The results of a nuclear magnetic resonance experiment are presented which directly demonstrate the spinor character of a spin \( \frac{1}{2} \) nucleus, \(^{13}C\). The interferometric spectroscopic technique used and its potential applications are discussed.
Explicit Demonstration of Spinor Character for a Spin $\frac{1}{2}$ Nucleus

Via NMR Interferometry

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Abstract

The results of a nuclear magnetic resonance experiment are presented which directly demonstrate the spinor character of a spin $\frac{1}{2}$ 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 wavefunction upon a $2\pi$ rotation, and that the phase factor comes back to itself only after a $4\pi$ rotation. A particle of integral spin (a boson) does not exhibit this behavior, and its phase factor comes back to itself in a $2\pi$ 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.\(^1\) clearly showed the spinor nature of neutrons. Such experiments had been suggested and discussed earlier (1967) by Bernstein\(^2\) and by Aharonov and Susskind\(^3\). We would like to present here the results of a somewhat analogous nuclear magnetic resonance experiment which graphically shows the spinor character of a spin $\frac{1}{2}$ particle. A similar technique could easily be used to show the spinor or non-spinor character of particles with spin greater than $\frac{1}{2}$. 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 wavefunction. However, this is difficult because any measurement involves $\Psi^{\dagger}\Psi$, 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 experiment of Werner$^1$, et al., 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 $2\pi$ rotation to one of these parts. The change in the "beating" pattern then signaled the change in the phase. In our experiment we have used the NMR analogue 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. In the particular case of a single spin $\frac{1}{2}$ particle, one has two eigenstates whose amplitudes have phases $\phi_A$ and $\phi_B$. The measurement of the transverse magnetization is proportional to $\cos (\phi_A - \phi_B)$, but the absolute phases $\phi_A$ and $\phi_B$ are indeterminable. In order for one to do NMR interferometry, it was necessary to split the Zeeman spin levels by the presence of another spin, and then, by applying a selective $2\pi$ rotation to only one transition, we observed a change in phase by watching an inversion of transverse magnetization.

The chemical system we chose for the demonstration was 91% $^{13}$C-enriched sodium formate (NaCHO$_2$) dissolved in D$_2$O 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 as shown in Figure 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 \( J \mathbf{I} \cdot \mathbf{S} \), where \( J \) is the coupling constant. The inequivalent \(^{13}\text{C}\) 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 Figure 2. The experiment
itself consisted of two parts. In the first part, we took a normal \(^1\text{H}\) Fourier-
transform echo spectrum of our liquid sample. This consisted of applying a
short (2 \(\mu\)sec) \( \pi/2 \) pulse to all the \(^1\text{H}\) transitions. A short (4 \(\mu\)sec) \(^1\text{H}\) \( \pi \)
pulse was applied at a time \( \Delta T \) 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
Figure 3. (Note that in this first part we have irradiated no \(^{13}\text{C}\) transitions.)
In this \(^1\text{H}\) spectrum the symmetric doublet results from the scalar coupling
between \(^1\text{H}\) and \(^{13}\text{C}\) in the 91\% of the formate ions which are isotopically
enriched with \(^{13}\text{C}\). The splitting here has a value of \( J = 195 \) Hz. The small
peak at the center of mass of the doublet results from the \(^1\text{H}\) nuclei in the
remaining 9\% of the formate ions which contain spinless \(^{12}\text{C}\) nuclei. The large
peak on the far right results from the \(^1\text{H}\) nuclei in the small amount of HDO in
the D\(_2\)O solvent.

In the second part of the experiment we repeated the scheme of the first
part but with one important addition. After the initial \(^1\text{H}\) \( \pi/2 \) pulse we
applied a long (\( \tau = 26 \) msec) low-power, selective, \(^{13}\text{C}\) \( 2\pi \) pulse to only one
of the the \(^{13}\text{C}\) transitions (the \(^{13}\text{C}\) rotating field equaled approximately 10\%
of the separation of the \(^{13}\text{C}\) lines). As before we recorded the spin echo
and Fourier transformed it to get the bottom spectrum shown in Figure 3. We
can see that the application of the selective \( 2\pi \) 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 spinor character of the $^{13}$C nucleus. (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 Figure 1. The effect of the initial $\pi/2$ 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 ($\alpha$ and $\beta$) 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 Figure 1). Let the phases of the amplitudes of the four states be $\phi_1$, $\phi_2$, $\phi_3$, and $\phi_4$. 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 $2\pi$ pulse to only the 3-4 $^{13}$C transition. (A $2\pi$ 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, i.e., $\Delta(\phi_3 - \phi_4) = 2\pi$.) However, one wishes to know by how much $\phi_3$ and $\phi_4$ have changed individually. Since no radiation was applied to the 1-2 transition, $\phi_1$ and $\phi_2$ have not been altered, and since the size of the $^1$H doublet lines are 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 Figure 3) to indicate that both $\phi_3$ and $\phi_4$ have each changed by $\pi$, 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 $\pi$ 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. In the experiment a slight lengthening of this $^{13}$C pulse was required to fully invert the $^1$H doublet, and in addition we note that the two peaks of the doublet in the bottom spectrum of Figure 3 do not have quite the same amplitude. According to preliminary calculations, neither of these minor effects has a trivial explanation. It appears that the difference in amplitude could be due to cross-correlation relaxation terms. We plan to discuss this in a forthcoming paper.

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$^4$). 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 than $\frac{1}{2}$. 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, which would allow one to obtain comparable information on such quantities as the electronic field gradient at a nuclear site.

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References

Figure Captions

Figure 1. Energy level diagram for two weakly coupled inequivalent spin \(1/2\) particles (\(^{13}\text{C}, {\text{H}}\)) in a strong magnetic field. The \(\alpha\) and \(\beta\) represent the two eigenstates spin up and spin down of the spin \(1/2\) particle. The first Greek letter represents the state of the \(^{1}\text{H}\) spin and the second represents the state of the \(^{13}\text{C}\) spin, so the two \(^{1}\text{H}\) transitions are shown with single arrows while the two \(^{13}\text{C}\) 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 \(^{1}\text{H}\) (56.4 MHz) and \(^{13}\text{C}\) (14.2 MHz) have been drawn to scale, but the effects of the weak coupling have been greatly exaggerated for emphasis.

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

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