PHYSICAL REVIEW
LETTERS

VOLUME 58 | 1 JUNE 1987 | NUMBER 22

Adiabatic Rotational Splittings and Berry's Phase in Nuclear Quadrupole Resonance

Robert Tycko
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 17 March 1987)

Sample rotation is shown to induce frequency splittings in nuclear-quadrupole-resonance spectra. The splittings are interpreted both as a manifestation of Berry's phase, associated with an adiabatically changing Hamiltonian, and as a result of a fictitious magnetic field, associated with a rotating-frame transformation. Real and fictitious fields are contrasted. Related effects are predicted in other magnetic resonance experiments that involve sample rotation.

PACS numbers: 03.65.−w, 33.30.+a

The evolution of a quantum-mechanical system under an adiabatically changing Hamiltonian is an important topic that is receiving renewed attention.[1-12] In particular, when the Hamiltonian follows a closed path in parameter space in the time interval $[0,T]$ [i.e., $\mathcal{H}(T)=\mathcal{H}(0)$] and when the system is initially in an eigenstate of $\mathcal{H}$ [i.e., $\mathcal{H}(0)\,|\,\psi(0)\rangle=E_n(0)\,|\,\psi(0)\rangle$], it has been recognized[1-3,8] that the system ends up in the state $|\,\psi(T)\rangle=e^{-i\beta_n}e^{-i\phi_n}\,|\,\psi(0)\rangle$. β_n, called the quantum adiabatic phase or Berry's phase, depends only on the path or certain geometric features of the path; ϕ_n, called the dynamical phase and equal to $\hbar^{-1}\int_0^T dt\,E_n(t)$, depends both on the path and on the rate at which the path is followed. Berry's phase has been invoked in discussions and experiments involving molecular spectroscopy,[3-7] atom-molecule scattering,[8] the quantum Hall effect,[2,9] and light propagation in optical fibers.[10,11] Spin problems have been used as solvable examples in theoretical treatments of Berry's phase.[1,2] Suggestions for experimental demonstrations of Berry's phase in magnetic resonance, involving *rotating external fields*, have been made.[1,7] In this Letter, an effect of Berry's phase on the magnetic resonance spectrum of a *rotating sample* is described and demonstrated with use of pure nuclear quadrupole resonance (NQR). This effect, which may be called the adiabatic rotational splitting, has important consequences in magnetic resonance in addition to serving as an interesting manifestation of Berry's phase.

Consider the experiment depicted in Fig. 1. A single-crystal sample containing nuclear spins S with an axially symmetric quadrupole coupling with coupling constant ω_Q and principal-axis direction z' is rotated about the z axis at angular velocity ω_R. The NQR spectrum is observed by applying radio-frequency (rf) pulses and detecting free-induction decay signals with a solenoid coil wound along z. Provided that $\omega_R \ll \omega_Q$, the nuclear-spin Hamiltonian is changing adiabatically. However, only the instantaneous eigenstates, and not the instantaneous energies, change with time since the NQR frequencies (in the absence of external static fields) are independent of orientation in a static sample. In other words, the dynamical phase evolution is unaffected by the rotational motion. Any observed rotational effects must arise from Berry's phase. Suppose that a superposition of two eigenstates $|\,\psi_1\rangle$ and $|\,\psi_2\rangle$ is created by a rf pulse at $t=0$. At time $mT=2\pi m/\omega_R$ later, the

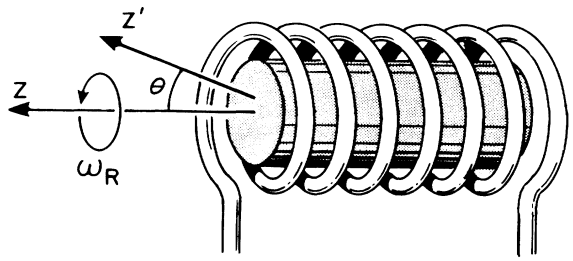
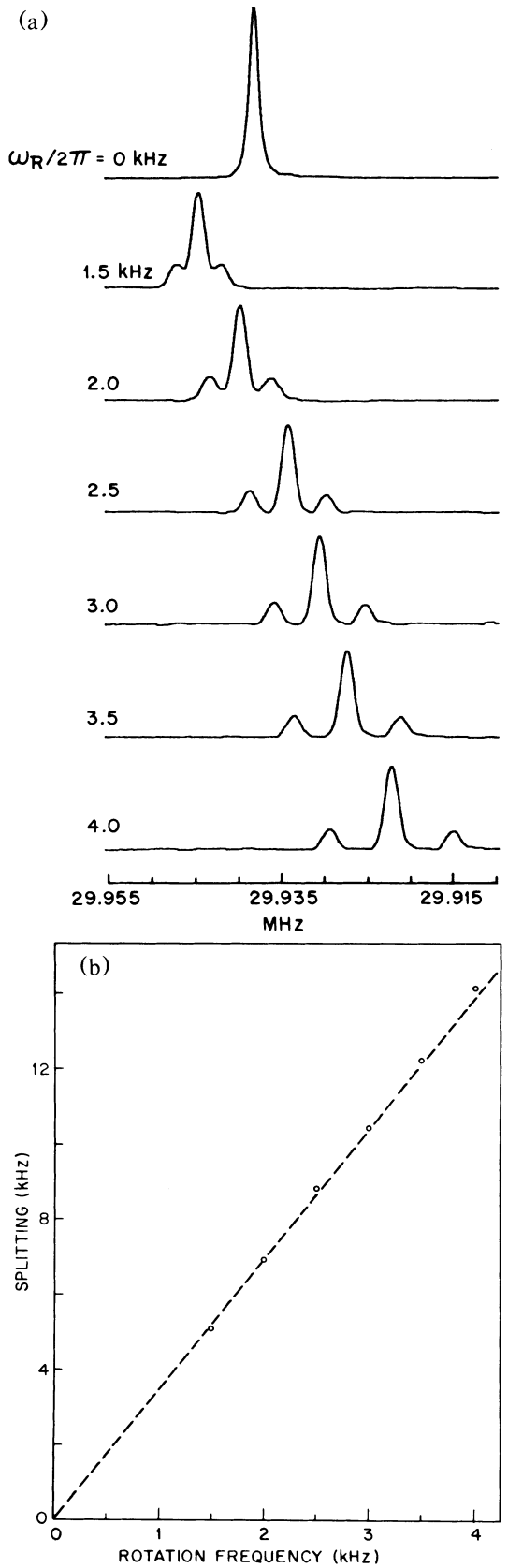


FIG. 1. Experimental arrangement for observation of adiabatic rotational splittings in NQR. z is the rotation axis and z' is the principal axis of the quadrupole coupling.



two eigenstates acquire a relative phase difference $(\beta_1-\beta_2)m$. The NQR signal phase is shifted by the same amount. Since a continuously increasing phase shift is equivalent to a frequency shift, Berry's phase is observable as a frequency shift of $(\beta_1-\beta_2)/2\pi T$. In the experiments described here, $S=\frac{3}{2}$ and there is a degenerate transition that exhibits a phase shift of $-(\beta_1-\beta_2)m$. Therefore, an adiabatic rotational splitting of the NQR line that is proportional to ω_R is expected.[13]

Figure 2(a) shows ^{35}Cl NQR spectra of $NaClO_3$ observed at various rotation frequencies. The 119-mg $NaClO_3$ crystal was oriented with a cleavage plane perpendicular to the rotation axis. At this orientation, the angle θ between z and z' satisfies $\cos^2\theta=\frac{1}{3}$ for all four Cl nuclei in the unit cell. A commercial nuclear-magnetic-resonance (NMR) probe designed for magic-angle spinning NMR experiments was used. The single NQR resonance observed when $\omega_R=0$ splits into three lines with relative areas 0.25, 1.00, and 0.22 when $\omega_R\neq 0$. Figure 2(b) shows that the splitting between the outer lines is well described by $\sqrt{3}\omega_R/\pi$. In addition to the splittings, overall shifts of the resonances are apparent in Fig. 2(a). These are artifacts due to changes in the crystal temperature that accompany sample spinning. At 23 °C, $\omega_Q/2\pi$ changes by 2.1 kHz/deg.[14]

The results in Fig. 2 can be predicted quantitatively from established formulas for Berry's phase.[1,2] The spin Hamiltonian is

$$\mathcal{H}(t)=\omega_Q S_{z'}^2(t), \tag{1}$$

$$S_{z'}(t)=S_z\cos\theta+S_x\sin\theta\cos\omega_R t+S_y\sin\theta\sin\omega_R t. \tag{2}$$

For reasons given below, it is convenient to use a basis of time-dependent eigenstates, written in terms of eigenstates of $S_{z'}(t)$ as follows:

$$|a\rangle=|\tfrac{3}{2}\rangle, \tag{3a}$$

$$|b\rangle=\cos(\tfrac{1}{2}\xi)|\tfrac{1}{2}\rangle-\sin(\tfrac{1}{2}\xi)|-\tfrac{1}{2}\rangle, \tag{3b}$$

$$|c\rangle=\sin(\tfrac{1}{2}\xi)|\tfrac{1}{2}\rangle+\cos(\tfrac{1}{2}\xi)|-\tfrac{1}{2}\rangle, \tag{3c}$$

$$|d\rangle=|-\tfrac{3}{2}\rangle, \tag{3d}$$

$$\tan\xi=2\tan\theta.$$

According to Simon[2] and Berry,[1] the adiabatic phase accumulated by a spin state $|\psi\rangle$ in one rotation is

$$2\pi\int_0^\theta d\theta'\sin\theta'\langle\psi|S_{z'}|\psi\rangle.$$

FIG. 2. (a) ^{35}Cl NQR spectra of a $NaClO_3$ crystal obtained at various sample rotation frequencies showing adiabatic rotational splittings. Ambient temperature is 23 ± 1 °C. Overall shifts of the resonances are due to crystal temperature variations. (b) Splitting between the countermost lines vs rotation frequencies. The dashed line has a slope of $2\sqrt{3}$.

Therefore,

$$\beta_a = 3\pi(\cos\theta - 1), \tag{4a}$$

$$\beta_b = -\pi[(4 - 3\cos^2\theta)^{1/2} - 1], \tag{4b}$$

$$\beta_c = \pi[(4 - 3\cos^2\theta)^{1/2} - 1], \tag{4c}$$

$$\beta_d = -3\pi(\cos\theta - 1). \tag{4d}$$

Possible phase differences, modulo 2π, are $\pm 2\sqrt{3}\pi$ and 0 at the crystal orientation used, corresponding to frequency shifts of $\pm\sqrt{3}\omega_R/2\pi$ and 0 as observed.

The observed spectra, including the relative intensities of the lines, can also be predicted from the quantum-mechanical expression for the free induction signal $F(t)$:

$$F(t) = \mathrm{Tr}\{S_z U(t)\rho(0)U(t)^{-1}\}, \tag{5}$$

$$U(t) = \mathbf{T}\exp\left[-i\int_0^t dt'\,\mathcal{H}(t')\right], \tag{6}$$

where $\rho(0)$ is the spin density operator after the rf pulse and $\mathbf{T}$ is the time-ordering operator. Since $\mathcal{H}(t)$ is related to $\mathcal{H}(0)$ by a rotation around z, the evolution operator $U(t)$ can be rewritten as

$$U(t) = e^{-i\omega_R S_z t} e^{-i\mathcal{H}t}, \tag{7}$$

$$\mathcal{H} = \mathcal{H}(0) - \omega_R S_z; \tag{8}$$

$\mathcal{H}$ is the Hamiltonian in a frame that rotates with the crystal. The signal becomes

$$F(t) = \mathrm{Tr}\{S_z e^{-i\mathcal{H}t}\rho(0)e^{i\mathcal{H}t}\}. \tag{9}$$

Equation (9) shows that the effect of Berry's phase on the signals can also be viewed as the effect of the "fictitious field" term $-\omega_R S_z$ that appears in the rotating frame. The adiabatic limit $\omega_R \ll \omega_Q$ corresponds to the first-order perturbation-theory limit. In that limit, and with an initial density operator $[S_z'(0)\cos\alpha + S_{y'}(0)\sin\alpha]^2$,

$$F(t) = -(\tfrac{2}{3})^{1/2}\sin 2\alpha(2 + \cos\sqrt{3}\omega_R t)\sin 2\omega_Q t, \tag{10}$$

showing that lines are expected at $(2\omega_Q - \sqrt{3}\omega_R)/2\pi$, ω_Q/π, and $(2\omega_Q - \sqrt{3}\omega_R)/2\pi$ with relative areas 0.25, 1.00, and 0.25.

In the general case of a system with a time-dependent Hamiltonian, the evolution operator can be written

$$U(t) = W(t)\mathbf{T}\exp\left\{-i\int_0^t dt'[A(t') + B(t')]\right\}, \tag{11}$$

$$A(t) = \sum_n \omega_n(t)\,|n(0)\rangle\langle n(0)|, \tag{12}$$

$$B(t) = i[dW^{-1}(t)/dt]W(t), \tag{13}$$

where $\{|n(t)\rangle\}$ and $\{\omega_n(t)\}$ are the instantaneous eigenstates and energies at time t and $W(t)$ is a unitary transformation between $\{|n(0)\rangle\}$ and $\{|n(t)\rangle\}$. Equation (11) is the generalization of Eq. (7), expressing $U(t)$ in terms of the Hamiltonian $A(t) + B(t)$ that appears in a frame that "follows" the time-dependent eigenstates of the original Hamiltonian. In the adiabatic limit, the generalized fictitious field $B(t)$ is a perturbation on $A(t)$ and β_n is given by

$$e^{-i\beta_n} = \langle n(0)|W(T)|n(0)\rangle\exp\left[-i\int_0^T dt\langle n(0)|B(t)|n(0)\rangle\right]. \tag{14}$$

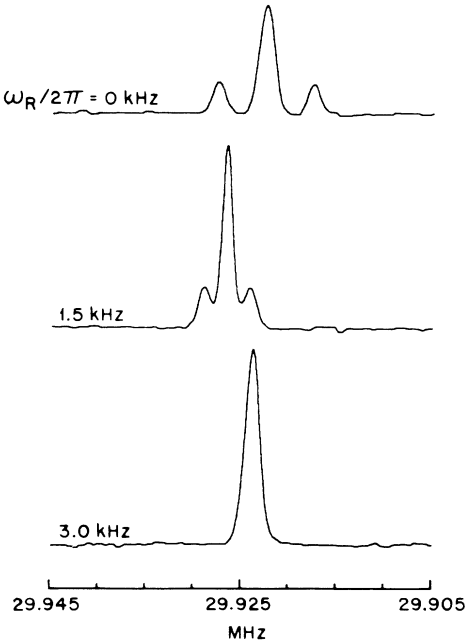


FIG. 3. As in Fig. 2(a), but with a 7.2-G static field applied along the rotation axis. The field is produced by Helmholtz coils coaxial with z and with the current direction opposite to the sample rotation direction.

An objection to the claim that Fig. 2 is a manifestation of Berry's phase may be raised. Since the instantaneous eigenstates of $\mathcal{H}(t)$ are two doubly degenerate pairs, it may be unclear whether a true adiabatic change is possible. However, provided that the instantaneous eigenstates are chosen so as to diagonalize S_z within each manifold of degenerate states, as has been done in Eqs. (3), transitions between degenerate eigenstates do not occur and Berry's phase remains meaningful. Wilczek and Zee[6] have treated degenerate systems in greater detail. Alternatively, a real static magnetic field H can be applied along z to lift the degeneracy of the states in Eqs. (3). As shown in Fig. 3, the linear dependence of the splitting of the NQR line on ω_R is unchanged. The real and fictitious fields can be made to

cancel one another.

The equivalence in NQR between rotation and the application of a field is not complete. For example, if the rf fields are applied and detected perpendicular to the rotation axis or static field direction, different signals will be observed in the two cases unless the rf coils rotate with the sample. In addition, the spin interaction with a real field depends on the gyromagnetic ratio γ, while the effect of the fictitious field induced by rotation is independent of γ. The absolute sign of γ can then be measured by determining which sense of rotation relative to the real field direction tends to cancel the real field. Figure 3 shows that γ is positive for ^{35}Cl, as expected.

Sample spinning is commonly used in solid-state NMR to obtain narrow lines.[15] It is generally assumed that the NMR spectrum of a rapidly rotating sample is simply the orientationally averaged spectrum. The results here show that this assumption is not always correct. In particular, whenever the spin eigenstates depend on the sample orientation, adiabatic rotational splittings or shifts may appear. Such effects may be expected in overtone NMR spectra[16] and NMR spectra of dipole-coupled nuclei when ω_R is small compared to the dipole couplings. It is also anticipated that the adiabatic rotational splitting may serve as a coherence dephasing mechanism, for example in NQR of randomly tumbling particles when the rotational correlation time is large compared to ω_Q^{-1}.[17] Finally, Pines and co-workers have provided independent experimental evidence for Berry's phase effects in magnetic resonance, using rotating rf fields in high field NMR.[18,19]

I thank D. C. Douglass and T. Sleator for many informative discussions and experimental assistance, L. W. Jelinski for the generator loan of a spectrometer, and J. P. Remeika for providing the $NaClO_3$ crystal.

[1]M. V. Berry, Proc. Roy. Soc. London, Ser. A **392**, 45 (1984).

[2]B. Simon, Phys. Rev. Lett. **51**, 2167 (1983).

[3]G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. **35**, 77 (1963).

[4]C. A. Mead, Chem. Phys. **49**, 23 (1980).

[5]G. Delacrétaz, E. R. Grant, R. L. Whetten, L. Wöste, and J. W. Zwanziger, Phys. Rev. Lett. **56**, 2598 (1986).

[6]F. Wilczek and A. Zee, Phys. Rev. Lett. **52**, 2111 (1984).

[7]J. Moody, A. Shapere, and F. Wilczek, Phys. Rev. Lett. **56**, 893 (1986).

[8]C. A. Mead and D. G. Truhlar, J. Chem. Phys. **70**, 2284 (1979).

[9]D. Arovas, J. R. Schrieffer, and F. Wilczek, Phys. Rev. Lett. **53**, 722 (1984).

[10]R. Y. Chiao and Y.-S. Wu, Phys. Rev. Lett. **57**, 933 (1986).

[11]A. Tomita and R. Y. Chiao, Phys. Rev. Lett. **57**, 937 (1986).

[12]H. Kuratsuji and S. Iida, Phys. Rev. Lett. **56**, 1003 (1986).

[13]Actually, this argument only determines the frequency shifts to within multiples of $\omega_R/2\pi$. The multiples that are observed depend on the orientation of the rf coils with respect to the spinning axis.

[14]H. S. Gutowsky and G. A. Williams, Phys. Rev. **105**, 464 (1957).

[15]M. Mehring, *Principles of High Resolution NMR in Solids* (Springer, New York, 1983).

[16]R. Tycko and S. J. Opella, J. Chem. Phys., to be published.

[17]S. Alexander and A. Tzalmona, Phys. Rev. **138**, A845 (1965). This paper treats longitudinal, not transverse, relaxation caused by slow rotation in terms of an effective field.

[18]D. Suter, G. Chingas, R. A. Harns, and A. Pines, to be published.

[19]D. B. Zax, A. Bielecki, K. W. Zilm, A. Pines, and D. P. Weitekamp, J. Chem. Phys. **83**, 4877 (1985). This paper predicts effects in zero-field NMR due to rapid, nonadiabatic sample rotation.