



## Berry dephasing due to diffusion in nuclear quadrupole resonance

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### Abstract

Berry's phase can give rise to coherence dephasing in optically detected nuclear quadrupole resonance of gaseous  $^{131}\text{Xe}$ . Diffusion of xenon atoms around a toroidal container should cause incoherent acquisition of Berry's phase, with consequent loss of phase coherence between atoms. This leads to signal loss which is equivalent to spin relaxation. The rate of dephasing is calculated by two different methods: first, using an exact treatment of diffusion, and secondly, using average propagators. Berry dephasing is predicted to be an important relaxation mechanism in this system.

If a system is prepared in a non-degenerate eigenstate of a Hamiltonian, and the Hamiltonian is slowly varied, the system remains in an eigenstate of the instantaneous Hamiltonian. Consequently, if the Hamiltonian is slowly changed along a cyclic path, the system will return to its original state, apart from a phase factor, when the Hamiltonian returns to its original form. Berry showed that, in addition to the normal dynamic phase factor, the system also acquires a 'geometric phase',  $\gamma$ , which depends on the geometry of the circuit [1]. Since then, several authors have published theoretical treatments, in which Berry's phase and similar phenomena are related to parallel transport in curved space and to gauge transformations [2,3]. Furthermore, the original limita-

tions of non-degenerate eigenstates and adiabatic changes in the Hamiltonian have been lifted [3,4].

Experimentally, Berry's phase has been observed in a wide range of systems [5,6], including nuclear quadrupole resonance (NQR). Tycko showed that if a crystal of  $\text{NaClO}_3$  is rotated rapidly about an axis while its zero-field  $^{35}\text{Cl}$  NQR spectrum is observed, the NQR line is split, with splittings proportional to the rotation rate [7]. These splittings arise from the linear accumulation of Berry's phase: after every rotation each eigenstate acquires a different phase, and so a coherent superposition of eigenstates acquires a frequency shift proportional to the rate of rotation. Appelt et al. have performed similar experiments using optically detected  $^{131}\text{Xe}$  NQR [8]. Gaseous  $^{131}\text{Xe}$  in a small container undergoes fast exchange between wall sites, and thus has an average quadrupolar interaction with the container's inner surface [9,10]; rotation of the container causes the quadrupole axis to rotate. The low magnitude of the

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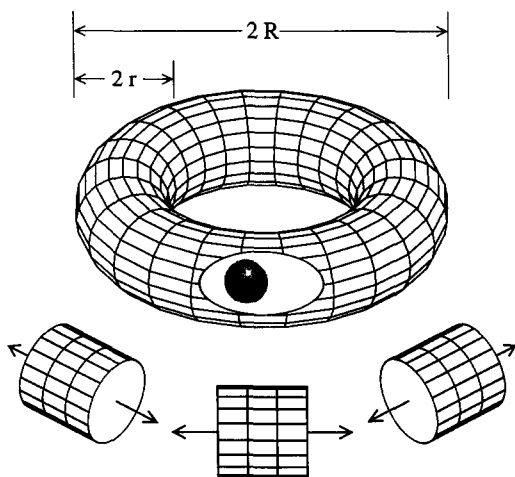


Fig. 1. Schematic depiction of a xenon atom in a toroidal container. As long as the tube radius,  $r$ , is small compared with the torus radius,  $R$ , the nucleus experiences an average electric field gradient with local cylindrical symmetry, and consequently has an axially symmetric quadrupolar coupling to the container with an axis directed along the local cylinder axis, that is tangential to the torus. As the atom moves around the torus the local cylinder axis changes, causing the quadrupole axis to rotate.

average quadrupole coupling (about 0.5 Hz) means that a wide range of adiabatic and non-adiabatic regimes may be readily achieved by macroscopic container motions.

If gaseous  $^{131}\text{Xe}$  is allowed to diffuse in a shaped container, it should be possible to observe Berry's phase effects without macroscopic motion of the container. For example, the local geometry of a torus is like a cylinder, and so a xenon atom at some point will experience an average quadrupolar coupling with a symmetry axis along the cylinder axis, that is, tangential to the torus (see Fig. 1). As any particular xenon atom diffuses around the torus, the direction of its quadrupolar axis will vary, and this variation can be described as a rotation around an axis threading the torus. This rotation will cause the xenon nuclei to acquire Berry phases, which depend only on the positions of the atoms. Two nuclei which start at the same position in the torus, but end up at different positions, will acquire a relative phase shift, which could be measured by exciting and detecting only selected regions of the torus. If the excitation and detection includes the whole torus, different

atoms will acquire different phases, and signals from them will interfere, resulting in signal loss.

This signal loss arises from a loss of phase coherence between different nuclei, and so can be considered as a form of geometric dephasing or spin relaxation. This Letter contains calculations of the rate of relaxation arising from these effects, which should be observable using optical pumping and detection [9,10]. The relaxation rate is calculated in two different ways: first, by considering the diffusive motion of individual atoms, and secondly, by calculating average propagators. Papers describing the related problems of exchange broadening and relaxation in electron spin resonance [11], and both electron and nuclear spin-rotation relaxation [12–14] have appeared in the literature.

The quadrupolar Hamiltonian for an individual nucleus is

$$\mathcal{H}_Q = \omega_Q \left[ I_z^2 - \frac{1}{3}I(I+1) \right], \quad (1)$$

where  $\omega_Q$  is the quadrupole coupling constant,  $z'$  is the (time dependent) quadrupole axis, and all energies are expressed in angular frequency units. During any short period of time, the motion of the quadrupole axis can be described as a steady rotation around an axis threading the torus, and it is convenient to transform into a frame rotating around this axis, such that the quadrupole axis is static. In this frame the Hamiltonian is given by

$$\mathcal{H}_Q^R = \omega_Q \left[ I_z^2 - \frac{1}{3}I(I+1) \right] + \omega_R I_x, \quad (2)$$

where the second term is a fictitious magnetic field (gauge field) along the rotation axis, and  $\omega_R$  is the rotation rate. For a nucleus with  $I = 3/2$ , such as  $^{131}\text{Xe}$ , the matrix representation of this Hamiltonian in the basis of  $I_z$  is

$$\mathcal{H}_Q^R = \begin{pmatrix} \omega_Q & \frac{1}{2}\sqrt{3}\omega_R & 0 & 0 \\ \frac{1}{2}\sqrt{3}\omega_R & -\omega_Q & \omega_R & 0 \\ 0 & \omega_R & -\omega_Q & \frac{1}{2}\sqrt{3}\omega_R \\ 0 & 0 & \frac{1}{2}\sqrt{3}\omega_R & \omega_Q \end{pmatrix}. \quad (3)$$

In the adiabatic limit (that is,  $\omega_R \ll \omega_Q$ ),  $\frac{1}{2}\sqrt{3}\omega_R \ll 2\omega_Q$ , and so four of the off-diagonal elements can be

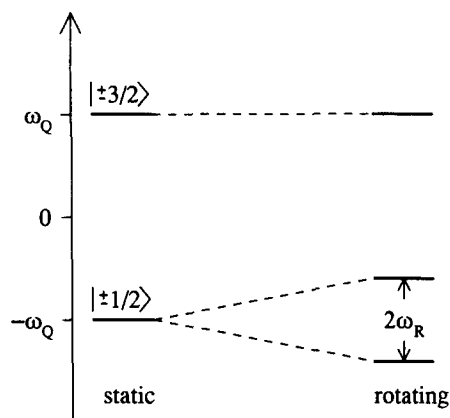


Fig. 2. The eigenstates of a spin-3/2 nucleus under an axially symmetric quadrupolar coupling. Rotation of the quadrupolar axis around an axis at  $90^\circ$  causes the  $|\pm 1/2\rangle$  states to split apart, with a splitting of  $2\omega_R$ . The  $|\pm 3/2\rangle$  states remain unaffected.

neglected. The other two off-diagonal elements, connecting the  $|\pm 1/2\rangle$  states, must be retained.

Within the adiabatic limit, it is clear that the  $|\pm 3/2\rangle$  states are completely unaffected by the fictitious field, and so remain degenerate at  $\omega_Q$ . It is initially tempting to treat the  $|\pm 1/2\rangle$  states as a fictitious spin-1/2, but this must be done with care. A true spin-1/2 nucleus would be split by the field to give two states, with eigenvalues split by  $\pm \frac{1}{2}\omega_R$ , but the  $|\pm 1/2\rangle$  states are in fact split by twice this amount, to give two new eigenstates,  $|\pm 1/2\rangle \pm | -1/2\rangle$ , with eigenvalues  $-\omega_Q \pm \omega_R$  (Fig. 2). This effect is analogous to a well-known effect in NMR of quadrupolar nuclei: when a half-odd-integer spin quadrupolar nucleus is excited with a weak radio frequency (RF) field, which is band selective for the central transition, the effective magnitude of the RF field is increased by a factor of  $I + 1/2$  [15]. One important consequence of this effect is that the Berry phases acquired by the  $|\pm 1/2\rangle$  states after one complete rotation are  $\pm 2\pi$ , but observable phase shifts can be detected as a result of fractional rotations.

In optically detected NQR, magnetization is created along some axis, allowed to evolve under a Hamiltonian, and then the magnetization remaining along the original axis is observed. This axis may be chosen at will by the experimenter, but for the present case a particularly simple choice is to ob-

serve magnetisation parallel to the rotation axis, that is perpendicular to the plane of the torus. Within the rotating frame, the initial state and final detection operator are then both  $I_x$ . Solving the Schrödinger equation gives for the observed signal

$$s(t) = 2 + 3 \cos(2\omega_Q t) \cos(\omega_R t), \quad (4)$$

where an initial intensity factor has been dropped and other forms of relaxation have been ignored. The offset corresponds to a line at zero frequency, while the oscillatory terms correspond to two groups of lines, centred at  $\pm 2\omega_Q$ , each of which comprises a pair of lines with splitting  $2\omega_R$  (see Fig. 3).

Over an extended period of time the rotation rate of any particular nucleus will vary. However the total phase acquired during a time period depends

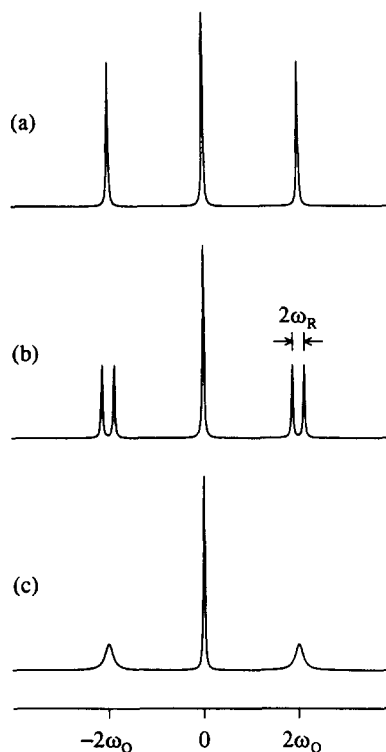


Fig. 3. Calculated spectra from  $^{131}\text{Xe}$  nuclei in a toroidal container. A static nucleus gives a simple three line spectrum (a). A nucleus moving round the container at a constant rate  $\omega_R$  (or, equivalently, a static nucleus in a container rotated at a rate  $\omega_R$ ) gives a five line spectrum (b), as the quadrupolar lines are split. Adiabatic diffusion of xenon atoms around the torus corresponds to an incoherent distribution of rotation rates, and so gives line broadenings (c) rather than splittings.

only on the average rotation rate,  $\bar{\omega}_R$ , over that time, even for the non-Abelian case of degenerate states, as discussed by Zee [16]. Hence the signal from an individual nucleus depends on the total winding,  $w = \bar{\omega}_R t$  achieved by the nucleus; in general we can write  $w = 2\pi n + \phi$ , where  $\phi$  is the additional fractional rotation. Consequently Eq. (4) and its generalisation may be simplified to give

$$s(t) = 2 + 3 \cos(2\omega_Q t) \cos(w). \quad (5)$$

The  $\cos(w)$  term arises from interference between signals from the two different quadrupolar transitions, which acquire equal and opposite phase shifts of  $\pm w$ .

In a gas sample different nuclei will move at different velocities, and so will acquire different windings. The motion of the atoms can be modelled as one dimensional diffusion, with a probability density function

$$\mathcal{P}(w) = (2\pi dt)^{-1/2} \exp(-w^2/2dt), \quad (6)$$

where  $d$  is the one dimensional diffusion coefficient measured in  $\text{rad}^2 \text{s}^{-1}$ . Multiplying Eqs. (5) and (6) and integrating over all possible windings gives the total observable signal

$$S(t) = 2 + 3 \cos(2\omega_Q t) \exp(-\frac{1}{2}dt), \quad (7)$$

showing that signal from the quadrupolar transitions decays exponentially with a time constant of  $2/d$  (the central line, which was not split by the fictitious field, remains unbroadened). The decay occurs not because nuclei acquire large winding numbers, but simply because at long times the distribution of fractional windings becomes flat.

The one dimensional diffusion coefficient,  $d$ , is related to the conventional three dimensional diffusion constant,  $D$ , by  $d = D/3R^2$ , where  $R$  is the radius of the torus (see Fig. 1). For xenon at standard temperature and pressure  $D \approx 5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  [17], so a torus with a radius of three millimetres will have a Berry dephasing time constant of about eleven seconds, shorter than that from other relaxation mechanisms. In such a torus the typical rotation rate is about 0.03 Hz, much smaller than the typical quadrupolar coupling (0.5 Hz), and so the adiabatic approximation is reasonable. Small deviations from adiabaticity should only result in a slightly faster loss

of signal, but at very high rotation rates ( $\omega_R \gg \omega_Q$ ) the signal should once again become sharp, as predicted by average Hamiltonian theory [18].

The coherence dephasing can also be calculated by a different method, involving average Liouvillian propagators [19], which is more reminiscent of conventional treatments of relaxation. Consider a short time  $\tau$  during which it may be assumed that any xenon atom has a fixed angular velocity around the torus, and so experiences a constant fictitious field. The evolution of the nuclear spin state during this period may be conveniently described by a Liouvillian propagator,  $\rho(\tau) = \bar{\mathcal{L}}(\tau)\rho(0)$ , where

$$\bar{\mathcal{L}}(\tau) = \exp\left[-i\hat{\mathcal{H}}(\omega_R)\tau\right]. \quad (8)$$

Different atoms possess different velocities, and so their nuclei will evolve under different propagators. Nevertheless, it is possible to calculate an average Liouvillian propagator, under which the whole system evolves. The angular velocities will be distributed with a one-dimensional Maxwell distribution,

$$\mathcal{P}(\omega_R) = (2\pi c^2)^{-1/2} \exp(-\omega_R^2/2c^2) \quad (9)$$

(where the root mean square velocity is  $c$ ), and the average propagator,  $\bar{\mathcal{L}}(\tau)$ , can be calculated by integrating Eq. (8) over this distribution. If  $c \ll \omega_Q$ , most of the nuclei will evolve adiabatically, and the approximate adiabatic Hamiltonian can be used in Eq. (8); this greatly simplifies the calculation of  $\bar{\mathcal{L}}(\tau)$ , and this approximation is used throughout the following sections.

Now suppose that at the end of a time period  $\tau$  all the atomic velocities instantly change, so that the velocity distribution retains the form of Eq. (9) but the velocities before and after the change are completely uncorrelated. In this case the same average propagator can be used during the two time periods. Hence

$$\rho(2\tau) = \bar{\mathcal{L}}(\tau)\bar{\mathcal{L}}(\tau)\rho(0) = \bar{\mathcal{L}}^2(\tau)\rho(0), \quad (10)$$

or, more succinctly,  $\bar{\mathcal{L}}(m\tau) = [\bar{\mathcal{L}}(\tau)]^m$ , for any integer  $m$ . For the approximate adiabatic Hamiltonian, the average propagator is sufficiently simple that the matrix power can be calculated analytically, allowing us to write an analytic formula for the

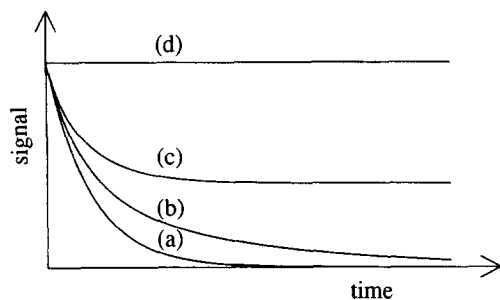


Fig. 4. Berry dephasing due to diffusion of xenon atoms around a torus causes the signal to decay exponentially to zero (a). The signal from a tube bent into a torus, but without the ends joined, decays more slowly but eventually reaches zero (b). If the tube is bent around an angle of  $180^\circ$ , forming a half torus, the signal decays to a constant value (c). If the tube is not bent at all, no decay due to Berry dephasing should be observed (d).

signal at time  $m\tau$ . For the experiment described previously,

$$s(m\tau) = 2 + 3 \cos(2\omega_Q m\tau) \exp\left(-\frac{1}{2}m\tau^2 c^2\right). \quad (11)$$

This can be simplified by writing  $t = m\tau$ , to give

$$s(t) = 2 + 3 \cos(2\omega_Q t) \exp\left(-\frac{1}{2}t\tau c^2\right), \quad (12)$$

which may be compared with Eq. (7). Clearly the equations have the same form, and equating terms gives  $d = \tau c^2$ , compatible with a random-walk diffusion model.

A related problem concerns the signal from xenon atoms diffusing in a tubular container which is bent around a circular arc, but whose ends are not joined to form a torus; this is most conveniently solved using the diffusion model for which problem can be solved numerically (Fig. 4). A simple equation may be obtained for the limiting signal at infinite time (as usual, neglecting other sources of relaxation). For this case the distribution of final angular positions is flat, as is that for initial positions. The distribution of acquired windings is not, however, flat, as the range of windings which may be acquired depends on the initial position. Integrating over all initial positions gives

$$\mathcal{P}_x(w) = (1 - |w|/\theta)/\theta, \quad -\theta \leq w \leq \theta, \quad (13)$$

where  $\theta$  is the arc subtended by the container (so that for a container wrapped into a torus, but with the

ends not joined,  $\theta = 2\pi$ , while for a true torus  $\theta = \infty$ ). Multiplying Eqs. (5) and (13) and integrating over all possible windings gives the total signal at long times,

$$S(t) = 2 + 3 \cos(2\omega_Q t) \operatorname{sinc}^2\left(\frac{1}{2}\theta\right), \quad (14)$$

where  $\operatorname{sinc}(x) = \sin(x)/x$ . Of course, other relaxation mechanisms will become significant at long times, and so the signal will eventually decay to zero.

The loss of signal coherence as a result of randomly acquired Berry phases is a novel spin relaxation mechanism which may also be relevant in other NMR and NQR experiments. In particular, the slow rotational diffusion of particles could be an important source of relaxation in conventional NQR studies of colloids. In this case it is necessary to consider the slow diffusion of the quadrupolar axis around the surface of a sphere, rather than around the edge of a circle.

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