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Orthogonal Indirect Detection of NMR Spinor Transitions

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Abstract

The behaviour of quantum mechanical state functions under selective rotations is discussed. If a two level transition is phase-shifted with composite z-pulses, the component state function shared with a connected transition can be multiplied by i, thereby shifting the corresponding coherence into an orthogonal channel. Application to the sensitive indirect detection of NMR transitions is demonstrated.

Orthogonal Indirect Detection of NMR Spinor Transitions

If a half-integer spin is rotated through an angle 2π it does not return to its original state, but its state function is multiplied by -1. The same holds for any two-level system. Although this change of sign is not observable in an isolated particle, it can be observed if the two levels are part of a larger system. The effect has been demonstrated in neutron interferometry [1, 2], molecular-beam resonance [3] and NMR interferometry [4]. In addition it has been shown recently that this spinor rotation may be utilized for enhanced sensitivity ENDOR experiments [5]. The typical situation is depicted in Figure 1. Suppose we wish to detect transition 2-3 by means of its effect on transition 1-2 which may be an ESR or optical transition, or another NMR transition. If a coherent superposition of 1-2 is prepared, followed by a 2π rotation on 2-3, the coherence of 1-2 is inverted. If the 2π rotation of 2-3 is performed during an electron spin echo sequence applied to 1-2, the amplitude of the echo is inverted, thereby creating a 200% ENDOR-effect. In crowded ESR spectra, however, the ESR transition which is used in the ENDOR experiment often coincides with resonances of electrons which are not coupled to nuclear spins and therfore create an unmodulated background signal which makes the observation of the spinor-ENDOR effect less sensitive. We propose here to circumvent this problem by a modified experiment which does not affect the amplitude, but the phase of the 1-2 signal. By using phase-sensitive detection it is then possible to observe exclusively those electrons which are coupled to nuclear spins.

The scheme is described by Figure 2. The coherent superposition and echo of states 1 and 2 may be written

$$\Psi = c_1|1> + c_2|2> . \quad (1)$$

In Figure 2(a), showing the normal spinor-ENDOR experiment [5], the 2-3 transition is rotated by 2π before the echo, thereby multiplying the coefficient of state function $|2>$ by -1

$$c_2|2> \longrightarrow -c_2|2>, \quad (2)$$

and so inverting the 1-2 coherence.

Suppose however that we rotate transition 2-3 by an angle ϕ around its z-axis. This corresponds to a phase shift of the 2-3 transition by ϕ and may be accomplished by a composite pulse [6], off-resonance irradiation, or differential precession [2]. The effect on c_2 in the 1-2 superposition is then

$$c_2|2> \longrightarrow e^{i\phi/2} c_2|2> . \quad (3)$$

If $\phi = \pi$, as in Figure 2(c), the 1-2 coherence is shifted by -$\pi/2$ into the orthogonal, otherwise empty detection channel:

$$\Psi = c_1|1> + ic_2|2> . \quad (4)$$

Using quadrature detection, it is therefore possible to observe in one of the two channels exclusively magnetization from transitions coupled to the irradiated transitions. The effect could also be observed on the 1-3 transition, which is phase shifted by $+\phi/2$.

An NMR version of the experiment was performed as follows. The system of Figure 1 was used, consisting of the totally symmetric part of two magnetically equivalent protons, coupled by dipolar interaction. This system allows observation not only of transition 1-2, but also the irradiated transition 2-3, and thereby direct experimental comparison of the effect of the phaseshift on the two transitions. The experimental scheme of Figure 2 with variable ϕ was applied. The nonselective $(\pi/2)_y$ pulse creates 1-2 coherence. After free precession for a time τ and a nonselective π-pulse the density operator of the system is given by

$$\rho(\tau+) = e^{-i\pi S_x} e^{-iH\tau} S_x e^{iH\tau} e^{i\pi S_x} , \tag{5}$$

where the three-level system is described as a virtual spin 1. During the second half of the experiment we apply a z-pulse selectively to the 2-3 transition. At the time of the echo we therefore have

$$\rho(2\tau) = e^{-iH\tau} e^{-i\phi S_z^{(2-3)}} \rho(\tau+) e^{i\phi S_z^{(2-3)}} e^{iH\tau} , \tag{6}$$

which is evaluated as

$$\rho(2\tau) = \surd 2[S_x^{(1-2)} \cos(\phi/2) - S_y^{(1-2)} \sin(\phi/2) + \\ + S_x^{(2-3)} \cos(\phi) + S_y^{(2-3)} \sin(\phi)] , \tag{7}$$

showing the ϕ shift in 2-3 and the $-\phi/2$ shift in 1-2. The resulting spectra are shown in Figure 3 together with the amplitude of the echo signal in the y channel of the 1-2 transition, which is empty if no phase shift or 2-3 irradiation is applied.

In summary, we have shown that it is possible to change the phase of coherence by applying a composite z-pulse to a connected transition. This experimental scheme may be used for indirect detection in a variety of applications like ENDOR, indirect detection of low-γ nuclei, multiple quantum transitions [7] or any other two level system, or optically detected magnetic and optical transitions [8,9]. The technique allows indirect detection with high sensitivity since the signal which is obtained, as in the case of spinor-ENDOR, is independent of the population difference across the irradiated 2-3 transition. Prerequisites for its applicability are a relaxation time of the 1-2 transition longer than the time needed to perform the z-rotation and quadrature detection of the echo signal. Alternative methods to shift the phase of the 2-3 transition include two π pulses, phase shifted by $(\pi-\phi)/2$ or separated by a period of free precession. In the latter case the phase shift is proportional to the resonance offset of the π-pulses and the length of the free precession period. This may therefore be the evolution time of a two-dimensional experiment which would combine high sensitivity with high resolution, avoiding the power broadening of the original method [5, 10]. The technique may also be used for spectral assignment and the sign of the observed phase shift contains information about the connectivity of the transitions. Generalisation to spins (or pseudospins) $S>1/2$ is also possible [4]. While half integer spins exhibit a 4π periodicity, integer spins return to the original state after a rotation through 2π. A rotation by an angle ϕ around the z-axis multiplies the component wave functions by a phase factor $\exp(-i\phi m)$, where m represents the magnetic quantum number characterizing the particular substate.

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FIGURE - CAPTIONS

Figure 1. Energy level scheme of the totally symmetric part of a dipolar-coupled A_2 system, corresponding to a spin 1. A similar energy level scheme applies also to spinor-ENDOR.

Figure 2. Experimental NMR scheme used for orthogonal spinor detection. The non-selective or 1-2 selective ($\pi/2$ - τ - π - τ) sequence is used to create an echo at time 2τ. During the second free-precession period a composite pulse is applied selectively to the 2-3 transition, changing its phase by ϕ.

Figure 3. NMR spectra of dichloromethane as a function of the flip angle ϕ of the composite z-pulse in Figure 2(c). The full phase shift ϕ appears in the low-frequency line while the high-frequency line shows only half of the phase shift $-\phi/2$. The left hand column shows the amplitude of the 1-2 signal in one of the two quadrature channels of the phase sensitive NMR detector. The phases have been adjusted such that the amplitude is zero if no z-pulse is applied.

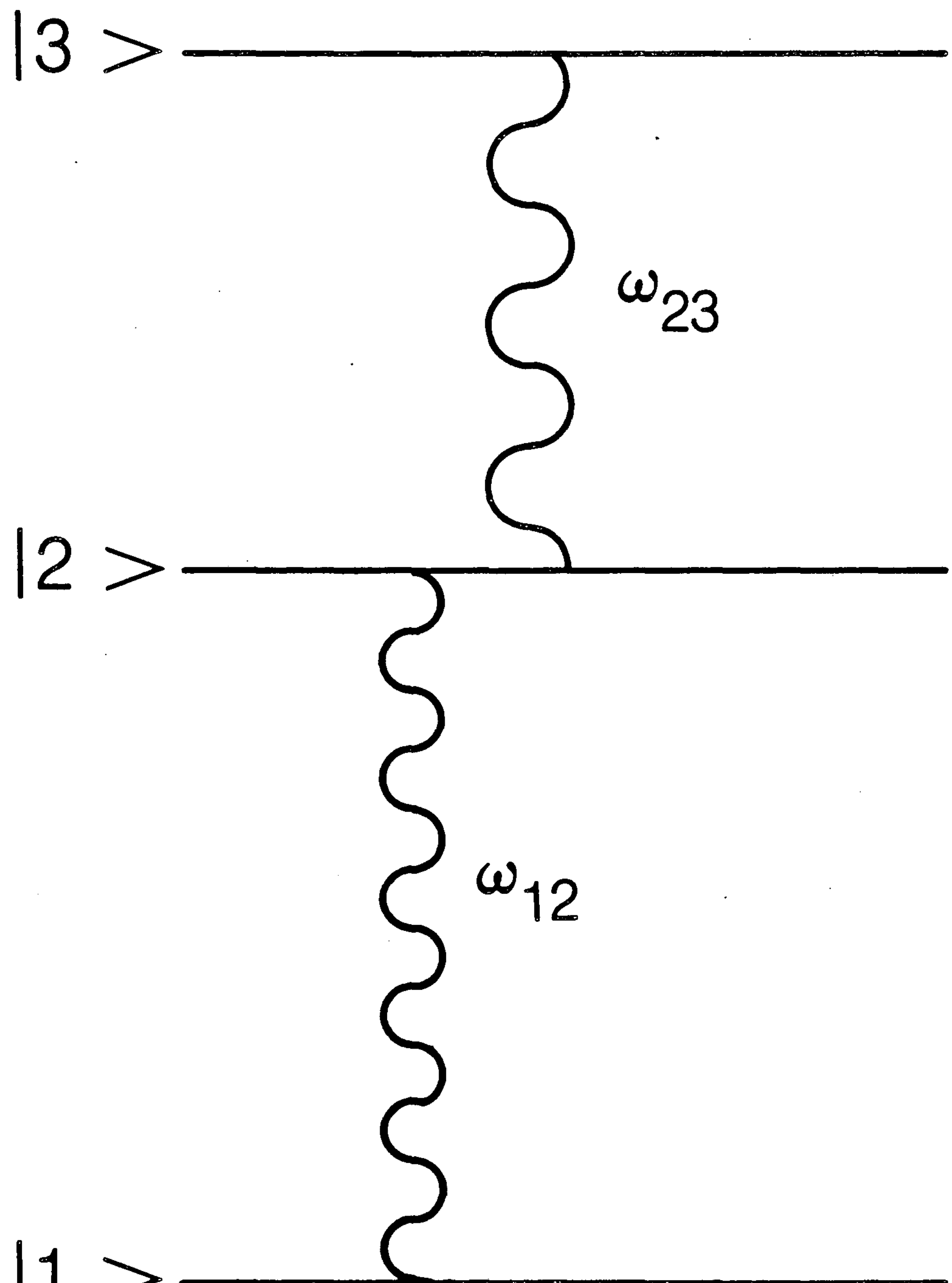

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Figure 1

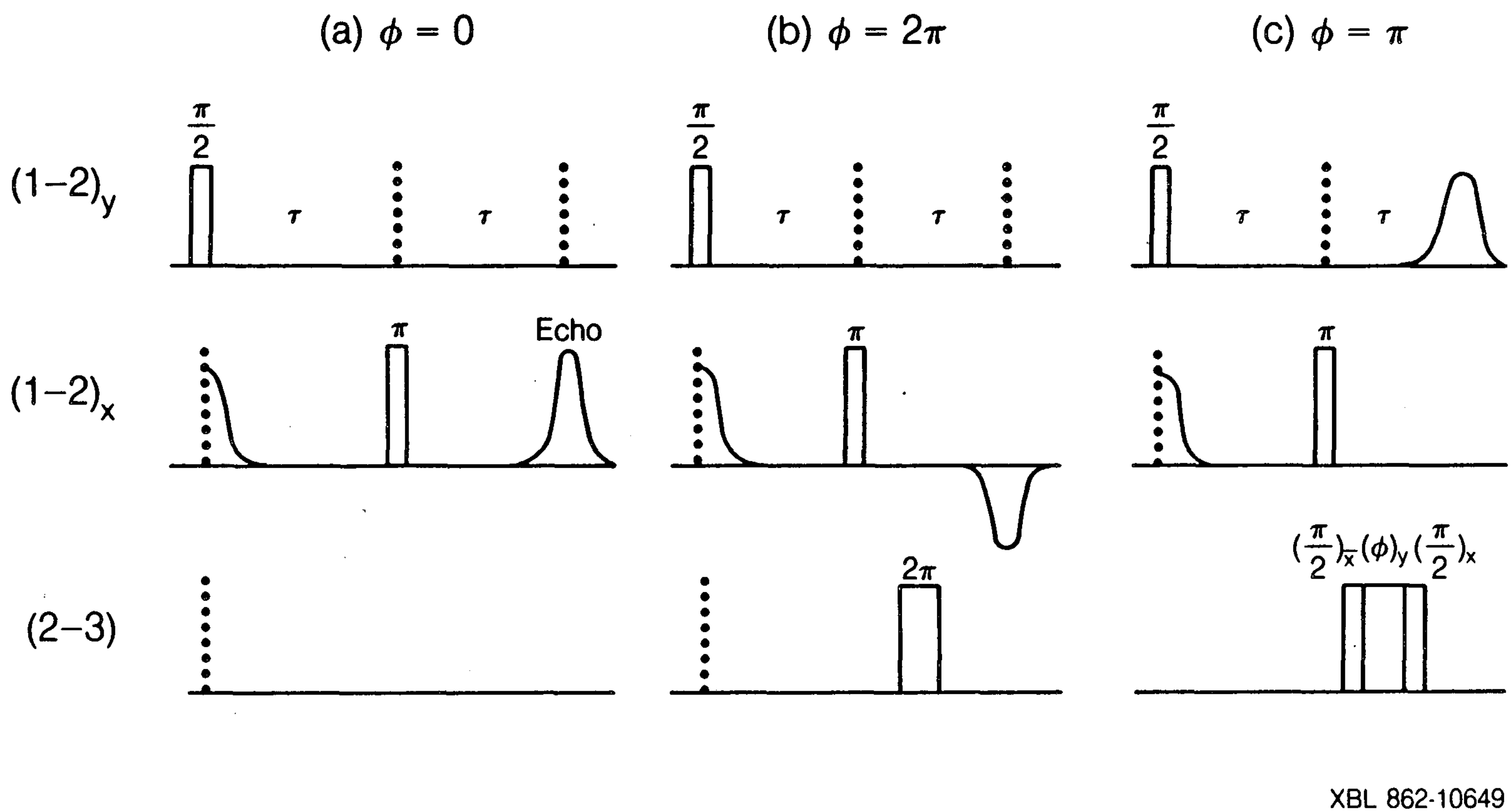
(a) $\phi = 0$
(b) $\phi = 2\pi$
(c) $\phi = \pi$
$(1-2)_y$
$(1-2)_x$
$(2-3)$
$\frac{\pi}{2}$
τ
π
Echo
2π
$(\frac{\pi}{2})_{\bar{x}} (\phi)_y (\frac{\pi}{2})_x$
XBL 862-10649

Figure 2

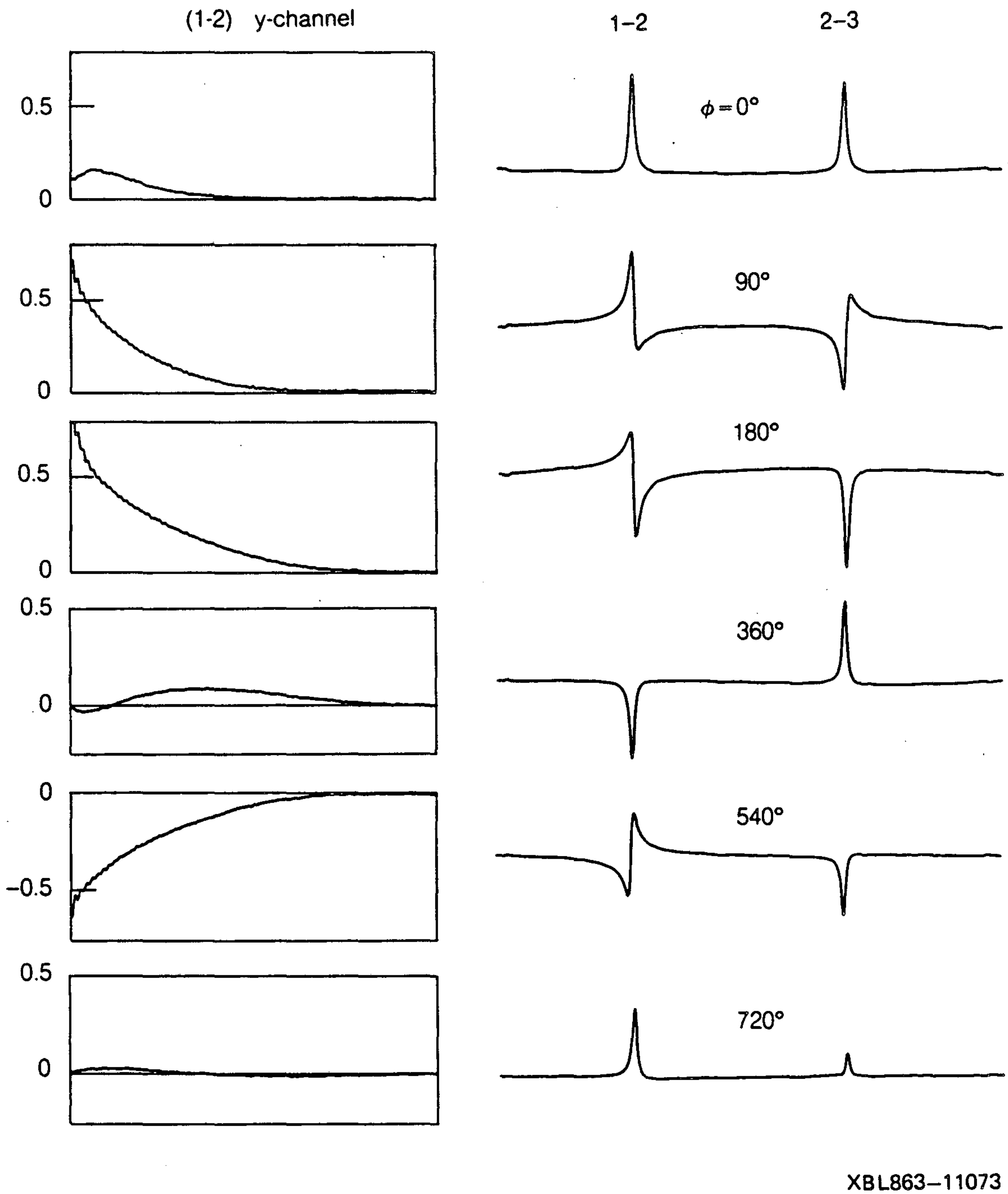

Figure 3