Explicit demonstration of spinor character for a spin-1/2 nucleus via NMR interferometry*

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The results of a nuclear-magnetic-resonance experiment are presented which directly demonstrate the spinor character of a spin-1/2 nucleus, ^{13}C. The interferometric spectroscopic technique used and its potential applications are discussed.

It has long been known that a particle of half-integral spin (a fermion) exhibits spinor character, which means that it changes the sign of its quantum-mechanical wave function upon a 2π rotation, and that the phase factor returns to its original value only after a 4π rotation. A particle of integral spin (a boson) does not exhibit this behavior, and its phase factor returns to its original value in a 2π rotation. While any number of experiments done over the years implicitly illustrate this concept, the first explicit demonstration came in 1975 when Werner *et al.*[1] and Rauch *et al.*[2] clearly showed the spinor nature of neutrons. Such experiments had been suggested and discussed earlier (1967) by Bernstein[3] and by Aharonov and Susskind.[4]

We present here the results of a somewhat analogous nuclear magnetic double-resonance experiment which graphically shows the spinor character of a spin-$\frac{1}{2}$ particle by observing the behavior under rotation of a pseudo-two-level system. A similiar technique could easily be used to study spinor character for spin $\frac{3}{2}$, $\frac{5}{2}$, etc., by observing the behavior under rotation of pseudo-4-, -6-, etc., level systems. Nonspinor character of spin 1, 2, etc., could be studied by choosing pseudo-3-, -5-, etc., level systems. In addition, this experiment embodies concepts which could be exploited in a variety of spectroscopic areas.

To observe spinor character, one must observe the phase of a wave function. However, this is difficult because any measurement involves $\psi^*\psi$, and thus the overall phase is unobservable. The only way for us to "see" the phase is then by some form of interferometry, i.e., by determination of the phase difference between the amplitude to be in the given state and the amplitude to be in some reference state. In order to measure this phase difference, we must measure a physical observable whose operator connects these same states, and furthermore, we must initially prepare the system in a linear combination of these states. Thus, it is in the off-diagonal elements of the density matrix that such relative-phase information is found and by doing experiments involving such off-diagonal elements that one can observe spinor character. Many previous experiments involving off-diagonal matrix elements then can be used as implicit evidence of this behavior. For example, the precession of a spin-$\frac{1}{2}$ particle in a strong magnetic field furnishes such implicit evidence.

In the neutron experiments[1,2] the relative-phase information was extracted by splitting a neutron beam into two parts and observing how the diffraction pattern changed upon application of a 2π rotation to one of these parts. The changes in the "beating" pattern then signaled the change in the phase. In our experiment, we have used the NMR analog of interferometry. For a spin in a strong magnetic field to have a transverse component of observable magnetization, it must not be in an eigenstate of the Zeeman Hamiltonian. In fact, the direction that the magnetization points in the x-y plane (the external field is assumed along z) is the direct manifestation of the phase difference between the various levels.

For the particular case of a spin-$\frac{1}{2}$ particle in a static magnetic field directed along the z direction, one has a two-level system where the spin wave function ψ can be written

$$\psi = ae^{i\phi_a}\alpha + be^{i\phi_b}\beta ,$$

where α and β are the eigenstates with quantized angular momentum along the z axis ($+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$, respectively). The complex coefficients, $ae^{i\phi_a}$ and $be^{i\phi_b}$, are amplitudes for eigenstates α and β, respectively, where a and b are chosen as real numbers with the normalization constraint, $a^2 + b^2 = 1$. The z component of the magnetization is $M_z \propto a^2 - b^2$, while the transverse components are $M_x \propto ab\cos(\phi_a - \phi_b)$ and $M_y \propto ab\sin(\phi_a - \phi_b)$, and thus it is apparent that observation of the transverse magnetization furnishes the phase difference, $\phi_a - \phi_b$, but the absolute phase, i.e., either ϕ_a or ϕ_b, is not determinable.

In order to perform the nuclear magnetic interferometric measurement, it is necessary to "split" the spin into two components, each of which is a two-level system and then to perform selectively a rotation on only one part. Then by observing the

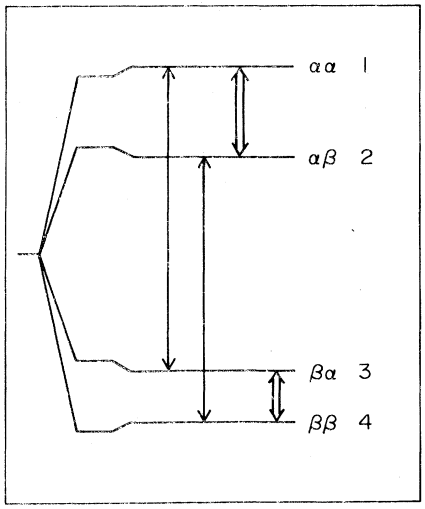

FIG. 1. Energy-level diagram for two weakly coupled inequivalent spin-$\frac{1}{2}$ particles (^{13}C, ^{1}H) in a strong magnetic field. The α and β represent the two eigenstates spin-up and spin-down of the spin-$\frac{1}{2}$ particle. The first Greek letter represents the state of the ^{1}H spin and the second represents the state of the ^{13}C spin, so the two ^{1}H transitions are shown with single arrows while the two ^{13}C transitions are shown with double arrows. The numbers 1, 2, 3, 4 are used to refer to the various energy levels or to the eigenstates to which they correspond. The relative Zeeman energies for ^{1}H (56.4 MHz) and ^{13}C (14.2 MHz) have been drawn to scale, but the effects of the weak coupling have been greatly exaggerated for emphasis.

interference between the two components both before and after the rotation one can determine the overall change in phase of the rotated component simply by using the phase of the unrotated component as a reference. This "splitting" was accomplished in the neutron experiment by splitting the neutron beam and spatially isolating it into two components which could be selectively rotated, and the beams were then spatially recombined to observe the interference. However, in the present experiment it was not necessary to split and isolate the spin spatially since we could use the presence of a second, different, spin to alter slightly the energy levels and thus accomplish the "splitting" energetically, rather than spatially. That is, by choosing a system with coupled pairs of spins, I and S, one naturally has a "split" system of two components; one consisting of the states α and β for the S spin with the I spin in the α eigenstate, and a second component consisting of the eigenstates α and β for the S spin with the I spin in the β eigenstate. The coupling between the I and S spins causes the transition frequencies of the S spin to be different for these two components, and thus it is possible to rotate selectively only one component and observe the interference effects.

The chemical system we chose for the demonstration was 91% ^{13}C-enriched sodium formate ($NaCHO_2$) dissolved in D_2O with a small amount of ^{1}H impurity. The ^{1}H (I spin) and ^{13}C (S spin) nuclei in the formate ion form a coupled system of two spin-$\frac{1}{2}$ particles, and their energy levels are shown in Fig. 1. The allowed transitions for the ^{1}H between levels 1-3 and 2-4 are inequivalent due to the presence of the secular part of a scalar coupling of the form $J\vec{I}\cdot\vec{S}$, where J is the coupling constant. The inequivalent ^{13}C transitions are between levels 1-2 and 3-4. This J coupling splits the spectroscopic lines and thus allows one to selectively irradiate transitions.

The rf pulsing scheme is illustrated in Fig. 2. The experiment itself consisted of two parts. In the first part, we took a normal ^{1}H Fourier-transform echo spectrum of our liquid sample. This consisted of applying a short (2 μsec) $\frac{1}{2}\pi$ pulse to all the ^{1}H transitions. A short (4 μsec) ^{1}H π pulse was applied at a time ΔT to create a spin echo at time $2\Delta T$ ($t=0$). This was convenient for reasons to be explained later. The time decay was then recorded from $t=0$ and Fourier transformed to yield the top spectrum in Fig. 3. (Note that in this first part we have irradiated no ^{13}C transitions.) In this ^{1}H spectrum, the symmetric doublet results from the scalar coupling between ^{1}H and ^{13}C in the 91% of the formate ions which are isotopically enriched with ^{13}C. The splitting here has a value of $J=195$ Hz. The small peak at the center of mass of the doublet results from the ^{1}H nuclei in the remaining 9% of the formate ions which contain spinless ^{12}C nuclei. The large peak on the far right results from the ^{1}H nuclei in the small amount of HDO in the D_2O solvent.

In the second part of the experiment, we repeated the scheme of the first part but with one important addition. After the initial ^{1}H $\frac{1}{2}\pi$ pulse we applied a long ($\tau=26$ msec) low-power, selective, ^{13}C 2π pulse to only one of the ^{13}C transitions (the

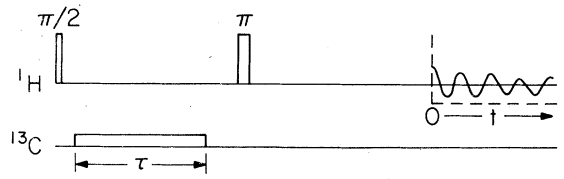

FIG. 2. Radiofrequency pulse sequence used. A $\frac{1}{2}\pi$ pulse and a π pulse were applied to the ^{1}H transitions and the resulting spin echo was recorded from time $t=0$ for Fourier transformation. The spectrum was obtained first with no ^{13}C irradiation ($\tau=0$) and second with a selective 2π pulse ($\tau=26$ msec) applied to only one ^{13}C transition.

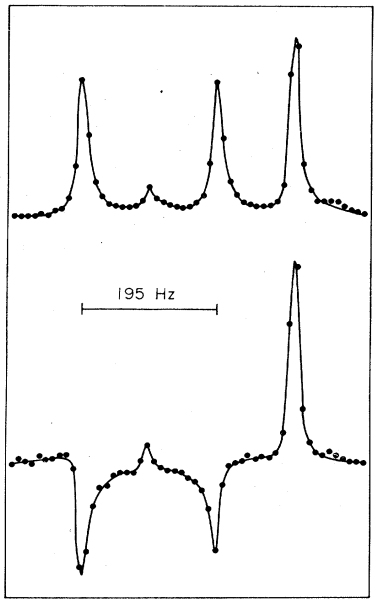

FIG. 3. ^{1}H Fourier-transform NMR spectra explicitly showing spinor character of a spin-$\frac{1}{2}$ particle. The top spectrum involved no ^{13}C irradiation, while the bottom spectrum utilized a selective 2π pulse applied to only one ^{13}C transition. The splitting of 195 Hz is between the two peaks of the doublet due to weak scalar coupling of the ^{1}H and ^{13}C in the formate ions containing ^{13}C. The small peak at the center of the doublet is due to ^{1}H in formate ions containing ^{12}C, while the large peak at the far right is due to the small amount of ^{1}H in the solvent.

^{13}C rotating field equaled approximately 10% of the separation of the ^{13}C lines). As before, we recorded the spin echo and Fourier transformed it to get the bottom spectrum shown in Fig. 3. We can see that the application of the selective 2π pulse to only one of the ^{13}C transitions caused the inversion of the peaks due to the ^{1}H coupled to the ^{13}C in the formate ions. This fact is the direct result of the fact that the ^{13}C is a two-level system and that two-level systems behave as spinors under rotation. (Note that the ^{1}H peaks due to the ^{1}H not coupled to the ^{13}C did not invert.) To understand this, one can refer to the energy-level diagram in Fig. 1. The effect of the initial $\frac{1}{2}\pi$ pulse applied to the ^{1}H 1-3 and 2-4 transitions was to place the ^{1}H spins in linear combinations of the eigenstates spin-up and -down (α and β) with a definite phase difference between them. This means that one has created linear combinations of the states 1 and 3 and also of the states 2 and 4 (see Fig. 1). Let the phases of the amplitudes of the four states be ϕ_1, ϕ_2, ϕ_3, and ϕ_4. The sizes of the ^{1}H doublet peaks are then proportional to $\cos(\phi_1 - \phi_3)$ and $\cos(\phi_2 - \phi_4)$. The phase difference between 1 and 3 and between 2 and 4 was then modified by the application of a selective 2π pulse to only the 3-4 ^{13}C transition. [A 2π pulse on the 3-4 transition is defined in the conventional way as one which causes $\cos(\phi_3 - \phi_4)$ to undergo one full cycle. However, one wishes to know by how much ϕ_3 and ϕ_4 have changed individually. Since no radiation was applied to the 1-2 transition, ϕ_1 and ϕ_2 have not been altered, and since the size of the ^{1}H doublet lines is a measure of $\cos(\phi_1 - \phi_3)$ and $\cos(\phi_2 - \phi_4)$, one can use the fact that both ^{1}H spectral lines inverted (see bottom spectrum in Fig. 3) to indicate that both ϕ_3 and ϕ_4 have each changed by π, i.e., a clear demonstration of spinor character.

With respect to more minor experimental details, a spin echo was used on the proton system to furnish ^{1}H spectra that could be directly compared. Had we not refocused the ^{1}H magnetization with the π pulse, we could have observed only the portion of the free-induction decay remaining after the end of the rather long selective pulse applied to the ^{13}C system, and this would have produced anomalous effects, making comparison of the ^{1}H spectra more complicated. We set the length of the selective ^{13}C pulse experimentally by observing the ^{13}C NMR signal from a different sample containing an unsplit ^{13}C spectrum.

We note that the two peaks of the doublet in the bottom spectrum of Fig. 3 do not have quite the same amplitude. This effect does not have a trivial explanation, and it appears that the difference in amplitude is due to relaxation. When a spin system has been prepared in a state not in thermal equilibrium, as ours has been, the various density matrix elements relax with characteristic times. The diagonal elements relax with time constants which are normally called T_1. A recent publication shows a clever way to measure all of these diagonal relaxation times, in the same system as we are using.[5] Off-diagonal elements relax with time constants called T_2. Usually, only relaxation times of off-diagonal elements corresponding to magnetic-dipole-allowed transitions contribute (e.g., T_2 of the ^{13}C is the relaxation time of elements 12 and 34, while the proton T_2 is that of elements 13 and 24). However, in this experiment, during the long 2π pulse, the spin system spends part of its time in states that are linear combinations of states 1 and 4 and states 2 and 3. These correspond to magnetic-dipole-forbidden transitions. The amplitudes of the two inverted lines in Fig. 3 are therefore partially determined by the relaxation rates of the normally not observable elements 14 and 23. Since the two peaks of the doublet have different amplitudes, these two T_2's are not equal. (The 14 and 23 relaxation rates are of special interest since they can depend on the cross correla-

tion between the fluctuating local fields at the two nuclei.) Thus, we are now able to map out all the relaxation times of the complete density matrix of a system like this. We will discuss this somewhat specialized spectroscopic idea in great detail in a later paper.

As mentioned earlier, this technique could be generalized to show explicitly the behavior of spins greater than $\frac{1}{2}$ under rotation. As an example, we could consider a system where a spin 1(e.g., ^{2}H, ^{6}Li, ^{14}N) is scalar coupled to a spin $\frac{1}{2}$(e.g., ^{1}H, ^{13}C, free electron). Provided the three energy levels of the spin 1 were equally spaced, we could accomplish a rotation of the nucleus as a whole by irradiating at the single resonance frequency. The presence of the spin $\frac{1}{2}$ would split this resonance line into a doublet, and the spin-$\frac{1}{2}$ spectrum would be a triplet. By first applying a $\frac{1}{2}\pi$ pulse to all of the three spin-$\frac{1}{2}$ transitions and then selectively applying a 2π pulse to only one of the lines in the spin-1 doublet, one would see the spin-$\frac{1}{2}$ triplet *not* invert but rather remain upright. A selective π pulse should cause an inversion, however. This is because a spin 1 does not exhibit spinor character. Thus, by choosing systems carefully, one should be able to examine spins with many different numbers of levels, and thus observe the spinor or nonspinor behavior of these systems. It is, in fact, just a property of Hilbert space that systems having an even number of levels behave as spinors and systems with odd numbers of levels behave as nonspinors. For instance, in the above example had the three levels of the spin 1 not been equally spaced due to quadrupolar interaction, then only transitions between one pair of levels might be irradiated by one pulse, and this two-level system would behave as a spinor. So it is because fermions have an even number of levels and bosons have an odd number that they behave as they do. A demonstration of the spinor behavior for a ^{13}C, as we have shown, is in fact valid as a demonstration for all two-level systems, of which spin-$\frac{1}{2}$ particles are particular examples.

Although used here for the demonstration of the spinor character of a spin-$\frac{1}{2}$ nucleus, the basic interferometric spectroscopic technique demonstrated here should have much wider applicability. In general, it is applicable whenever we have a system with two or more inequivalent transitions having one quantum-mechanical level in common. An obvious application could involve indirect detection of low-magnetogyric-ratio spins, where this technique can have a signal-to-noise advantage over schemes which depend on diagonal elements of the density matrix, since the ^{1}H spectrum is totally inverted independent of the ratio of the two magnetogyric ratios (related phase effects have been observed in a different context by Ferretti and Ernst[6]). The scheme can, in addition, be applied to a variety of spin systems; for example, inequivalent transitions with a common level could be formed by interaction of two nuclear spins, by electron-nuclear spin interactions, or by magnetic dipole and electric quadrupole interactions of a particle with spin greater then $\frac{1}{2}$.[7] With only slight additional complication, one can envision experiments developed using concepts of recently published schemes for extracting geometrical and orientational information in polycrystalline solids,[8,9] which would allow one to obtain comparable information on such quantities as the electric field gradient at a nuclear site.

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