NMR Spin-Spin Relaxation as Kinetics in Spin Phase Space

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A new approach is presented that treats NMR spin-spin relaxation as kinetics in spin phase space. The approach is applied to free induction decay (FID) in solids containing equivalent nuclear spins 1/2. The description obtained does not involve adjustable parameters. As an example, the calculation is performed for $^19$F FID in CaF$_2$, and the results are in good agreement with experiment.

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We present a new approach to the problem of free induction decay (FID) in the lattice of equivalent spin 1/2 nuclei, where nuclear spin-spin interaction is responsible for the relaxation. The approach applies the framework of the Boltzmann kinetic description beyond the limit of instantaneous collisions. The resulting method is formally comparable to the original treatment of Lowe and Norberg in the sense that it starts from the Ising-like Hamiltonian, matches the second and the fourth moments, and does not involve adjustments to experimental data. Moreover, the $T$-criterion, which is introduced in this work, is also satisfied in the Lowe and Norberg calculation. The difference is that our mathematical construction is based on physical arguments, which give better control over the calculation, and, in principle, allow a routine analysis of experiments to be performed to extract unknown microscopic parameters. None of the approximate methods suggested so far has been generally accepted for such a task.

A typical FID formulation in solids assumes that each nucleus is at rest on its site in the crystal lattice, and the following conditions are fulfilled:

$$\frac{k_B T}{\hbar} \gg \Omega \gg \frac{1}{T_2} \gg \frac{1}{T_1}, \quad (1)$$

where $T$ is the temperature of the initial equilibrium distribution, $\Omega$ is the Larmor frequency in the static magnetic field, $T_2$ is the time scale of the nuclear spin-spin interaction, and $T_1$ is the spin-lattice relaxation time. The spin-lattice relaxation can be neglected, since the time range of interest is of the order of $T_2$.

We consider FID in the Larmor rotating reference frame, where the Hamiltonian is

$$\mathcal{H} = \sum_{k<n} \left[ A_{kn} I_k z I_n z + B_{kn} I_k \cdot I_n \right], \quad (2)$$

$I_k$ is the spin 1/2 operator of the $k$th nucleus, and $A_{kn}$ and $B_{kn}$ are the interaction coefficients. The $z$-axis is chosen along the direction of the Larmor precession.

The FID is measured as a spin response to $\pi/2$ radio frequency pulse. The $\pi/2$ pulse rotates the equilibrium spin system so that immediately after the pulse, all spins are uniformly polarized in the direction perpendicular to the static magnetic field. We choose the $x$-axis along the magnetization at this moment of time. After the pulse, the $x$-component of the magnetization $M_x$ decays as a result of the spin-spin interactions. The leading term in the high temperature expansion gives

$$M_x(t) = \frac{\gamma \hbar^2 \Omega}{k_B T} \text{Tr} \{ e^{i \mathcal{H} t} \sum_k I_k x \ e^{-i \mathcal{H} t} \sum_n I_n x \}, \quad (3)$$

where $\gamma$ is the gyromagnetic ratio. Usually, FID is presented as a normalized function $G(t) = M_x(t)/M_x(0)$.

Since all spins are equivalent, each of them equally contributes to the magnetization. For the purposes of the forthcoming consideration, we express $G(t)$ in terms of the average magnetic moment $m$ of one spin:

$$G(t) = m_x(t)/m_x(0). \quad (4)$$

We outline our approach by comparing it with the derivation of the Boltzmann kinetic equation (BKE) in the Ising-like Hamiltonian. The BKE can be considered as a modification of the exact equation for the system of noninteracting classical particles. In our method, we modify the exactly soluble case of the Ising-like Hamiltonian. The BKE is derived by counting particles entering and leaving small volumes of the phase space. Similarly, we analyze the averaged spin behaviour in a given configuration of neighbors. The configuration of neighbors refers to the phase space domain arising in the context of the Ising-like Hamiltonian.

The derivation of BKE is based on the approximation of instantaneous collisions, which is not applicable to the nuclear spin-spin interaction in solids. Instead, we substantiate the quantitative claim of our approach by adopting the criteria presented below.

The first criterion is that the mathematical construction of our theory has to be time reversible. This allows a well-defined correspondence to be established between the parameters of the theory and the time reversible microscopic dynamics. In particular, it enables us to match the exactly calculated momenta $M_2 = -\frac{\partial^2 G}{\partial t^2}|_{t=0}$ and $M_4 = \frac{\partial^4 G}{\partial t^4}|_{t=0}$, which can be obtained by the direct trace evaluation of the first terms in the time expansion of Eq.(3). Time reversibility implies abandoning simple first-order differential rate equations. Consequently, the
minimal description has to be based on time-reversible second-order differential rate equations.

Among the various dynamical correlations that complicate the analysis, the most important are the two-spin correlations. If an approximate calculation can accurately take the two-spin correlations into account, then it is reasonable to expect that the contribution from the higher order correlations is more random, i.e. better averageable. The criterion, which at least partially guarantees that the two-spin correlations are respected, is as follows: The FID shape obtained by the effective calculation is the function of the microscopic coefficients $A_{kn}$ and $B_{kn}$. We require that if in this function all $A_{kn}$ and $B_{kn}$, except for the coefficients describing the interaction between any given pair of spins, equal zero, then the function reproduces the exact FID shape of the two-spin system

$$G(t) = \cos \left( \frac{1}{2\hbar} A_{12} t \right).$$

We call this the “T-criterion.”

The FID can be evaluated in a closed form in the Ising-like case when all $B_{kn} = 0$. We use the Lowe and Norberg interpretation of this evaluation to initially motivate the formalism of our description.

In the Ising-like Hamiltonian, the operator of the local field, which affects the $k$th spin, is

$$h_k = \frac{1}{\gamma_0 \hbar} \sum_n A_{kn} I_{nz}.$$

Since the $z$-component of each spin is the constant of motion, Eq. (6) implies that each spin is rotated by a constant local field created by spin’s neighbors.

If all operators $I_{nz}$ are diagonal in the basis chosen for the trace evaluation in Eq. (3), the contributions to the trace can be interpreted as a result of spin precessions in classical local fields. The possible values of these fields are the eigenvalues of the field operator $h_k$.

We introduce index $C$ to refer to the configurations of neighbors, and define configuration as a particular set of the eigenvalues of operators $I_{nz}$ in Eq. (6). The description can be restricted to a finite number of neighbors $N_0$. Consequently, there are infinitely many spins surrounded by a given configuration $C$ of $N_0$ neighbors. In the following we use notation $(...)_C$ to indicate averaging over all configurations.

For configuration $C$, we define $m_{Cz}(t)$ as the average magnetic moment of nuclei that are surrounded by neighbors with the specified set of instantaneous spin projections on the $z$-axis. The initial uniform polarization implies that $m_{Cz}(0) = m_z(0) = \frac{\hbar \omega c}{4k_B T}$.

The evolution of $m_{Cz}$ is governed by the equation

$$\frac{d^2 m_{Cz}}{dt^2} = -\omega_c^2 m_{Cz},$$

where $\omega_c$ is the precession rate in configuration $C$:

$$\omega_c = \frac{1}{2\hbar} \sum_n \pm A_{kn}.$$

Each configuration of neighbors uniquely specifies the combination of signs in Eq. (8).

As a result, $m_{Cz}(t) = m_{Cz}(0) \cos(\omega_c t)$, and Eq. (9) with $m_z(t) = (m_{Cz}(t))_C$ leads to

$$G(t) = \prod_n \cos \left( \frac{1}{2\hbar} A_{kn} t \right).$$

The right-hand side (RHS) of Eq. (3) is the Fourier transform of the discrete distribution of $\omega_c$, which can be considered as a sum of random quantities $\pm A_{kn}/(2\hbar)$. Therefore, according to the central limit theorem, the distribution approaches Gaussian when

$$\text{max} \{|A_{kn}|\} < < 2\hbar \sqrt{M_2},$$

where $M_2 = \frac{1}{4\hbar^2} \sum_n A_{kn}^2$. In this case, the RHS of Eq. (3) can be approximated as $\exp(-M_2 t^2/2)$.

Apart from the Ising-like case, the evolutions of $m_{Cz}$ in different configurations of neighbors are mutually dependent. We employ the following generalization of Eq. (3)

$$\frac{d^2 m_{Cz}}{dt^2} = -(W_{C+} P_{Cz+} - W_{C-} P_{Cz-}) m_0,$$

where $P_{Cz+}$ and $P_{Cz-}$ are the probabilities that the spin projections on the $x$-axis are positive and negative, respectively; $W_{C+}$ is the effective rate of the transition from a state where the spin is oriented positively along the $x$-axis to the state where the spin is oriented negatively along the same axis; $W_{C-}$ is the rate of the reverse transition; $m_0 = \gamma_0 / 2$ is the maximum magnetic moment of one spin. The probabilities obey the relationships:

$$P_{Cz+} + P_{Cz-} = 1, \quad m_0 (P_{Cz+} - P_{Cz-}) = m_{Cz}.$$ (13)

The rates in Eq. (13) characterize the net effect of two factors: the direct influence of neighbors and the flux of spin polarization to and from configuration $C$. When the spin system is weakly polarized, each of these factors can lead to a slight asymmetry between $W_{C+}$ and $W_{C-}$.

The first factor can be understood after we rewrite the two-spin Hamiltonian extracted from Eq. (2) as

$$H_{kn} = B_{kn} I_{nx} I_{nz} - \frac{1}{4} A_{kn} (I_z + I_{n+} + I_{k-} - I_{n-}) + \frac{1}{4} (A_{kn} + 2B_{kn})(I_{k+} I_{n-} + I_{k-} I_{n+}),$$

where $I_+ = I_y + iI_z$, and $I_- = I_y - iI_z$. The second and the third terms in Eq. (14) lead to the double-flip of two parallel spins and the flip-flop of two antiparallel spins, respectively. If the $k$th spin is parallel to the average spin polarization, it is more probable that the $n$th spin will be parallel to the $k$th spin. This effectively increases
the influence of the double-flip term on the kth spin and reduces the influence of the flip-flop term. If the kth spin is antiparallel to the average polarization, the opposite effect would occur. When \( m_x > 0 \), the double-flip correlation increases \( W_{C+}^2 \) and reduces \( W_{C-}^2 \) in Eq.(19). The flip-flop correlation leads to the opposite result.

The other factor mentioned above is frequently referred to as motional narrowing. In terms of our description, this means that the faster the time variations of the real local fields, the greater the difference between the chosen configuration of neighbors and those configurations that actually drove the spin to its current surroundings. One can conclude that spins coming to configuration \( C \) from other configurations tend to be slightly polarized in the direction of the average magnetization. This reduces \( W_{C+}^2 \) and increases \( W_{C-}^2 \), provided \( m_x > 0 \).

We define the average rate as
\[
W_C^2 = \frac{1}{2} (W_{C+}^2 + W_{C-}^2),
\]
(15)
The high temperature condition guarantees that the difference between \( W_{C+}^2 \) and \( W_{C-}^2 \) is small. The basic assumption of our analysis is that the leading term of this difference can be expressed as
\[
\frac{1}{2} (W_{C+}^2 - W_{C-}^2) = \alpha W_C^2 \frac{m_x}{m_0},
\]
(16)
where \( \alpha \) is a configuration independent parameter, which is determined by the average of all factors considered. The status of assumption (14) is somewhat similar to the self-consistent relaxation time approximation, which is frequently adopted to solve BKE.

The substitution of Eqs.(12,13,15,16) into Eq.(11) yields
\[
\frac{d^2 m_{Cz}}{dt^2} = -W_C^2 m_{Cz} - \alpha W_C^2 m_x.
\]
(17)

Given the initial uniformly polarized state, the solution of Eq.(17) is
\[
m_{Cz}(t) = m_{Cz}(0) \cos(W_C t) - \alpha \int_0^t m_x(t' - t') W_C \sin(W_C t') dt'.
\]
(18)

Since \( m_x(t) = \langle m_x(t) \rangle \), the averaging of Eq.(18) over all configurations, together with Eq.(8), results in the integral equation
\[
G(t) = g(t) + \alpha \int_0^t G(t' - t') \frac{dg(t')}{dt'} dt',
\]
(19)
where \( g(t) = \langle \cos(W_C t) \rangle \).

We choose \( g(t) \) and \( \alpha \) such that the second and the fourth momenta obtained from Eq.(19) match the exact calculation. Matching the second moment gives
\[
M_{2g} = \frac{M_2}{1 + \alpha}.
\]
(20)

where \( M_{2g} = -\frac{d^2}{dt^2} |_{t=0} \langle W_C^2 \rangle_\alpha \). Matching the fourth moment, combined with Eq.(20), allows \( \alpha \) to be expressed as
\[
\alpha = \frac{M_{4g} - M_2^2}{M_2^2 - 1},
\]
(21)
where \( M_{4g} = \frac{d^4}{dt^4} |_{t=0} \langle W_C^4 \rangle_\alpha \).

Eqs.(20,21) relate the shape and the scale of the acceptable distributions of \( W_C \). Namely, the shape specifies the ratio of \( M_{4g}/M_{2g}^2 \), which enters Eq.(21) and determines the value of \( \alpha \). With a known \( \alpha \), Eq.(20) gives the value of \( M_{2g} \), which defines the scale of the distribution.

An important property of Eqs.(20,21) is that they guarantee the fulfillment of the T-criterion for any shape of the distribution of \( W_C \) with finite moments. The exact solution (3) for the system of two spins 1/2 always gives the ratio \( M_4/M_2^2 = 1 \), which formally leads to an infinite value of \( \alpha \) in Eq.(21). The divergence does not appear in the solution of Eq.(19b), because, according to Eq.(20), it is offset by the small value of \( M_{2g} \). When the two-spin problem is considered as a limit of the many-spin problem with \( A_{1n}, B_{kn} \rightarrow 0 \), except for \( A_{12} \) and \( B_{12} \), the solution of Eq.(19c) converges to the RHS of Eq.(3), independently of the shape of the distribution of \( W_C \).

The relevance of the T-criterion is supported by the fact that the observable part of \( G(t) \) obtained from Eqs.(19,20,21) is weakly sensitive to the variations of the input shape of the \( W_C \) distribution. Thus relatively crude assumptions about this shape still should lead to good accuracy in the result.

Since the fulfillment of the T-criterion is guaranteed, and the many-spin correlations are taken into account by the choice of parameter \( \alpha \), we assume that the distribution of \( W_C \) is produced by uncorrelated contributions from spin neighbors. As a result, this distribution has a tendency to be Gaussian. However, in the presence of a few strongly interacting neighbors, it can have a peaked structure originating from the Ising-like part of Hamiltonian (3). This part alone would produce the discrete distribution of the static rates \( \omega_C \) given by Eq.(3). The discrete structure, presumably, propagates to the distribution of \( W_C \), but it has to be “washed out” by the polarization flux between different configurations. The proper scale this “lifetime” effect is given by
\[
M_{2f} = -\frac{1}{f(0)} \left. \frac{d^2 f(t)}{dt^2} \right|_{t=0},
\]
(22)
where \( f(t) = \text{Tr} \{ e^{i \hat{H} t} \hat{h}_k e^{-i \hat{H} t} \hat{h}_k \} \).

We choose the input shape of the \( W_C \) distribution to be the convolution of the distribution of \( \omega_C \) with a Gaussian that has the second moment \( M_{2f} \). Based on this shape,
$g(t)$ becomes a renormalized product of a Gaussian and the RHS of Eq. (19):

$$g(t) = \exp[-\frac{1}{2}M_2f(\eta t)^2]\prod_n \cos\left(\frac{1}{2\eta}\alpha_{kn}\right), \quad (23)$$

where $\eta = \sqrt{\frac{M_2}{1+\alpha(M_2+M_f)}}$ is the renormalization factor required by Eq. (20). If the large number of neighbors criterion (10) is satisfied, $g(t)$ becomes Gaussian.

Eqs. (19,21,22,23) form a closed system, which allows $G(t)$ to be calculated.

We apply the method to CaF$_2$, where FID is observed on $^{19}$F nuclei ($\gamma = 25166.2$ rad s$^{-1}$ Oe$^{-1}$), which form a simple cubic lattice having near-neighbor separation of $d = 2.72325$A. The spin-spin interaction is assumed to be magnetic dipolar [3].

The calculation is performed with the static magnetic field oriented along the [100], [110] and [111] crystal directions. Evaluating $g(t)$ according to Eq. (23), we individually include 50 cosines with the interaction constants making the largest contribution to $M_{2g}$, and approximate the product of other cosines by the Gaussian exponent, which adds the remaining contribution to $M_{2g}$. We also approximate $M_{2f}$ by the second moment of one spin correlation function $\text{Tr}\{e^{iH_1t}I_{nz}e^{-iH_1t}I_{nz}\}$, which is sufficient given the alternating signs of $\alpha_{kn}$. This gives $M_{2f} = \frac{\eta}{2}M_2$. Variations of $M_{2f}$, even by a factor of 2, result in a negligible difference in the observable part of FID. In Eq. (21), we take the exact ratios $M_2/M_2$ from Ref. [3] and obtain the values of $\alpha$: (0.54, 0.42, 0.42) for the [100], [110] and [111] directions, respectively.

When $g(t)$ and $\alpha$ are known, Eq. (19) is easily soluble numerically. The solutions are plotted in Fig. 1, together with the experimental data of Engelsberg and Lowe [3].

The microscopic coefficients originating from the magnetic dipolar interaction have the relation $B_{kn} = -\frac{1}{4}A_{kn}$. As a result, the double-flip correlation, which is discussed after Eq. (14), is sufficiently strong to outweigh the flip-flop correlation and the motional narrowing. Consequently, $\alpha > 0$, which leads to the oscillating FID shape.

The value of $\alpha$ can also be negative, e.g. when $A_{kn}$ and $B_{kn}$ have the same sign for each pair of spins. If $g(t)$ is Gaussian, and $\alpha$ changes from 0 to $-1$, the shape of $G(t)$ obtained from Eq. (19) evolves from Gaussian to nearly exponential. The minimum possible value of $\alpha$ is $-1$, which leads to $G(t) = 1$ for any $g(t)$. This limit arises as the interaction approaches the Heisenberg form with all $A_{kn} = 0$.

In summary, we presented a kinetic FID theory, which reproduced the exact results of the two-spin problem with Hamiltonian (2) and many-spin problem with Ising-like and Heisenberg Hamiltonians. Based on the physical arguments, the theory extended the above exactly soluble cases in the space of all possible interaction coefficients $A_{kn}$ and $B_{kn}$. Given also the fact that the first four derivatives of $G(t)$ at $t = 0$ obtained from Eq. (14) coincide with the exact calculation, we conclude that in most cases, the solution of Eq. (19) approximates the observable part of FID with good accuracy. The accuracy is mainly limited by the adequacy of assumption (10).

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FIG. 1. FID in CaF$_2$ with static magnetic field along [100], [110] and [111] crystal directions. Solid lines are the solutions of Eq. (19). Dashed lines are experimental data from Ref. [3].

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