6$ kHz; ■, experimental data (Ref. 3), $T_1 = 0.5$ ms.

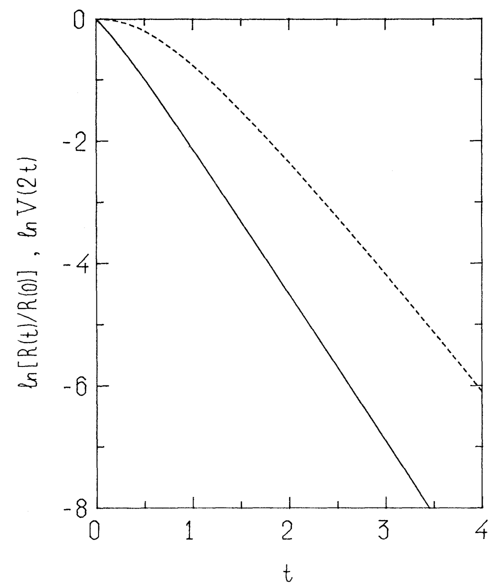


FIG. 7. Logarithmic dependence of the FID signal at $\chi \to 0$: ——, $R(t)/R(0)$, Eq. (5.9); and of the echo signal — — —, $V(2t)$, Eq. (6.9); $a_0 = b_0$, $q = a_0\tau_0 = 2.3$, $\tau_0 = 22$ μs, $T_1 = 0.5$ ms.

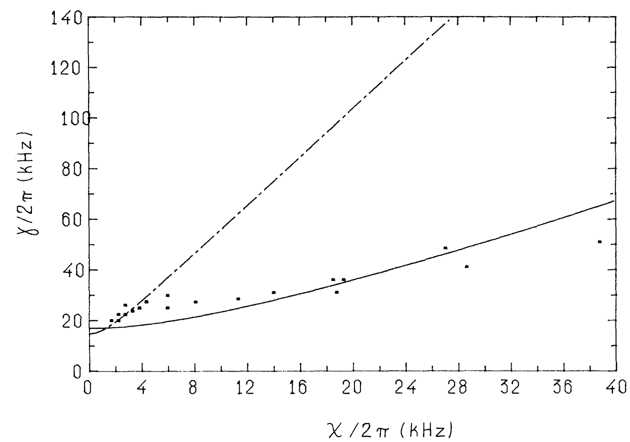


FIG. 8. Field dependence of the FID rate. —·—·—·, Bloch theory; ——, exact theory [Eq. (6.2)] $q = 400$, $\tau_0 = 22$ μs, $a_0 = b_0$, $a_0/2\pi = 2.9$ MHz; ■, experimental data (Ref. 3), $T_1 = 0.5$ ms.

asymptotic decay, which is τ_0. But the deviations from exponential echo kinetics were not observed experimentally. If the reason for this is that only the exponential asymptotic regions can be measured, then the value $\tau_0 = 21.7$ μs found in this way agrees well with the one obtained by fitting the field dependence $\gamma(\chi)$. However, if not only the asymptotic behavior is exponential, but all the kinetics from the very beginning to the end, it certainly proves that the modulation is either too fast or too slow. The first possibility should be rejected at once, as it does not describe field dependence $\gamma(\chi)$. Concerning that, the second one is preferable, since in the deep quasistatics $\gamma(\chi)$ is approximated even better than in the moderate one (Fig. 8). But for such a great $q = 400$ magnetic static broadening $a_0/2\pi = 2.9$ MHz is much greater than its real value.[15]

Therefore, it is rather difficult to describe both experiments in the framework of the model employed here. At least we have to consider other types of static contour, which are different from the bi-Lorentzian one. Besides, it is necessary to remember that the frequency migration can be a correlated process as well, which for the Gaussian contour is described by the Focker-Planck equation. This latter case was considered in Ref. 16, but did not allow us to eliminate the discussed contradictions. It is quite possible that the physical model of modulation must be revised even more seriously due to the rejection of the Kielson-Storer kernel for the description of the correlated frequency migration.

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