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Long-lived NMR echoes in solids

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ABSTRACT

A new type of long-lived NMR echo in solids with homogeneously broadened dipolar spectra is discussed. The echo can be generated by a simple two-pulse Hahn sequence in solid samples, where dipolar-coupled nuclei have different chemical shifts. We present general considerations and simple theoretical models which explain some features of this phenomenon.

1. Introduction

It has been known that, for homogeneously broadened dipolar NMR spectra of solids, weak and long pulses can excite sharp response signals, which are orders of magnitude narrower than the conventional spectra [1–3]. So far, the attempts of explaining this phenomenon have not been very successful. Very recently, it has been found that the underlying mechanism is a new type of long-lived echo, based on broken symmetry [4]. Whenever a single long pulse can produce long free-induction decay (FID) signal, there also exists a long-lived echo, generated by the two-pulse Hahn sequence [5]. This long-lived echo can be found in all homonuclear samples with non-equivalent nuclei (different chemical shifts) coupled by dipole–dipole interactions, as well as in heteronuclear systems. Why this type of long-lived echo, observed in a simple two-pulse experiment, waited so long to be discovered? Probably, each time when such small-amplitude echoes have been observed in experiments, they were misinterpreted as coming from "liquid"-phase contamination. However, many features of the new echo are inconsistent with an explanation by a presence of inhomogeneously broadened signal from "liquid". Besides that, for inhomogeneous broadening, dephasing/refocusing of individual spectral components of magnetization takes place in the x–y plane of the rotating frame. For the echo we discuss, dephasing/refocusing occurs is a more complex space of many-spin operators. This difference can be easily verified in experiments.

The purpose of this paper is to supplement Ref. [4] by providing more explanations, theoretical considerations, and model calculations. In the next section we derive expressions for the signal excited by a soft pulse followed by a hard refocusing pulse. Compared to Ref. [4], the calculation is done in a more explicit and general way, and the result is obtained in a simpler form. Section 3 contains exact calculations for the three-level model, introduced in [4]. We also present some additional qualitative considerations related to the echo amplitude, decay rate, shape, and the role of molecular motions.

Even though not all characteristics of the long-lived echo are well understood at this moment, we feel that the discussion below may be useful. The new type of long-lived NMR echo in solids is a manifestation of complex collective many-spin dynamics. Therefore, explicit models, like the three-level model in Section 3, will be necessarily oversimplified and capable of grasping only few features of the real spin dynamics.

2. Selective echo

We will start by explaining why a soft selective pulse cannot produce slowly decaying magnetization unless there also exists a long-lived echo, excited by a sequence of two hard pulses. In this section, we consider the signal generated by a sequence of a soft (weak and long) y-pulse with the amplitude $f(t)$, followed by a hard refocusing pulse. For simplicity, the soft pulse will be symmetric: $f(t) = f(-t)$, and it will be also assumed that the total flip angle of the soft pulse is small: $\varphi = \int_{-T}^{T} dt\, f(t) \ll 1$, where $2T$ is the pulse duration.

In the first part of this section we reproduce some calculations in Ref. [4] in order to introduce more convenient notations, and also to show the calculations and results in a more explicit way. Suppose that a spin system evolves under the time-independent Hamiltonian H, and both the initial density matrix $\rho(0)$ and the observable are S_X. Then x-component of magnetization $M(t)$, or the free-induction decay (FID) signal, is

$$M(t) = \langle S_X|\rho(t)\rangle = \langle S_X|S_X(t)\rangle, \quad \text{where } |S_X(t)\rangle = \exp(L_H t)|S_X\rangle. \quad (1)$$

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Here $L_H = -i[H, \ldots]$ is the Liouvillian, the binary product for the two operators A and B is defined as $\langle A|B\rangle = Tr(A^+B)$, and A^+ is the Hermitian conjugate of A. We will also use normalization $\langle S_X|S_X\rangle = 1$, so that the FID signal in Eq. (1) is normalized. It is convenient to introduce the spectral components $|\omega\rangle$ of the operator $|S_X(t)\rangle$ as

$$|\omega\rangle = \int dt \exp(-i\omega t)|S_X(t)\rangle, \qquad |S_X(t)\rangle = \int d\omega \exp(i\omega t)|\omega\rangle. \quad (2)$$

Here and below the integration symbol without limits means integration between $-\infty$ and ∞.

Now let us assume that the equilibrium density matrix is S_Z and the signal is created by a soft y-pulse with the amplitude $f(t)$ and small total flip angle. The linear-response density matrix created by the pulse at time $t = T$ is

$$|\rho(T)\rangle = \int d\omega \int_{-T}^{T} dt f(t) \exp(i\omega(T-t))|\omega\rangle, \quad (3)$$

i.e. each spectral component of the linear response, created at time t with the rate $f(t)$, has evolved during time T–t after its creation. Since $f(t) = 0$ at $|t| > T$, the integration limits in (3) can be omitted:

$$|\rho(T)\rangle = \int d\omega \exp(i\omega T) \int dt f(t) \exp(-i\omega t)|\omega\rangle$$
$$= \int d\omega \exp(i\omega T) f(\omega)|\omega\rangle, \quad (4)$$

where $f(\omega)$ is the Fourier transform of $f(t)$. The phase factors in Eq. (4) are the same as resulting from δ-excitation at $t = 0$ (compare to Eq. (2)), but the excitation profile is "tailored" by the function $f(\omega)$. It is easy to see that, without the refocusing pulse at $t = T$, the signal is zero at $t > T$ if the spectral width of $f(\omega)$ is much narrower than that of the conventional spectrum:

$$M(t > T) = \langle S_X|\rho(t)\rangle = \int d\omega_1 d\omega exp(i\omega t) f(\omega)\langle\omega_1|\omega\rangle$$
$$= \int d\omega I_0(\omega) \exp(i\omega t) f(\omega) \approx I_0(0) \int d\omega \exp(i\omega t) f(\omega)$$
$$= I_0(0) f(t) = 0. \quad (5)$$

Here the projector $\langle\omega_1|\omega\rangle = \delta(\omega_1 - \omega)\ I_0(\omega_1)$ can be calculated directly from Eqs. (1) and (2), and $I_0(\omega)$ is the conventional line shape.

Let us suppose that after the soft excitation pulse, at the moment $t = T$, the Hamiltonian changes from H to H', and the subsequent evolution happens with the Hamiltonian H'. Similar to the spectral components $|\omega\rangle$, we can introduce the operator S'_X and its spectral components $|\omega'\rangle$ for the Hamiltonian H'. Magnetization at time $t > T$ is contributed only by the operators $|\omega'\rangle$. Projection of the density matrix on this subspace at $t = T$ can be represented as

$$|\rho'(T)\rangle = \int d\omega'' a(\omega'', T)|\omega''\rangle, \quad (6)$$

where $a(\omega'',T)$ are numerical coefficients. The coefficients $a(\omega'',T)$ can be calculated from equal projections of $|\rho\rangle$ and $|\rho'\rangle$ on the subspace $|\omega'\rangle$:

$$\langle\omega'|\rho(T)\rangle = \langle\omega'|\rho'(T)\rangle = \int d\omega'' a(\omega'', T)\langle\omega'|\omega''\rangle$$
$$= \int d\omega'' \delta(\omega' - \omega'') I'_0(\omega') a(\omega'', T) = I'_0(\omega') a(\omega', T). \quad (7)$$

Therefore, the coefficients are

$$a(\omega', T) = \langle\omega'|\rho(T)\rangle (I'_0(\omega'))^{-1}. \quad (8)$$

By inserting the density matrix $|\rho(T)\rangle$ from Eq. (4) into Eq. (8), and using Eq. (6), one can now calculate the signal at $t > T$:

$$M(t > T) = \int d\omega' d\omega'' \langle\omega''| \exp(i\omega'(t-T)) a(\omega', T)|\omega'\rangle$$
$$= \int d\omega' d\omega'' \langle\omega''| \exp(i\omega'(t-T))|\omega'\rangle\langle\omega'|\rho(T)\rangle (I'_0(\omega'))^{-1}$$
$$= \int d\omega' d\omega'' \langle\omega''| \exp(i\omega'(t-T))|\omega'\rangle\langle\omega'|$$
$$\times \int d\omega \exp(i\omega T) f(\omega)|\omega\rangle (I'_0(\omega'))^{-1}$$
$$= \int d\omega d\omega' \exp(i\omega'(t-T)) \exp(i\omega T) f(\omega)\langle\omega'|\omega\rangle. \quad (9)$$

In Eqs. (7)–(9) we used for the "new" operators $\langle\omega''|\omega'\rangle = \delta(\omega'' - \omega') I'_0(\omega'')$, where $I'_0(\omega)$ is the conventional line shape with the Hamiltonian H'. The projections $\langle\omega'|\omega\rangle$ of "new" operators on "old" operators in Eq. (9) can be calculated by using their definition in Eqs. (2) and (1):

$$\langle\omega'|\omega\rangle = \int d\tau' d\tau \exp(i\omega'\tau') \exp(-i\omega\tau)\langle S'_X(\tau')|S_X(\tau)\rangle, \quad (10)$$

where the time dependence of $|S'_X(\tau)\rangle$ is defined by the Hamiltonian H'. Since the operators $|\exp(L_H t) S_X\rangle$ in Eq. (1) are Hermitian, the transformation from "ket" to "bra" operators requires only a complex conjugation for the phase factors $\exp(-i\omega t)$. Then, by substituting Eq. (10) into Eq. (9) and integrating over ω and ω', one obtains

$$M(t > T) = \int d\omega' d\omega \exp(i\omega'(t-T)) \exp(i\omega T) f(\omega)$$
$$\times \int d\tau' d\tau \exp(i\omega'\tau') \exp(-i\omega\tau)\langle S'_X(\tau')|S_X(\tau)\rangle$$
$$= \int d\tau' d\tau \delta(\tau' + t - T) f(T - \tau)\langle S'_X(\tau')|S_X(\tau)\rangle$$
$$= \int d\tau f(T - \tau)\langle S'_X(T - t)|S_X(\tau)\rangle. \quad (11)$$

This simple equation in time domain could be written directly by using the same reasoning as we did to introduce Eq. (3). The purpose of switching to frequency domain and then back to time domain was to learn several things on the way. First, a long weak pulse selects spectral components with arbitrarily narrow spectral range (Eq. (4)), and the created long-lived state is far from equilibrium. Second, the spectral components are perfectly dephased (Eq. (5)) and, therefore, no linear response signal can be observed. This is true for arbitrary pulse shape and the system's Hamiltonian (including also the systems with inhomogeneous broadening). Third, sudden change of the Hamiltonian does not do any magic in refocusing these spectral components unless there exists an echo for a sequence of two hard pulses (see below).

There are two simple cases of Eq. (11):

(1) $H' = H$. In this case $\langle S'_X(T-t)|S_X(\tau)\rangle = M_0(T - t - \tau) = M_0(t - T + \tau)$, and Eq. (11) becomes

$$M(t > T) = \int d\tau f(T - \tau) M_0(t - T + \tau) \approx I_0(0) f(t) = 0. \quad (12)$$

Eq. (12) is an expected summation of free induction signals, created at earlier moments of time. There is no echo signal.

(2) $H' = -H$. In this case $\langle S'_X(T-t)|S_X(\tau)\rangle = M_0(-T + t - \tau)$, and Eq. (11) becomes

$$M(t > T) = \int d\tau f(T - \tau) M_0(-T + t - \tau) \approx I_0(0) f(2T - t), \quad (13)$$

describing an ideally refocused echo at $T < t < 3T$, which replicates the (time-reversed) excitation profile $f(t)$.

In general, Eq. (11) shows that a long-lived echo, centered at $t = 2T$, can exist only when the correlator $\langle S'_X(T-t)|S_X(\tau)\rangle$ has a long-lived component at $t = T + \tau$: