

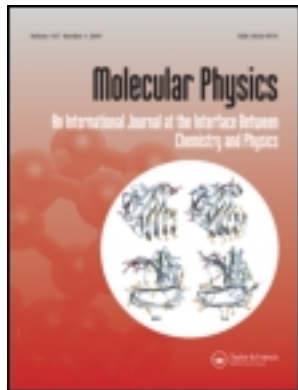
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## Berry's phase in magnetic resonance

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According to Berry, quantum states of a hamiltonian which varies adiabatically through a circuit  $C$  in parameter space may acquire geometrical phase factors  $\exp(i\gamma(C))$  in addition to the normal dynamical phase factors  $\exp((-i/\hbar) \int E(t) dt)$ . We present N.M.R. experiments in the rotating frame which bear out these predictions for simple conical circuits, and point out that they are related to familiar behaviour based on the classical Bloch equations and on Haeberlen-Waugh coherent averaging theory. Extensions to coupled spins and electric quadrupolar effects are discussed.

### 1. Introduction

A system prepared in an eigenstate of a slowly varying hamiltonian remains in an eigenstate of the instantaneous hamiltonian [1]. In 1984, Berry pointed out [2] that in a cyclic adiabatic process, that is one in which the slowly time varying hamiltonian returns to its original form via a circuit  $C$ , a quantum state may acquire a 'geometrical' phase factor  $\exp(i\gamma(C))$  in addition to the 'normal' dynamical phase factor  $\exp((-i/\hbar) \int E_m(t) dt)$ . In an elegant calculation, Berry showed that if the circuit occurs in the vicinity of a degeneracy of the hamiltonian in parameter space, then the geometrical phase is proportional to the solid angle  $\Omega$  subtended by the circuit at the degeneracy.

As an illustrative example, Berry considered spins in a magnetic field characterized by slowly varying parameters  $R$  as depicted in figure 1. The hamiltonian for this system has a degeneracy at  $R = 0$  where  $B = 0$ . For the simplest case of a cone,  $\theta$  constant, the solid angle is  $\Omega = 2\pi(1 - \cos \theta)$ . Imagine that such a conical circuit is traversed adiabatically, that is with small  $\delta$ , where  $\delta = 2\pi/T$  and  $T$  is the period of the circuit. A spin eigenstate with magnetic quantum number  $m$  should accumulate a geometrical phase  $\gamma(C) = 2\pi m(1 - \cos \theta)$  in addition to the dynamical phase  $m\gamma_I \int B(t) dt$ , where  $\gamma_I$  is the magnetogyric ratio.

Wilczek and co-workers [3] and Cina [4] have suggested that a manifestation of the geometrical phase should be observed in interference between eigenstates, for example in the evolution of a coherent superposition of states  $m$  and  $m'$ . Such a superposition corresponds to magnetization or to higher rank tensor coherences [5] and the phase changes of such coherences have been observed for states in N.M.R. undergoing non-adiabatic circuits [6]. Upon completion of an adiabatic circuit, a coherence should acquire a geometrical phase change or extra rotation,  $\phi_g = \gamma_m(C) - \gamma_{m'}(C)$ , in addition to the dynamical precession angle  $\phi_d$ . For the case of a

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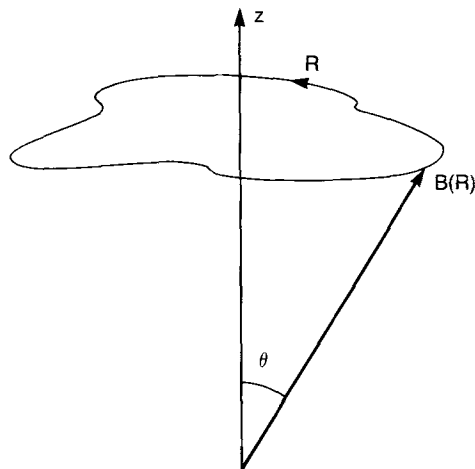


Figure 1. Berry's experiment for spins in a magnetic field. A field of magnitude  $B$  moves adiabatically through a circuit of parameters  $R$  in the laboratory. The experiments in this paper deal with simple conical circuits in the rotating frame for which  $|B|$  and  $\theta$  are constant. The considerations are similar if  $B$  is the axis in zero field of a dipolar coupled spin-1/2 pair or spin-1 with electric quadrupole coupling.

magnetic field of constant magnitude  $|B| = \omega_d/\gamma_I$  and constant angle  $\theta$  in figure 1

$$\phi_d = (m - m')\gamma_I BT = \Delta m \omega_d T, \quad (1)$$

$$\phi_g = (m - m')\Omega = 2\pi\Delta m(1 - \cos \theta). \quad (2)$$

Chiao *et al.* [7] have reported a classical optical version of such an experiment in which the plane of linearly polarized light (which corresponds to a superposition of the  $m = \pm 1$  photon states) was rotated by a geometrical phase imposed by helically wound optical fibers. Tycko [8] has recently performed a nuclear quadrupole resonance experiment in which the geometrical phase of a spin-3/2 was observed during rotation of a crystal, thereby moving the quantization axis of the electric field gradient in a cone. The geometrical phase is also related to early work on fractional quantum numbers [9] in molecules and the classical work on conical intersections by Herzberg and Longuet-Higgins [10]. Indeed, Mead and Truhlar had earlier used the concept of a geometrical phase in their discussion of conical intersections [11].

In the present paper we outline N.M.R. experiments that measure the geometrical phase acquired by a spin-1/2 in a magnetic field of constant magnitude and varying direction in the rotating frame [3]. The experiments and corresponding treatment cover the range from the adiabatic limit ( $\delta$  small), which yields Berry's geometrical phase, to the non-adiabatic regime characteristic of resonant processes. Such circuits are well known in N.M.R. experiments which involve precisely such combinations of static and rotating fields. We also relate the adiabatic behaviour to well-known coherent averaging phenomena in pulsed and iterative N.M.R. schemes which exploit geometrical scaling of resonance frequency differences and spin-spin couplings [12, 13].

2. N.M.R. experiment

The experiment might be conducted in the laboratory frame using the methods of pure N.Q.R. [14] or zero field N.M.R. [15], but we prefer the inherently greater sensitivity of high frequency N.M.R. in a high field magnet as suggested by Wilczek and co-workers [3]. To recall how the adiabatic circuits of figure 1 can be implemented in such circumstances, we refer to figure 2. An ensemble of spin-1/2 nuclei  $I$  is immersed in a large static magnetic field  $B_0$  along the  $z$  axis so that their Larmor frequency is given by  $\omega_0 = \gamma_I B_0$  where  $\gamma_I$  is the magnetogyric ratio. The spins develop an equilibrium magnetic polarization described by the reduced high temperature density operator [16]

$$\rho(0) = I_z, \tag{3}$$

where we have omitted, as usual, the unity operator and all proportionality constants.

The spins are irradiated at a frequency  $\omega_{rf}$  near  $\omega_0$  with a circularly polarized radio-frequency (rf) field of magnitude  $B_1$  such that  $\gamma_I B_1 = \omega_1$ . The evolving

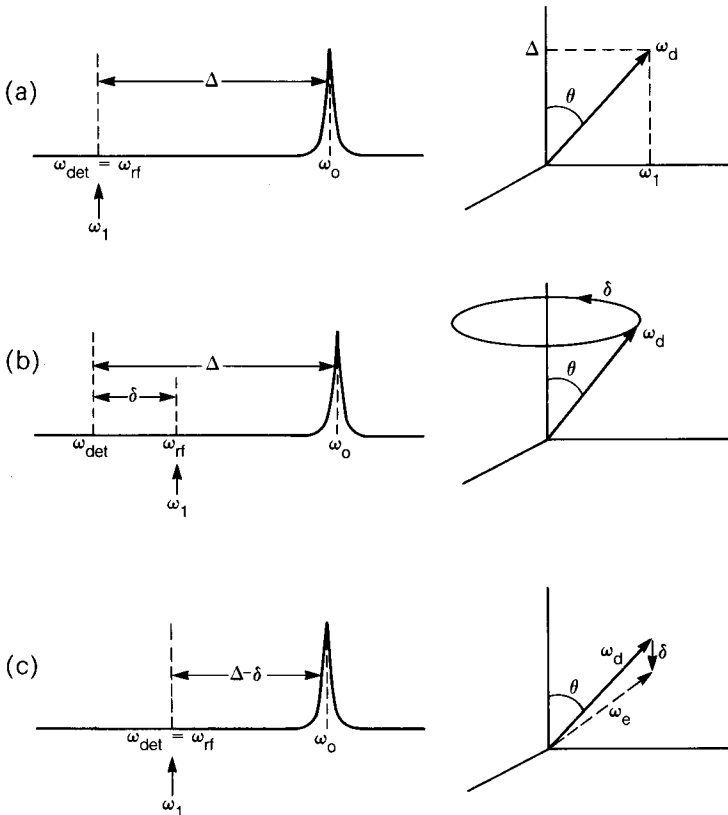


Figure 2. Rotating (detector) frame pictures of spins irradiated at frequency  $\omega_{rf}$  near resonance ( $\omega_0$ ) with a circularly polarized radio-frequency field of magnitude  $B_1 = \omega_1/\gamma_I$ . A phase sensitive detector at frequency  $\omega_{det}$  is responsible for recording the transverse magnetization. (b) shows that in the detector frame we have implemented, for high field N.M.R., a situation equivalent to the laboratory picture ( $\omega_{det} = 0$ ) of figure 1 for simple conical circuits.

magnetization is detected with a phase sensitive detector operating at frequency  $\omega_{\text{det}}$  such that

$$\omega_0 - \omega_{\text{det}} = \Delta, \quad (4)$$

$$\omega_{\text{rf}} - \omega_{\text{det}} = \delta. \quad (5)$$

We consider the case of simple conical circuits for which  $\omega_0$  and  $\omega_1$  are constant in time. In figure 2(a)  $\omega_{\text{rf}}$  has been set equal to  $\omega_{\text{det}}$  so that  $\delta = 0$ , whereas figure 2(b) reflects the general situation in which  $\delta \neq 0$ . The frequency  $\omega_{\text{det}}$  can be thought of as the reference or zero of the frequency scale. A laboratory frame experiment of the type in figure 1 with a constant field  $|B| = \omega_d/\gamma_I$  (here  $\omega_d$  denotes the dynamical frequency) moving with constant  $\theta$  at frequency  $\delta$  around  $z$  would correspond to  $\omega_{\text{det}} = 0$  in Figure 2(b).

In a frame of reference rotating with the detector [17], we term this the ‘detector frame’, the effective static field along the  $z$  axis is  $B_0 - \omega_{\text{det}}/\gamma_I$  so the effective Larmor frequency is  $\Delta$ , given by equation (4), and the effective rotation frequency of the rf field  $B_1$  is  $\delta$ , given by equation (5). The situation in figure 2(b) is thus equivalent to a magnetic field of magnitude  $B = \omega_d/\gamma_I$  moving in a cone of angle  $2\theta$  around the  $z$  axis at frequency  $\delta$ . The effective hamiltonian in the detector frame is given by

$$\tilde{\mathcal{H}}(t) = -\hbar\omega_d[\cos\theta I_z + \sin\theta(I_x \cos\delta t + I_y \sin\delta t)], \quad (6)$$

where

$$\omega_d = (\Delta^2 + \omega_1^2)^{1/2}, \quad (7)$$

$$\theta = \tan^{-1}(\omega_1/\Delta), \quad (8)$$

and  $I_\alpha$  are the spin angular momentum operators. But this is precisely the arrangement corresponding to figure 1 for the case of constant  $|B|$  and  $\theta$ . Thus figure 2(b) is the high field detector frame equivalent of conical circuits in the laboratory. To implement the general circuits of figure 1 in the rotating frame  $\omega_d$  and  $\theta$  can be varied by modulating  $\omega_0$ ,  $\omega_{\text{rf}}$  and  $\omega_1$ .

To calculate the evolution of the magnetization in the detector frame of figure 2(b) it is convenient to transform temporarily to a frame rotating at frequency  $\delta$  with respect to the detector frame [17] as shown in figure 2(c); we imagine moving the detector frequency to  $\omega_{\text{rf}}$ . In the laboratory case  $\omega_{\text{det}} = 0$ , this corresponds to a frame rotating at frequency  $\delta$  around the laboratory  $z$  axis. In this rotating frame the total effective magnetic field is static with a magnitude  $\omega_e/\gamma_I$  where the effective frequency  $\omega_e$  is given by

$$\omega_e = ((\Delta - \delta)^2 + \omega_1^2)^{1/2}. \quad (9)$$

The adiabatic limit corresponds to

$$\delta \ll \omega_d, \quad (10)$$

in which case the quantization axis remains along the direction of  $\omega_d$  to first order and the magnetization precesses at frequency  $\omega_e$  given by expanding equation (9) in  $\delta/\omega_d$  and using equations (7) and (8) to give

$$\omega_e \approx \omega_d - \delta \cos\theta. \quad (11)$$

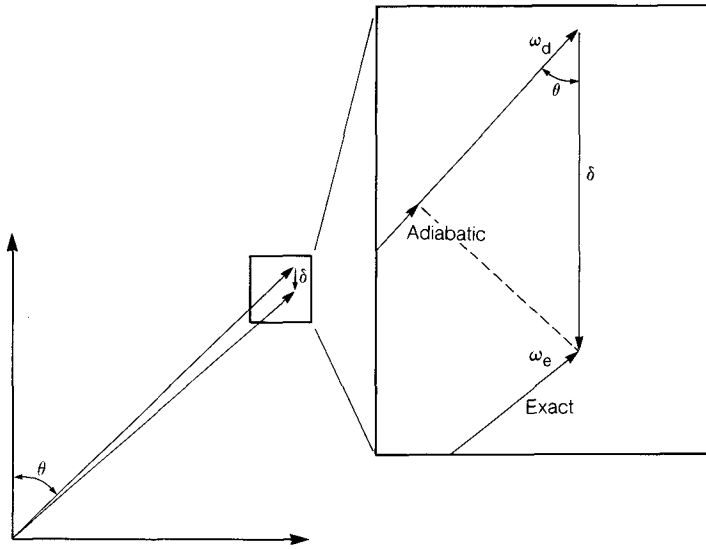


Figure 3. Expansion of figure 2(c) showing a view of the effective static fields in a frame rotating at frequency  $\delta$  with respect to the Berry situation in figures 1 and 2(b). The adiabatic limit corresponds to taking the projection of  $\delta$  onto  $\omega_d$ .

Details of the relevant geometry and the adiabatic projection of  $\delta$  onto  $\omega_d$  are shown in figure 3.

The phase  $\phi'$  accumulated after one adiabatic circuit,  $\delta T = 2\pi$ , in the rotating frame of figure 2(c) is given according to equation (11) by

$$\phi' = \omega_e T \approx \omega_d T - 2\pi \cos \theta, \quad (12)$$

which corresponds in the original detector frame of figure 2(b) to an accumulated phase  $\phi$  of

$$\phi = \phi' + 2\pi = \phi_d + \phi_g = \omega_d T + 2\pi(1 - \cos \theta), \quad (13)$$

with  $\phi_d$  and  $\phi_g$  corresponding to the dynamical and geometrical phases of equations (1) and (2) with  $\Delta m = 1$ . Thus it is possible to determine Berry's geometrical phase, corresponding to 'stroboscopic' observations (once per circuit), by measuring  $\omega_e$  and  $\delta$ .

The exact expression for the evolving density operator in the detector frame, beginning with initial condition equation (3), is given by the well-known transient solution to the Bloch equations [17] neglecting relaxation:

$$\begin{aligned} \rho(t) = & \sin \theta I_x [\cos \theta (1 - \cos \omega_e t) \cos \delta t + \sin \omega_e t \sin \delta t] \\ & + \sin \theta I_y [\cos \theta (1 - \cos \omega_e t) \sin \delta t - \sin \omega_e t \cos \delta t] \\ & + I_z [\cos^2 \theta - \sin^2 \theta \cos \omega_e t], \end{aligned} \quad (14)$$

from which the adiabatic and non-adiabatic regimes can be inferred. Experimentally a linearly polarized rf field was used, invoking the rotating wave approximation. The phase sensitive detector measures  $\langle I_x \rangle$ ,  $\langle I_y \rangle$  and, upon Fourier transformation of the signal,  $\omega_e$  can be determined. Experiments were performed on the proton

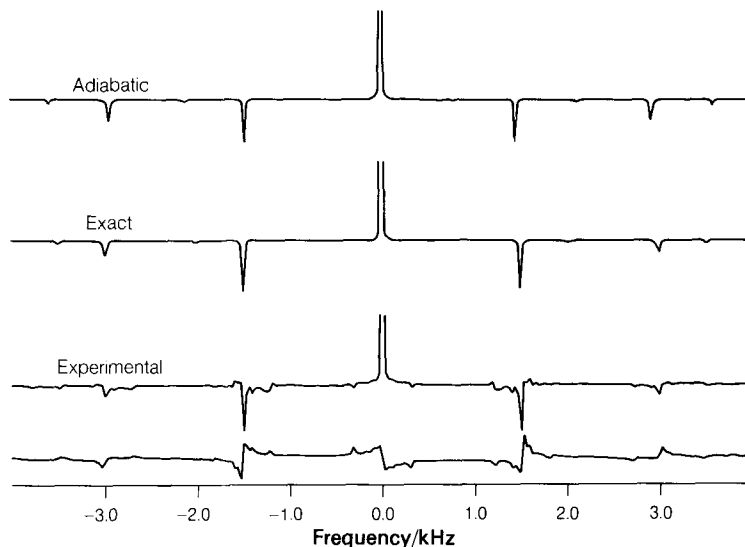


Figure 4. Fourier transform spectra of the detected transverse magnetization signal in an experiment of the type shown in figure 2(b) with  $\theta = 62.1^\circ$ ,  $\omega_d/2\pi = 1.31$  kHz,  $\delta/2\pi = -0.33$  kHz. Adiabatic and exact simulations are shown as well as the complex experimental signal. Deviations from adiabatic behaviour are visible since  $\delta \cong 0.25 \omega_d$ .

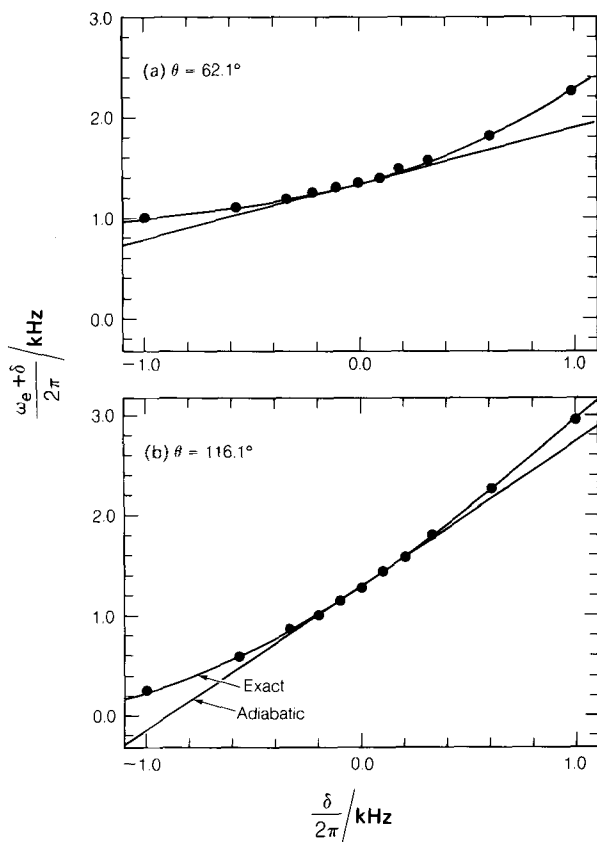


Figure 5. Experimental measurements of  $\omega_e + \delta$  versus  $\delta$  for two values of  $\theta$ . According to equation (15), in the adiabatic regime ( $\delta \ll \omega_d$ ) the data should conform to  $\omega_e + \delta \approx \omega_d + \delta(1 - \cos \theta)$ , which is shown as the straight lines. The adiabatic behaviour holds quite well for  $\delta < 0.2 \omega_d$ .

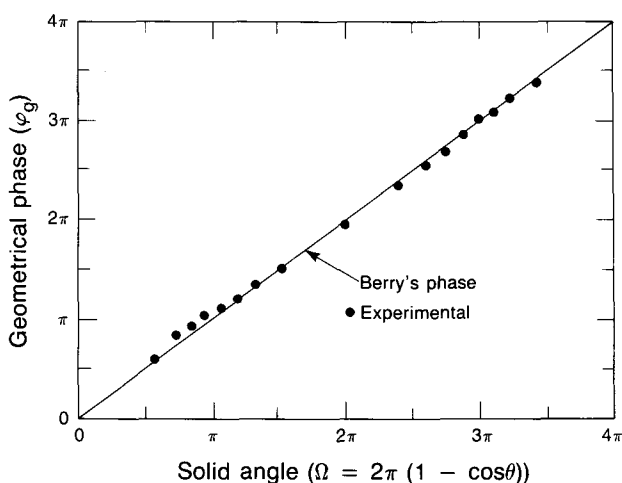


Figure 6. Plot of experimental geometrical phase (extra rotation angle of the magnetization per circuit) extracted from least squares linear fits to the adiabatic ( $\delta < 0.2\omega_d$ ) data of figure 5 versus solid angle. The straight line with slope 1 corresponds to Berry's geometrical phase.

spins of a water/acetone sample in a superconducting magnet with  $\omega_0/2\pi = 500$  MHz,  $\omega_1/2\pi = 1.16$  kHz and various values of  $\theta$  and  $\delta$ . An example of the Fourier transform of the detector signal is shown in figure 4 together with exact and adiabatic simulations for  $\theta = 62.1^\circ$ ,  $\omega_d/2\pi = 1.31$  kHz and  $\delta/2\pi = -0.33$  kHz. In figure 5 we plot  $\omega_e + \delta$ , as determined from spectra such as the one shown in figure 4, as a function of  $\delta$  for two values of  $\theta$ , using calibrated oscillators to vary  $\delta$ . According to equation (11), in the adiabatic limit this should be given by

$$\omega_e + \delta \approx \omega_d + \delta(1 - \cos \theta). \quad (15)$$

Indeed, for small values of  $\delta$  the data are linear, and the geometrical phase  $\phi_g$  is determined by the slope of the adiabatic straight line in figure 5 multiplied by  $T = 2\pi/\delta$  and is plotted versus the solid angle  $2\pi(1 - \cos \theta)$  in figure 6. The behaviour is similar to that observed in the optical rotation [7] and N.Q.R. [8] experiments.

In these experiments the geometrical phase is present as a small factor in the presence of the large dynamical phase. The effects of the dynamical phase may be removed either by stroboscopic observation commensurate with the dynamical period, or by periodically (for example once in the middle of the circuit, or just prior to repeating the circuit) reversing the direction of  $B$ . In the latter case the dynamical phase is refocused as an echo [17(b)] at the end of the circuit leaving only the pure geometrical phase.

The  $\cos \theta$  factor which derived from the projection of the small vector  $\delta$  onto the large  $\omega_d$  is familiar in N.M.R. [5]. It corresponds to the secular approximation or average hamiltonian [11, 12]. What we have done in going from the laboratory or detector frame to the rotating frame is to transform a large slowly time varying hamiltonian into a large time independent hamiltonian plus a small additional term which is treated by perturbation theory. This is explained in more detail in the next section. We have used a time independent perturbation  $\delta I_z$  as the generator of the adiabatic circuit whereas Cina [4] used a time dependent generator orthogonal to the field  $\omega_d$  at all times to express the problem as one of parallel transport [2].



The scaling of chemical shifts by  $\cos \theta$ , for example  $1/\sqrt{3}$  at the ‘magic angle’ [18], is related to the frequency differences predicted by Wilczek and co-workers [3] and observed in this work. Dipolar couplings between spins and other higher rank interactions are correspondingly scaled by higher order Legendre polynomials as predicted by the coherent averaging theory of Haeblerlen and Waugh [12]. The treatment and experiments in this paper are of course applicable to spins greater than  $1/2$  or to any multilevel quantum system which can be cast in the framework of a fictitious spin [5, 19]. Finally, we note that the effects measured in this work can be interpreted classically and are equivalent to the accumulation of phase due to Coriolis forces in accelerated frames of reference [20]. They would occur for an inclined top spinning on a slowing rotating platform. Quantum mechanical effects due to non-integral  $m$  values of the spin could be observed in adiabatic versions of the N.M.R. interference experiments [6].

### 3. General circuits and coherent averaging

In this section we discuss the relationship between the adiabatic theorem and well-known coherent averaging effects in N.M.R. Consider a ‘large’ hamiltonian  $\tilde{\mathcal{H}}(t)$  with a slow time dependence characterized by a small parameter  $\delta$ . We assume that  $\tilde{\mathcal{H}}(t)$  is cyclic and that it goes through one cycle or circuit:

$$\tilde{\mathcal{H}}(T) = \tilde{\mathcal{H}}(0). \quad (16)$$

Such cyclic hamiltonians are familiar in pulsed N.M.R. When the time dependence is rapid then coherent averaging theory [12] is directly applicable, but here we are interested in adiabatic processes for which a change of picture may be appropriate. An eigenstate  $|0\rangle$  of  $\tilde{\mathcal{H}}(0)$  will evolve by the end of the circuit to

$$|T\rangle = \tilde{U}(T)|0\rangle, \quad (17)$$

where the circuit propagator  $\tilde{U}(T)$  is given by

$$\tilde{U}(T) = \mathcal{T} \exp(-i/\hbar) \int_0^T \tilde{\mathcal{H}}(t) dt \quad (18)$$

and  $\mathcal{T}$  is a time ordering operator [21]. If the change is adiabatic then

$$|T\rangle = \exp\{i(\gamma_d + \gamma(C))\} |0\rangle \quad (19)$$

where  $\gamma_d$  and  $\gamma(C)$  are the dynamical and geometrical phases [2] respectively. Taking only the dynamical phase  $\gamma_d$  is tantamount to assuming that the eigenvalues of the average hamiltonian  $\tilde{\mathcal{H}}$  [12] are the same as the average eigenvalues of  $\tilde{\mathcal{H}}(t)$ , namely  $\langle 0|\tilde{\mathcal{H}}|0\rangle = \langle t|\tilde{\mathcal{H}}(t)|t\rangle$ . The circuit propagator  $\tilde{U}(T)$  in equation (18) can be factored [22]

$$\tilde{U}(T) = R_\delta^\dagger(T)U(T), \quad (20)$$

where

$$R_\delta(t) = \mathcal{T} \exp(-i/\hbar) \int_0^t \mathcal{H}_\delta(t') dt', \quad (21)$$

$$U(T) = \mathcal{T} \exp(-i/\hbar) \int_0^T (\mathcal{H}(t) + \mathcal{H}_\delta(t)) dt, \quad (22)$$

and

$$\mathcal{H}(t) = R_\delta(t)\tilde{\mathcal{H}}(t)R_\delta^\dagger(t). \tag{23}$$

The hamiltonian  $\mathcal{H}_\delta(t)$  in equation (21) can be regarded as the generator of an interaction picture [1] in which the effective hamiltonian is  $\mathcal{H}(t) + \mathcal{H}_\delta(t)$  and the effective circuit propagator is  $U(T)$  in equation (22). In such an interaction picture

$$R_\delta(T)|T\rangle = U(T)|0\rangle. \tag{24}$$

Now, the objective is to find a 'small'  $\mathcal{H}_\delta(t)$  and thus an  $R_\delta(t)$  such that  $\mathcal{H}(t)$  in equation (23) is time independent or commutes with itself at different times. If  $\mathcal{H}(t)$  is time independent (this is easily generalized to a commuting hamiltonian), namely

$$\mathcal{H}(t) = \mathcal{H}_d \tag{25}$$

where  $\mathcal{H}_d$  is a large 'local' hamiltonian giving rise to normal dynamical evolution of the eigenstates with a characteristic frequency

$$\omega_d = 2\pi/t_d, \tag{26}$$

then equation (22) can be written

$$U(T) = \mathcal{T} \exp(-i/\hbar \int_0^T (\mathcal{H}_d + \mathcal{H}_\delta(t) dt). \tag{27}$$

Of course the choices of  $R_\delta$  and  $\mathcal{H}_d$  are not unique and it is the different pictures and local hamiltonians which give rise to the choice of dynamical phases and fractional quantum numbers. Now, since  $\mathcal{H}_\delta$  is small,  $\|\mathcal{H}_\delta\| \ll \|\mathcal{H}_d\|$ , we use coherent averaging theory [12], retaining only the zero order average hamiltonian  $\bar{\mathcal{H}}_\delta$  in the Magnus expansion [23], that is the part of  $\mathcal{H}_\delta(t)$  which is secular or commutes with  $\mathcal{H}_d$ . This is given by

$$\bar{\mathcal{H}}_\delta = \frac{1}{t_d} \int_0^T \int_0^{t_d} \exp((-i/\hbar)t\mathcal{H}_d)\mathcal{H}_\delta(t') \exp((i/\hbar)t\mathcal{H}_d) dt dt'. \tag{28}$$

$\bar{\mathcal{H}}_\delta$  is a generalization of the vector projection proportional to  $-\delta \cos \theta$  of the previous section where the hamiltonians  $\mathcal{H}_d$  and  $\mathcal{H}_\delta$  correspond to magnetic field vectors. Corrections to  $\bar{\mathcal{H}}_\delta$  which correspond to non-adiabatic deviations are provided by the correction terms  $\bar{\mathcal{H}}_\delta(k)$  [12, 23].

The adiabatic circuit propagator  $\tilde{U}(T)$  in equation (20) is thus given by combining equations (20), (21), (27) and (28):

$$\tilde{U}(T) = R_\delta^\dagger(T)\bar{R}_\delta(T) \exp((-i/\hbar)T\mathcal{H}_d), \tag{29}$$

where

$$\bar{R}_\delta(T) = \exp((-i/\hbar)T\bar{\mathcal{H}}_\delta). \tag{30}$$

The dynamical and geometrical phase factors in equation (19) can now be recognized as

$$\exp((-i/\hbar)T\mathcal{H}_d)|0\rangle = \exp(i\gamma_d)|0\rangle, \tag{31}$$

$$R_\delta^\dagger(T)\bar{R}_\delta(T)|0\rangle = \exp(i\gamma(C))|0\rangle. \tag{32}$$

Parallel transport corresponds to a choice of  $\mathcal{H}_\delta(t)$  orthogonal to  $\mathcal{H}_d$  so that  $\bar{\mathcal{H}}_\delta = 0$  and  $\bar{R}_\delta(T) = 1$ . The geometrical phase is then given entirely by  $R_\delta^\dagger(T)$  in equation (32) acting on  $|0\rangle$ . This relates the adiabatic behaviour to the general case of parallel transported circuits due to Aharonov and Anandan [24].

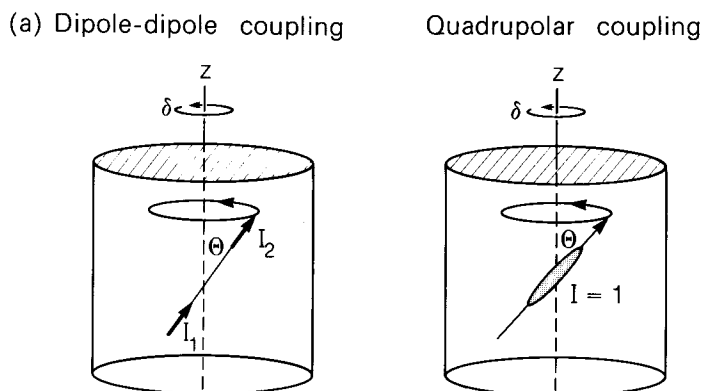


Figure 7. Adiabatic rotation of a sample can generate a geometrical phase for (a) dipole-coupled spins or (b) spins  $I = 1$  subject to electric quadrupole coupling.

Equation (29) makes clear the contributions to the phase factor in a circuit. The dynamical phase of equation (31) derives from the static hamiltonian  $\mathcal{H}_d$  which corresponds in the magnetic field case to a static magnetic field or  $\omega_d$  in figure 2. Any mystery in the geometrical phase is a consequence of the seductive intuition that in the transformed picture, or local coordinates, the evolution, boundary conditions and quantization should be the same as if  $\mathcal{H}_d$  were originally static. The terms  $\bar{R}_\delta(T)$  and  $R_\delta^\dagger(T)$  in equation (32) give rise respectively in the magnetic field case to the  $-2\pi \cos \theta$  term of equation (12) and the  $2\pi$  term of equation (13). The case  $\theta = 0$  in § 2 corresponds here to  $R_\delta^\dagger(T)\bar{R}_\delta(T) = 1$  which can be achieved for example (not necessarily) if

$$[\mathcal{H}_d, \mathcal{H}_\delta] = 0. \quad (33)$$

In this case equation (27) can be factored exactly and the adiabatic approximation is not necessary. The magnetic case  $\theta = \pi/2$  corresponds to  $\bar{R}_\delta(T) = 1$  in which case  $R_\delta^\dagger(T)$  is responsible for the geometrical phase and gives rise to the familiar spinor sign changes under  $2\pi$  rotations [2, 6]. Such considerations also apply to the case of molecules with coupled rotors [9].

Interesting versions of the geometrical phase occur for coupled spins or for spins greater than  $\frac{1}{2}$ . Suppose two spins 1 and 2 are coupled by magnetic dipolar interactions in the absence of a static external field. In the principal axis system ( $x'$ ,  $y'$ ,  $z'$ ) of the dipolar tensor, the coupling hamiltonian is

$$\mathcal{H}_d = \frac{2}{3}\hbar\omega_d[(3I_{1z'}I_{2z'} - I_1 \cdot I_2) + \eta(I_{1x'}I_{2x'} - I_{1y'}I_{2y'})]. \quad (34)$$

Similarly, for a spin  $I = 1$  in the principal axis system of the electric field gradient tensor

$$\mathcal{H}_d = \frac{1}{3}\hbar\omega_d[(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)]. \quad (35)$$

In the case of axial symmetry ( $\eta = 0$ ), a component of magnetization perpendicular to the symmetry ( $z'$ ) axis oscillates linearly at the dynamical frequency  $\omega_d$  [15] so the total magnetization evolves in a plane, the polarization plane. A superposition of the  $m = \pm 1$  eigenstates, corresponding to double quantum coherence, would remain constant in time [5]. Imagine that the symmetry axis ( $z'$ ) is now rotated adiabatically in a cone at frequency  $\delta$ , for example by physically rotating a solid

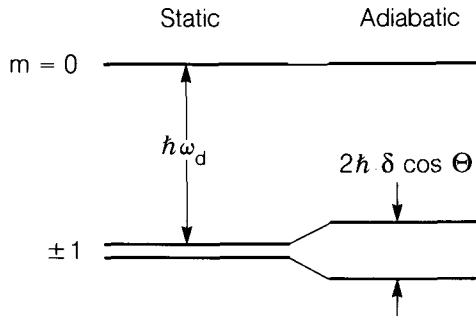


Figure 8. The degeneracy of the  $m = \pm 1$  levels is lifted by sample rotation.

sample around an axis tilted at an angle  $\theta$  with respect to  $z'$ , as shown in figure 7. The evolution of the spin system can then be described in a frame rotating at  $\delta$  with the crystal or spin pair by a time independent hamiltonian (equation (34) or (35)) with an additional term  $\hbar\delta[\cos\theta(I_{1z'} + I_{2z'}) + \sin\theta(I_{1x'} + I_{2x'})]$  or  $\hbar\delta[\cos\theta I_{z'} + \sin\theta I_{x'}]$ . The term  $\mathcal{H}'_\delta$  of equation (28) is given by the projection of this term onto the symmetry axis, i.e.  $\hbar\delta\cos\theta(I_{1z'} + I_{2z'})$  for the dipolar case, and  $\hbar\delta\cos\theta I_{z'}$  for the quadrupolar case (see figure 8), again violating the intuitive notion that if we 'run around' with the pair of spins then the local dynamics should look the same as they would for a static pair in the laboratory. This is identical to the consideration of §2 and so the phase at the end of the circuit is given precisely by equation (13). Thus the polarization plane of the magnetization is now rotated by the geometrical phase and the orientation of the  $\pm 1$  superposition by twice the geometrical phase when the crystal is rotated adiabatically. This is analogous to the rotation of the optical polarization plane in the experiments of Chiao and co-workers [7] and will give rise to effective Zeeman splittings in the N.M.R. experiments or powder patterns in the zero field spectra [15]. Similar considerations hold for a spin-1 with an axially symmetric electric quadrupole coupling or for spin-3/2 [8]. If the coupling for spin-1 is not axially symmetric  $\eta \neq 0$ , and  $\delta \ll \eta\omega_d$ , then we find  $\mathcal{H}'_\delta = 0$  and the geometrical phase is  $2\pi m$ . This corresponds to the situation in which the effective rotation in parameter space occurs in a plane containing the degeneracy.

If the dipolar coupled spin pair described by equation (34) is in the presence of a large magnetic field it is known that the dynamical phase due to the secular dipolar coupling  $\mathcal{H}'_d$  can be eliminated by rotating the sample adiabatically in circuits around an axis inclined at the magic angle ( $\theta_m = \cos^{-1}(1/\sqrt{3})$ ) relative to the magnetic field [18]. Dynamical phases due to quadrupolar couplings and anisotropic chemical shifts are similarly removed. Since  $\mathcal{H}'_d$  commutes with itself at different times, the geometrical phase is also zero so that only isotropic Zeeman couplings or chemical shifts remain. Instead of moving the sample relative to the field, similar effects can be achieved by rotating the field in a cone of angle  $2\theta_m$  with the sample fixed [25]. In this latter case, however, there will be frequency shifts due to the geometrical phase factors given by equation (2). These will add to the isotropic shifts of the magic angle spectra.

Finally, by combining dipolar or quadrupolar couplings together with magnetic fields, for example spin  $I = 1$  with

$$\mathcal{H}_d = \frac{1}{3}\hbar\omega_d[(3I_z^2 - I^2) + 3I_{z'}], \tag{36}$$

where, again, the  $z'$  axis is moved in a circuit, the non-abelian case of Wilczek and Zee [3] can be investigated [26]. In fact, such a possibility also exists for the  $\pm\frac{1}{2}$  manifold of the spin  $-\frac{3}{2}$  N.Q.R. [8], but, for the case of conical circuits, could be treated by Tycko as adiabatic Berry phases on diagonal states.

#### 4. Conclusions

When two systems are coupled together, the eigenstates of the total hamiltonian do not in general exhibit statistical independence in the separate systems. That is, the probability amplitudes are not the product of probability amplitudes for each system. Often the states may be exactly, or approximately, separated into states which are functions of variables involving both systems. It is often the case that one or more of the degrees of freedom describing one of the systems goes through a sequence of values, for example, an angle. Although the overall wave function must be single valued when the hamiltonian repeats itself, there is no reason for the individual amplitudes which make up the products above to be single valued. This partial multivaluedness was pointed out and analysed in the early treatments of the coupling of internal rotations to overall rotations [9] showing that fractional quantum numbers were a natural consequence of multivaluedness.

An extreme example of strong coupling is the Born–Oppenheimer approximation. In the electronic wave functions, the nuclear coordinates are parameters. An overall wave function is the product of the electronic wave function times the nuclear wave function. Again there is no *a priori* reason for the electronic wave function and the nuclear wave function to be separately single valued in the nuclear coordinates. Herzberg and Longuet-Higgins [10] pointed out that near a conical intersection of a triatomic molecule the electronic wave function would be multivalued. Thus fractional quantum numbers could be expected in certain vibration states of triatomic species such as  $(\text{Na})_3$ , and indeed appear to have been observed [27]. In the later 1970s and early 1980s, Mead and Truhlar [11] pointed out that the partial multivaluedness could be removed by multiplying both nuclear and electronic amplitudes by a phase which countered the multivalued real amplitudes. Thus, in the nuclear Schrödinger equation one restored single-valuedness at the cost of introducing a ‘vector potential’. Mead and Truhlar dubbed this construct the molecular ‘Bohm–Aharonov’ [28] effect and proceeded to relate the form of the vector potential to certain circulation integrals over the nuclear potential energies. A related approach was discussed recently by Wilczek and co-workers [3].

The papers of Berry and Simon [2] are in essence a complete analysis of the time dependent adiabatic theorem. When the adiabatic eigenstates are complex and single valued, the diagonal phase factors, usually discarded [1], must be retained. Not surprisingly, the amplitudes may be multivalued. Also not surprisingly, the phase is identical to that derived by Mead and Truhlar. In fact, the additional phase required to restore the single valuedness of the eigenstates is the geometrical phase of Berry. Thus there may be observable effects in the dynamics. In particular, Berry suggested a series of experiments including one involving the polarization of light and the one investigated in the present paper involving adiabatic rotation of the spatial degrees of freedom of a magnetic system.

Although Berry used quantum mechanical arguments to obtain his phase, it is clear that the dynamical manifestation of this phase is classical in nature since the magnetization or the polarization of any fictitious spin satisfies the Bloch equations

[17], and, in fact, Cina [4] obtained the Berry phase from classical arguments. Thus for spins and other systems which undergo rotation, Berry's effect is entirely analogous to evolution under Coriolis forces in an accelerating non-planar reference frame [20]. Since the polarization of light may be described in terms of the Stokes parameters, the experiments of Chiao and co-workers [7] is another manifestation of this idea.

In this paper we have related the effects for spin-1/2 to well-known behaviour in N.M.R. involving continuous irradiation of spins near resonance. The experiments were carried out for conical circuits over a range of parameters which include both adiabatic and non-adiabatic effects. In addition we have invoked the known solutions to the Bloch equations for the evolution of magnetization with arbitrary values of the parameters, and hence were able to compare the exact results both with the experiment and with the general adiabatic theory. Finally, the relationship between geometrical phase in general adiabatic circuits and the average hamiltonian in an interaction picture was outlined. Such an approach to adiabatic N.M.R. experiments is useful because it lends to the processes a deeply geometrical view [2] in the spirit of the topological arguments of Berry and Simon.

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