NMR Addendum

Experiment NA-QT

Theory

In the Pauli representation the spin-1/2 angular momentum operator $\mathbf{s}$ is represented in a cartesian basis

$$\mathbf{s} = \frac{\hbar}{2}\,\boldsymbol{\sigma} = \frac{\hbar}{2}\left(\sigma_x\,\hat{\mathbf{x}} + \sigma_y\,\hat{\mathbf{y}} + \sigma_z\,\hat{\mathbf{z}}\right) \tag{1}$$

where the two-by-two Pauli spin matrices are given explicitly by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{2}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{3}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{4}$$

The spin operator $\boldsymbol{\sigma}$ is thus the spin angular momentum operator in units of $\hbar/2$.

The eigenstates of s_z having eigenvalues $\pm\hbar/2$ (eigenstates of σ_z having eigenvalues ± 1) are

$$\psi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \psi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{5}$$

An arbitrary spin wavefunction ψ is a superposition of these basis states $\psi = C_+\psi_+ + C_-\psi_-$

$$\begin{aligned} \psi &= C_+\begin{pmatrix} 1 \\ 0 \end{pmatrix} + C_-\begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ &= \begin{pmatrix} C_+ \\ C_- \end{pmatrix} \end{aligned} \tag{6}$$

where C_+ and C_- are the complex amplitudes "c-numbers" whose squared magnitude give the probability for observing the spin in the spin-up (+) or spin-down (-) states. Note that

$$C_+^* C_+ + C_-^* C_- = 1 \tag{7}$$

specifies the wavefunction normalization.

It will be useful to have explicit formulas for the expectation values of the spin components for the wavefunction $\psi = C_+\psi_+ + C_-\psi_-$, i.e., Eq. 6.

$$\begin{aligned} \langle\sigma_z\rangle &= \psi^*\sigma_z\psi = && C_+^* C_+ - C_-^* C_- \\ \langle\sigma_x\rangle &= \psi^*\sigma_x\psi = && C_+^* C_- + C_-^* C_+ \\ \langle\sigma_y\rangle &= \psi^*\sigma_y\psi = && -i(C_+^* C_- - C_-^* C_+) \end{aligned} \tag{8}$$

where $\psi^* = C_+^*\psi_+^* + C_-^*\psi_-^*$ is the row vector

$$\psi^* = \begin{pmatrix} C_+^* & C_-^* \end{pmatrix} \tag{9}$$

and ordinary vector and matrix multiplication apply.

The spin manifests itself not only by its association with angular momentum but also through its association with the particle's magnetic dipole moment $\boldsymbol{\mu}$ which is aligned with the angular momentum with a proportionality constant γ called the gyromagnetic ratio

$$\boldsymbol{\mu} = \gamma\,\mathbf{s} = \frac{1}{2}\gamma\hbar\,\boldsymbol{\sigma} \tag{10}$$

In a constant magnetic field $\mathbf{H}_0$, the Hamiltonian $\mathcal{H}_0$ is

$$\mathcal{H}_0 = -\boldsymbol{\mu}\cdot\mathbf{H}_0 \tag{11}$$

Defining the z-axis along $\mathbf{H}_0$,

$$\mathbf{H}_0 = H_0\ \hat{\mathbf{z}} \tag{12}$$

gives

$$\mathcal{H}_0 = -H_0\boldsymbol{\mu}\cdot\hat{\mathbf{z}} = -\frac{1}{2}\hbar\gamma H_0\sigma_z \tag{13}$$

or with $\omega_0 = \gamma H_0$ (the Larmor frequency)

$$\begin{aligned}\mathcal{H}_0 &= -\frac{\hbar\omega_0}{2}\sigma_z \\ \mathcal{H}_0 &= -\frac{\hbar\omega_0}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\end{aligned} \tag{14}$$

The eigenstates of s_z — ψ_+ and ψ_- — are thus also eigenstates of $\mathcal{H}_0$ with eigenenergies (Zeeman levels)

$$E_\pm = \mp\frac{1}{2}\hbar\omega_0 \tag{15}$$

Under the influence of the constant field, the time evolution of the wave function ψ, i.e., of the c-numbers C_+ and C_-, is governed by the Schroedinger equation

$$i\hbar\frac{d\psi}{dt} = \mathcal{H}_0\psi \tag{16}$$

or

$$i\hbar\begin{pmatrix}\dot{C}_+\\ \dot{C}_-\end{pmatrix} = -\frac{\hbar\omega_0}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\begin{pmatrix}C_+\\ C_-\end{pmatrix} \tag{17}$$

having the solution

$$\psi(t) = \begin{pmatrix}C_+(0)e^{i\omega_0 t/2}\\ C_-(0)e^{-i\omega_0 t/2}\end{pmatrix} \tag{18}$$

showing that the upper and lower components of the wavefunction acquire phase factors $e^{-iE_\pm t/\hbar}$.

Using Eqs. 8 to evaluate the spin components of the time dependent wavefunction (Eq. 18) gives:

$$\begin{aligned}\langle\sigma_z\rangle &= C_+^*(0)C_+(0) - C_-^*(0)C_-(0) \quad (19)\\ \langle\sigma_x\rangle &= C_+^*(0)C_-(0)e^{-i\omega_0 t}\\ &\quad +C_-^*(0)C_+(0)e^{i\omega_0 t}\\ \langle\sigma_y\rangle &= -iC_+^*(0)C_-(0)e^{-i\omega_0 t}\\ &\quad +iC_-^*(0)C_+(0)e^{i\omega_0 t}\end{aligned}$$

The first equation shows that the z-component is time independent and taking the time derivatives of each of the other two gives

$$\frac{d\langle\sigma_x\rangle}{dt} = \omega_0\langle\sigma_y\rangle \tag{20}$$

$$\frac{d\langle\sigma_y\rangle}{dt} = -\omega_0\langle\sigma_x\rangle \tag{21}$$

These last two equations can be used to show that the magnitude of the spin component in the xy-plane is also constant and rotates in the clockwise direction at an angular frequency ω_0. This is the Larmor precession of the spin vector $\boldsymbol{\sigma}$.

Note that the constant-field Hamiltonian $\mathcal{H}_0$ does not cause transitions between the eigenstates (they are stationary states). But a weak oscillating magnetic field $\mathbf{H}_1$ superimposed on the static field $\mathbf{H}_0$ can cause transitions. In an NMR spectrometer $\mathbf{H}_1$ is produced by an alternating voltage (at an angular frequency near the Larmor frequency) applied to a solenoidal coil oriented with its axis perpendicular to the constant field $\mathbf{H}_0$. This creates a linearly polarized magnetic field which oscillates back and forth along the coil axis and can be considered as the sum of two counter-rotating circularly polarized components each with half the amplitude of the total oscillating field.

Formally, with the x-axis defined along the coil axis and $\mathbf{H}_1$ taken as varying as $\cos\omega t$

with an amplitude $2H_1$

$$\begin{aligned} \mathbf{H}_1 &= 2H_1 \cos\omega t\ \hat{\mathbf{x}} \\ &= H_1 \left[(\cos\omega t\ \hat{\mathbf{x}} - \sin\omega t\ \hat{\mathbf{y}}) + \right. \\ &\qquad \left. (\cos\omega t\ \hat{\mathbf{x}} + \sin\omega t\ \hat{\mathbf{y}}) \right] \end{aligned} \tag{22}$$

Split up this way, the first component rotates in the same direction as the Larmor precession and the second in the opposite direction.

We next form the Hamiltonian including both the static and oscillating components $\mathcal{H} = -\boldsymbol{\mu}\cdot(\mathbf{H}_0 + \mathbf{H}_1)$. When this is put in operator form using $\boldsymbol{\mu} = \gamma\hbar/2\ \boldsymbol{\sigma}$, the explicit forms for $\mathbf{H}_0$ (Eq. 12) and $\mathbf{H}_1$ (Eq. 22), and the Pauli matrices for $\boldsymbol{\sigma}$, the Hamiltonian becomes

$$\begin{aligned} \mathcal{H} &= -\frac{\hbar\omega_0}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + \\ &\quad -\frac{\hbar\omega_1}{2}\begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix} + \\ &\quad -\frac{\hbar\omega_1}{2}\begin{pmatrix} 0 & e^{-i\omega t} \\ e^{+i\omega t} & 0 \end{pmatrix} \end{aligned} \tag{23}$$

where $\omega_1 = \gamma H_1$. The first matrix arises from the $\mathbf{H}_0$ field, the middle matrix arises from the $\mathbf{H}_1$ component rotating in the direction of the Larmor precession, and the the last matrix from the counter rotating component.

The time dependence of the wavefunction $\psi(t)$ is again obtained from the Schroedinger equation $i\hbar\ d\psi/dt = \mathcal{H}\psi$. The math will simplify somewhat by assuming a solution of the form

$$\psi(t) = \begin{pmatrix} c_+(t)e^{i\omega t/2} \\ c_-(t)e^{-i\omega t/2} \end{pmatrix} \tag{24}$$

The explicit phase factors represent a frame transformation rotating about the z-axis (at the angular frequency of the $\mathbf{H}_1$ field) in the direction of the Larmor precession.

Differentiating $\psi(t)$ and performing the matrix multiplications involved in the Schroedinger equation leads to

$$\begin{aligned} i\hbar\begin{pmatrix} \dot{c}_+ \\ \dot{c}_- \end{pmatrix} &= \frac{\hbar}{2}\left[(\omega-\omega_0)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\right. \\ -\omega_1\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} &- \left.\omega_1\begin{pmatrix} 0 & e^{-i2\omega t} \\ e^{i2\omega t} & 0 \end{pmatrix}\right]\begin{pmatrix} c_+ \\ c_- \end{pmatrix} \end{aligned} \tag{25}$$

The first matrix arises from the $\mathbf{H}_0$ field and the frame transfomation. It appears as if arising from an effective static field along the z-axis of field strength $H_0 - \omega/\gamma$.

The frame transformation also eliminates the time dependence of the second matrix arising from the properly rotating $\mathbf{H}_1$ component and makes it appear as a constant field (of magnitude H_1) in the x-direction. The last matrix, arising from the counter-rotating component rotates at 2ω in the rotating frame and has little effect. The rotating-wave approximation amounts to dropping this last part of the Hamiltonian.

Using the rotating-wave approximation, c_+ and c_- — the c-numbers in the rotating-frame — appear to obey a Schroedinger equation for a constant field having an x and z component.

$$\mathbf{H}' = \left(H_0 - \frac{\omega}{\gamma}\right)\hat{\mathbf{z}} + H_1\hat{\mathbf{x}} \tag{26}$$

and, in fact, on resonance ($\omega = \omega_0$) $\mathbf{H}'$ is entirely along the x-axis. Tidying up Eq. 25 gives

$$i\hbar\begin{pmatrix} \dot{c}_+ \\ \dot{c}_- \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} (\omega-\omega_0) & -\omega_1 \\ -\omega_1 & -(\omega-\omega_0) \end{pmatrix}\begin{pmatrix} c_+ \\ c_- \end{pmatrix}$$

Thus solutions to the following first order differential equations are needed

$$\begin{aligned} \dot{c}_+ &= -\frac{i}{2}\left[(\omega-\omega_0)c_+ - \omega_1 c_-\right] \\ \dot{c}_- &= \frac{i}{2}\left[\omega_1 c_+ + (\omega-\omega_0)c_-\right] \end{aligned} \tag{27}$$

Eliminating c_- gives the harmonic osillator equation for c_+

$$\ddot{c}_+ + \frac{1}{4}\left[\omega_1^2 + (\omega - \omega_0)^2\right] c_+ = 0 \tag{28}$$

having the general solution which can be written in the form

$$c_+(t) = A_+ e^{i\mu t/2} + A_- e^{-i\mu t/2} \tag{29}$$

where

$$\mu = \sqrt{\omega_1^2 + (\omega - \omega_0)^2} \tag{30}$$

is called the Rabi frequency. Using this in the first of Eqs. 27 and solving for c_- gives

$$\begin{aligned} c_-(t) &= A_+ \frac{\mu + (\omega - \omega_0)}{\omega_1} e^{i\mu t/2} \\ &\quad - A_- \frac{\mu - (\omega - \omega_0)}{\omega_1} e^{-i\mu t/2} \end{aligned} \tag{31}$$

In particular, suppose $c_+(0) = 1$ and $c_-(0) = 0$ (spin initially aligned in z-direction). Equation 29 at $t = 0$ gives

$$A_+ + A_- = 1 \tag{32}$$

and Eq. 31 gives

$$\frac{\mu}{\omega_1}(A_+ - A_-) + \frac{\omega - \omega_0}{\omega_1}(A_+ + A_-) = 0 \tag{33}$$

Solving these equations gives

$$\begin{aligned} A_+ &= \frac{1}{2}\left(1 - \frac{\omega - \omega_0}{\mu}\right) \\ A_- &= \frac{1}{2}\left(1 + \frac{\omega - \omega_0}{\mu}\right) \end{aligned} \tag{34}$$

and substituting these into Eqs. 29 and 31 gives

$$\begin{aligned} c_+(t) &= \cos\frac{\mu t}{2} - i\frac{\omega - \omega_0}{\mu}\sin\frac{\mu t}{2} \\ c_-(t) &= i\frac{\omega_1}{\mu}\sin\frac{\mu t}{2} \end{aligned} \tag{35}$$

These are easily checked to satisfy the Schroendinger equation (Eq. 27), the initial conditions $c_+(0) = 1$ and $c_-(0) = 0$ and are properly normalized. They can be expected to describe a spin vector that precesses about the effective total field in the rotating frame.

In the rotating frame (i.e., using c_+ and c_-) the component expectation values (Eqs. 8) become

$$\begin{aligned} \langle\sigma_z\rangle &= \cos^2\frac{\mu t}{2} - \frac{\omega_1^2 - (\omega - \omega_0)^2}{\mu^2}\sin^2\frac{\mu t}{2} \\ \langle\sigma_x\rangle &= -\frac{2\omega_1(\omega - \omega_0)}{\mu^2}\sin^2\frac{\mu t}{2} \\ \langle\sigma_y\rangle &= \frac{\omega_1}{\mu}\sin^2\frac{\mu t}{2} \end{aligned} \tag{36}$$

On-resonance ($\omega = \omega_0$, $\mu = \omega_1$) we get

$$\langle\sigma_z\rangle = \cos\mu t \tag{37}$$

showing that $\langle\sigma_z\rangle$ oscillates completely between between the extremes ± 1 as μt goes from 0 to π. If the alternating field is pulsed on and off for an interval t satisfying $\mu t = \pi$, it is said to be a π-pulse and on-resonance causes a complete inversion of the spin.

Off resonance, complete inversion does not occur (the Rabi precession axis has a z-component and is therefore not perpendicular to the initial spin). The minimum $\langle\sigma_z\rangle$ is easily shown to still occur for a $\mu t = \pi$-pulse reaching the value

$$\langle\sigma_z\rangle_{\rm min} = -\frac{1 - (\Delta\omega/\omega_1)^2}{1 + (\Delta\omega/\omega_1)^2} \tag{38}$$

where $\Delta\omega = \omega - \omega_0$ is the frequency mismatch.