Quantum interference phenomena in the local polarization dynamics of mesoscopic systems: an NMR observation

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Abstract

It has been predicted that local spin polarization in a ring of five dipolar coupled spins should present a particular fingerprint of quantum interferences, reflecting both the discrete and finite nature of the system. We report its observation for the proton system of a \((C_5H_5)_2Fe\) molecule using the rare \(^{13}C\) as local probe. Novel high frequency \((\approx 60 \text{ kHz})\) polarization oscillations appear because incomplete \(^{13}C\)–\(^1H\) cross-polarization transfer splits the polarization state into a portion that wanders in the proton system and one that remains in the \(^{13}C\). They interfere with each other after rejoining.

1. Introduction

Mesoscopic systems [1] constitute an active topic because their transport properties manifest quantum mechanics in its full splendor and open new possibilities for the design of devices and finely tailored systems which started with the tunnel diode [2]. These involve interference processes both in the space and time domains. The last case includes the consequences of a finite tunneling time in resonant devices [3] and the propagation of a localized excitation in finite random media. Here, a simple average over impurity configurations produces an apparent diffusion; however, a non-linear \(\sigma\)-model calculation [4] predicts strong long time correlations, meaning that a local excitation returns as a mesoscopic dynamical echo after diffusing away and reaching the system boundaries. The observation of these effects in the time domain is difficult because excitations propagate through the system on a timescale that is in the frontier of present technological possibilities. However, a similar phenomenon was also predicted [5] for local excitation in a system of nuclear spins with a magnetic dipolar interaction, which evolves with characteristic times of hundreds of microseconds and can be tested by NMR spectroscopy. While the discrete nature of spin systems leads to a fingerprint of quantum interferences in the spin dynamics of both finite [6] and infinite systems, the survival of mesoscopic phenomena might not seem obvious since, at high temperature, different configurations must be averaged and it is often described as a diffusive process. Therefore, in order to illustrate the physics we resort to an XY model, where exact analytical results can be obtained (technical details sketched below). Fig. 1 shows the evolution of the local magnetic polarization \(M(t)\) for a ring of 21 spins and an infinite chain at high temperature. At short times a series of quantum beats, associated with the discrete nature of the system, are developed. At around 2300 \(\mu\text{s}\) there appears a revival of the polarization. A study of the polarization at other sites shows that the wave packet splits in two parts winding around

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Fig. 1. Evolution of the local magnetic polarization \( M(t) \) for a ring of \( N = 21 \) spins at infinite temperature with an XY (\( \alpha = 0 \)) interaction \( d = 1576 \text{ Hz} \times 2\pi \hbar \). The fine line is the square modulus of the \( J_0 \) Bessel function, exact solution of an infinite chain. At short times a series of quantum beats (at around \( t_n \approx z_n \hbar/d \) with \( z_n \) the zeroes of \( J_1 \)) are developed which decay with a \( t^{-1/2} \) law, indicating the excitation propagation. At around \( 2330 \mu s = t_{\text{m,b}} \) there appears a revival of the polarization corresponding to the excitation winding around the ring. The inset shows the mesoscopic beat time, \( t_{\text{m,b}} \), for different ring sizes. Notice that \( t_{\text{m,b}} \propto N^2 \), where \( N \) is the lattice constant and \( v \approx \alpha d/\hbar \) is the effective group velocity.

The NMR radiofrequency pulse sequence developed by Zhang, Meier and Ernst [7] (ZME), involves cross-polarization (CP) [9], to achieve a two-way transfer of polarization [10] among the spins \( S \) of the rare \( ^{13}C \) (1.1% abundance) and the \( I_1 \) spin of a directly bonded \( ^1H \). Then, the \( ^{13}C \) can be used as a local probe that injects magnetization in the proton and later captures it. The set of coupled protons within a molecule constitutes the mesoscopic system where the spin dynamics can be monitored, while the rest of the crystal constitutes a 'weakly' interacting reservoir.

We measure this spin dynamics in a polycrystalline sample of ferrocene, \((C_5H_5)_2Fe\) (Fig. 2). Since the dipolar interaction depends on the angle between the internuclear vector and the magnetic field, in a general molecule each pair of nuclei can have a different interaction parameter. Therefore, the resulting Hamiltonian is a particular case of

\[
\mathcal{H}_H = \sum_{j > k} \sum_k d_{j,k} [\alpha 2\mathbf{l}^j \cdot \mathbf{l}^k - \frac{1}{2} (\mathbf{l}^j_+ \mathbf{l}^k_- + \mathbf{l}^j_- \mathbf{l}^k_+)],
\]

(1)

where subscripts indicate spins. For \( \alpha = 0 \), it defines an XY model. \( \alpha = -\frac{1}{2} \) describes the J-coupling or Heisenberg model, and \( \alpha = 1 \) is the truncated dipolar.

Fig. 2. Ferrocene molecule in a staggered configuration. The Fe atom is at the center. The hydrogen atoms are labeled starting from the one which has a rare \(^{13}C \) directly bonded. The eclipsed configuration is obtained rotating any ring 36° around the \( C_5 \) axis.
Hamiltonian. In ferrocene at room temperature, the
ing rings perform fast rotations around the C5 molecular
axis ($\tau_R \approx 10^{-12}$ s) [11]. In this last case $d_{ik}$ are
time-averaged [12] interaction parameters depending
only upon the angle between the rotation axis and the
magnetic field. For each initial state, $|i\rangle$, with site
1 polarized, the probability of finding the same site
polarized in state $|f\rangle$ after a time $t$ is

$$P_{f,i}(t) = |\langle f | \exp[-(i/h)\mathcal{H}_{II}t] | i\rangle|^2,$$

from which the polarization can be calculated sum-
ing over all the $N_i$ and $N_f$ possible initial and final
states:

$$M^I(t) = 2 \left[ \sum_{f} \sum_{i} \frac{1}{N_i} P_{f,i}(t) - \frac{1}{2} \right].$$

This is the magnitude which presents quantum meso-
sopic beats as a function of $t$. For the case $\alpha = 0$,
(XY-model) an exact mapping [13] to a non-
interacting fermion system, allows one to sum up the
terms in Eq. (3) and write the magnetization just as

$$M^I(t) = |\langle 1 | \exp[-(i/h)\mathcal{H}_I] | 1\rangle|^2,$$

the square modulus of a single particle wavefunction, where state
$|1\rangle$ has spin $I_1$ ‘up’ and all the others ‘down’. Even
when the $\alpha \neq 0$ cases map to interacting
particles, the essence of this excitation dynamics is retained un-
til intermediate times.

The best condition for observing quantum beats [5]
occurs when the polarization is quantized along the
external magnetic field (laboratory frame). This is be-
cause the neglect of non-secular terms in the dipolar
Hamiltonian is better justified and, since the dipolar
interactions are maximized, the timescale of the
quantum dynamics shrinks minimizing the effects of
other interactions leading to relaxation. The complete
pulse sequence is schematized in Fig. 3. A $(\pi/2)_x$
pulse on the abundant $^1$H spins system creates a polari-
zation that is transferred during $t_c$ to the rare
$^{13}$C system when both are irradiated at their respective
resonant frequencies with field strengths fulfilling the
Hartmann–Hahn [9] condition $\gamma_1B_{11}^y = \gamma_S B_{13}^z \equiv \omega_{31}$
(here $\omega_{31} = 2\pi \times 44.6$ KHz). After decay of the pro-
ton spin coherence during time $t_S = 1$ ms the most
relevant part begins. (A) The magnetization from an
initially $y$ polarized $S$ spin is transferred to the $y$-axis
of the $I_1$ spin through a CP pulse of duration $t_d =
85 \mu$s (the shortest maximizing the polarization trans-
fer [14] for the selected orientation). (B) A $(\pi/2)_x$
pulse tilts the polarization to the laboratory frame. (C) The
$I$-spins evolve freely during a time $t_2$. Thus, the
relevant evolution of the spin-diffusion sequence oc-
curs in the laboratory frame while $S$-irradiation pre-
vents the system–probe coupling. (D) A $(\pi/2)_{-x}$
pulse tilts the polarization back to the rotating $xy$
plane. (E) Another CP pulse of length $t_p = t_d$ is ap-
plicated to transfer back the polarization to the $x$-axis
of $S$. (F) The $S$ polarization is detected while the $I$-
system is kept irradiated (high-resolution condition).
An important feature in the pulse sequence of Fig. 2
is that while during $t_2$ the spins evolve with Hamilto-
nian (1), during CP periods $t_d$ and $t_p$ the proton spins
evolve with a Hamiltonian which after truncation is

$$\mathcal{H}_I = -\frac{1}{2} \mathcal{H}_{II}.$$ 

Thus a part of the free evolution time $t_2$ (around $t_m = [\frac{1}{2}] (t_d + t_p) / 2 = 42.5 \mu$s) is spent going backwards in time (Loschmidt’s daemon [15]
is working!) compensating the undesired evolution. In the
ZME experiment an additional polarization evolution
in the rotating frame is allowed by keeping the rf in the proton system during a time $t_1$ (i.e. after CP
shown in A and before the tilting pulse B). Therefore,
a time $t_2 = \frac{1}{2} t_1 + t_m$ is required to reach the local
polarization maximum (polarization echo), after which
it evolves according to Eq. (3).
3. Results and discussion

In a polycrystal all the angles between the molecular rotation axis and the magnetic field are equally present. Therefore the $^{13}$C spectrum has a shape typical of axially symmetric systems with a well developed peak corresponding to molecules with their rotational axis lying in a plane perpendicular to the field. Then, if we select the signal intensity at this exact frequency, we are monitoring the spin dynamics only on those molecules which have the same intramolecular interactions ($d_{1,2} = 1576 \text{ Hz} \times 2\pi\hbar$). Moreover, the carrier frequency is set to have this peak exactly on-resonance avoiding time evolution with chemical shift. The experimental results with the sequence of Fig. 3 are shown in Fig. 4 with circles. Diamonds correspond to a run with the full sequence [7] of ZME with $t_1 = 80 \mu s$. It is presented here as a function of $t_2$ with a shift $-t_1/2$ and properly normalized. The line is obtained by a spline fitting. For short times we see that superimposed to a parabolic curve with a maximum (polarization echo) around $t_m$ there are high frequency oscillations. This is a novel quantum phenomenon that we discuss below. Local polarization decreases until a quantum beat appears with a clearly developed maximum at $\approx 370 \mu s$. A second maximum which, on the basis of numerical analysis, we identify with the mesoscopic beat, develops at $520 \mu s$ but it is overcome by an overall attenuation with a characteristic time of about $500 \mu s$. This attenuation contains both the interaction with neighbor molecules and decoherent processes. The inset shows a sequence of ideal (without couplings to $^{13}$C) evolutions, $M^I(t)$, calculated with Hamiltonian (1) for a single ring and complete molecule (10 spins in Fig. 2) as described in Ref. [5]. The single ring is the upper dotted curve and is the case where our previous study of different correlation functions allowed the identification of the second peak at $580 \mu s$ as a mesoscopic beat [5]. For the molecule we distinguish four situations: rings rotating independently but keeping: (a) a staggered configuration, or (b) an eclipsed one; the molecule rotating rigidly with their rings in (c) a staggered configuration or (d) an eclipsed one. Each of these gives different sets of time averaged interaction parameters and represents a progressive increase in the inter-ring interactions which produce the consequent attenuation of the interference phenomena. An important conclusion to be drawn from this sequence is that while changes in the short time evolution, $M^I(t) \approx 1 - \frac{1}{2} \Delta \omega^2 \times t^2$, are not much apparent, the effect of those interactions in blurring out the long range interferences is decisive. This is evident in the decrease of the mesoscopic beat. The above arguments also lead to an interpretation of the additional attenuation shown up in the experimental curve as being due to intermolecular interactions. Therefore, although the experimental data cannot be fitted to our simulation with a small number of spins, the comparison of these theoretical curves with the experimental one establishes that the rings rotate independently, a result compatible with conclusions drawn from proton $T_1$ measurements [16], but cannot distinguish between staggered and eclipsed configurations. The clear correlation between the positions of the experimental and calculated peaks indicates that this is the first observation of a mesoscopic beat in a system of spins with magnetic dipolar interactions.

The short time oscillations can be explained as follows: the polarization initially at the $^{13}$C nuclei has to be transferred to the proton system. Since systems with more than one proton have an energy uncertainty due to the interproton interaction, it is not possible to obtain an 'exact' Hartmann–Hahn condition [10]. Therefore, the initial $S$ polarized state splits in two: the polarization stays at $S$ (State A) with a probabili-
ity amplitude $a = \cos \phi$, or it jumps to the proton system (state $B$) with a probability amplitude $b = i \sin \phi$. During the free evolution time the state $A$ acquires an additional phase factor due to the spin lock field. When a new CP pulse allows these states to rejoin, the phase produces an oscillation in the measured intensity. The simplest model showing this phenomenon considers a situation in which the incomplete ($|b|^2 < 1$) CP transfer occurs instantaneously, with both polarization transfers along the $y$-direction, and the spin dynamics of only two $^1\text{H}$ with an XY interaction. Then the polarization injected in one of them at time $t_2 = 0$ will be found again with a probability amplitude $m_B(t) = \cos[\frac{1}{2} \Omega_0 t]$, with $\Omega_0$ obtained as the difference between singlet and triplet eigenenergies. The ideal magnetization is then $M^I(t) = |m_B(t)|^2$. Because of rf irradiation during $t_2$, the $A$ polarization amplitude is $m_A(t) = \exp[ia_0 t]$. The magnetization measured at the $^{13}\text{C}$ non-ideal probe after a new contact pulse can be written, after some algebra, as

$$M^S(t) = |b|^4 \left( M^I(t) + 2b^2 \cos[\frac{1}{2} \Omega_0 t]a^2 \cos[\omega_{15} t] \right) + |a|^4.$$

(4)

Here we identify an interference term proportional to the waiting amplitude, $m_B(t)$. To emphasize the effect we re-write this as: $M^S(t) = |b|^2 m_B(t) + a^2 m_A(t)|^2$. The first term represents the probability amplitude for the $S$ polarization to be transferred to the proton system multiplied by the probability amplitude for the magnetization to remain in the original proton site (waiting amplitude), multiplied by the probability amplitude for the polarization to remain in $S$, evolve and still remain in the $^{13}\text{C}$. In the actual experiment (Fig. 3) the second transfer is to the $x$-axis; this cancels out the last term in Eq. (4) and decreases the interference term by a factor of 2. That gives a coefficient $|a|^2/|b|^2$ for the relative importance of the oscillations. From these considerations, the experimental oscillation amplitude implies that there is about 90% efficiency in the polarization transfer from $^{13}\text{C}$. This is also consistent with the experimental lower bound of 85% efficiency for each CP transfer obtained from the ratio of intensities measured with $t_2 = 0$ and with a sequence in which the portions A–E have been suppressed. This simple case has the virtue of presenting a structure that is maintained for more complex proton systems: the first and third terms in Eq. (4) represent the classical effect of the sum of probabilities, the second term is an interference one. In general, the frequencies involved in the first two terms are not the same. Those contributing to the first have the form $\Omega_{ij} = (E_i^N - E_j^N)/\hbar$, where the superscript in the eigenenergies of Hamiltonian (1) indicates the number of "up" spins in the proton system, while the interference term contains the frequencies $\Omega_{ij}' = (E_i^{N+1} - E_j^N)/\hbar$, i.e., the subspaces mixed by CP. Hence the expression of the observed polarization $M^S(t_2)$ is not simple. A better model takes into account the evolution in the proton system during the CP periods. Its numerical integration gives, in agreement with the experiments, both an overall shift in the oscillation toward frequencies higher than $\omega_{15}$ and an oscillation maximum which precedes that of $M^I(t_2 - t_m)$. Further comparisons between models and experiments in simple systems should provide useful information about decoherence processes and efficiency of cross polarization pulses. On a more speculative scope, we notice that the described manipulation of polarization is of the type proposed to implement simple quantum computations [17] and its further understanding could also contribute to this developing field.

One might wonder why these wealth of quantum phenomena were not seen in the ZME experiments performed in a single crystal [7]. In order to observe the interference between polarization pathways it is important to take data at short enough time intervals. The experiments of ZME were performed at about the characteristic period $(2\pi/\omega_{15})$ and that explains why they could not see this phenomenon. Note that the use of higher rf power would make the observation even more elusive. Finally, as mentioned above, in a polycrystal we are observing simultaneously all the molecules which have their rotational axis in the plane perpendicular to the magnetic field; among them there are some molecules that have the interactions with their neighbors minimized while others have them maximized (in a single crystal this shows up as an orientation dependent second moment $\Delta \omega^2$). While rings with a stronger interaction contribute with polarization evolutions which do not have quantum beats but decay steadily such as plots (c) and (d) in the inset of Fig. 3, the molecules in which the characteristic inter-
ring vectors form an angle close to the magic angle can contribute with well defined quantum beats. The importance of the interaction of neighbor molecules is appreciated in the overall decay of polarization observed in the experimental data in contrast with the finite asymptotic polarization in the exact solution of an isolated molecule. While our experimental data are a superposition of these typical behaviors, the reported single crystal data, are probably arising from an orientation favoring intermolecular interactions. Therefore we expect that by choosing the appropriate orientation in the single crystal a mesoscopic beat better developed than the one shown here should be observed.

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