Nuclear Magnetic Resonance (MRI scans)

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1 Larmor Precession

Consider a spin-1/2 particle with a gyromagnetic ratio γ, at rest in a static magnetic field $B_0\hat{k}$. The Hamiltonian for this system is

$$\hat{H} = -\gamma B_0 \hat{S}_z = \frac{\gamma B_0 \hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{1}$$

Evidently, the eigenstates of $\hat{H}$ are

$$\begin{cases} \chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, & \text{with energy } E_+ = -(\gamma B_0 \hbar)/2 \\ \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, & \text{with energy } E_- = +(\gamma B_0 \hbar)/2 \end{cases} \tag{2}$$

As expected from classical mechanics, energy is lowest when the dipole moment is parallel to the field. We note that the Hamiltonian is time-independent, which means the general solution to the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial \chi}{\partial t} = \hat{H}\chi \tag{3}$$

can be expressed in terms of the stationary states:

$$\chi(t) = a\chi_+ e^{-iE_+t/\hbar} + b\chi_- e^{-iE_-t/\hbar} = \begin{pmatrix} ae^{i\gamma B_0 t/2} \\ be^{-i\gamma B_0 t/2} \end{pmatrix} \tag{4}$$

To determine the constants a and b, we impose the initial conditions:

$$\chi(0) = \begin{pmatrix} a \\ b \end{pmatrix} \tag{5}$$

where normalisation requires $|a|^2 + |b|^2 = 1$. Writing $a = \cos(\alpha/2)$ and $b = \sin(\alpha/2)$, where α is a fixed angle whose physical significance will be clear in a moment. We have

$$\chi(t) = \begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix}. \tag{6}$$

To see what's happening here, lets calculate the expectation value of $\hat{S}$ in different directions:

$$\left\langle \hat{S}_x \right\rangle = \chi(t)^\dagger \hat{S}_x \chi(t) how = \begin{pmatrix} \cos(\alpha/2)e^{-i\gamma B_0 t/2} & \sin(\alpha/2)e^{i\gamma B_0 t/2} \end{pmatrix} \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \cos(\alpha/2)e^{i\gamma B_0 t/2} \\ \sin(\alpha/2)e^{-i\gamma B_0 t/2} \end{pmatrix} \tag{7}$$

$$= \frac{\hbar}{2}\sin\alpha\cos(\gamma B_0 t) \tag{8}$$

By similar calculations,

$$\left\langle \hat{S}_y \right\rangle = \chi(t)^\dagger \hat{S}_y \chi(t) = -\frac{\hbar}{2}\sin\alpha\sin(\gamma B_0 t) \tag{9}$$

and

$$\left\langle \hat{S}_z \right\rangle = \chi(t)^\dagger \hat{S}_z \chi(t) = \frac{\hbar}{2}\cos\alpha. \tag{10}$$

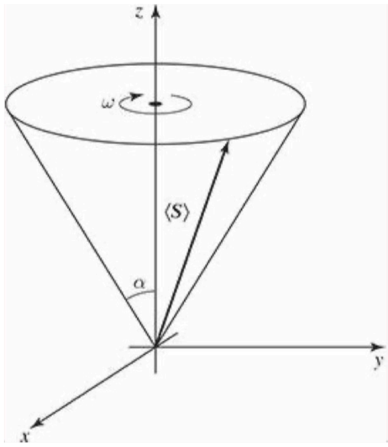

Figure 1: Spin precession around the z-axis at an angle α due to a static magnetic field $B_0\hat{z}$

Thus, $\left\langle \hat{S} \right\rangle$ is tilted at a constant angle α to the z-axis, and precesses about the z-axis at the Larmor frequency $\omega = \gamma B_0$, just as it would classically as predicted by the Ehrenfest theorem:

$$\frac{d}{dt}\left\langle \hat{A} \right\rangle = -i\hbar\left\langle \left[\hat{A}, \hat{H}\right] \right\rangle + \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle \tag{11}$$

for some operator $\hat{A}$. You can see this by trying $\hat{A} = \hat{x}$ or $\hat{A} = \hat{p} = -i\hbar\frac{\partial}{\partial x}$ to show that expectation values reconcile quantum mechanical equations with classical equations.

2 Nuclear Magnetic Resonance

We saw in the last section that a spin-1/2 particle with gyromagnetic ratio γ is at rest in a static magnetic field $B_0\hat{k}$, it precesses at the Larmor frequency. Now, consider turning on a small transverse radio frequency field, $B_{\text{rf}}\left[\cos(\omega t)\hat{\imath} - \sin(\omega t)\hat{\jmath}\right]$, so the total field is

$$\vec{B} = B_{\text{rf}}\cos(\omega t)\hat{\imath} - B_{\text{rf}}\sin(\omega t)\hat{\jmath} + B_0\hat{k}. \tag{12}$$

The Hamiltonian is given by

$$\hat{H} = -\gamma\vec{B}\cdot\vec{S} = -\frac{\gamma\hbar}{2}(B_x\sigma_x + B_y\sigma_y + B_z\sigma_z) = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_0 & B_{\text{rf}}e^{i\omega t} \\ B_{\text{rf}}e^{-i\omega t} & -B_0 \end{pmatrix}. \tag{13}$$

The difference between this Hamiltonian and the Hamitonian for the static field case in the previous section is that we now have time-dependence so we can no longer use the stationary states. We need to solve the time-dependent Schrödinger equation for a general state $\chi = \begin{pmatrix} a(t) \\ b(t) \end{pmatrix}$:

$$i\hbar\begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_0 & B_{\text{rf}}e^{i\omega t} \\ B_{\text{rf}}e^{-i\omega t} & -B_0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix} B_0 a + B_{\text{rf}}e^{i\omega t}b \\ B_{\text{rf}}e^{-i\omega t}a - B_0 b \end{pmatrix}. \tag{14}$$

This gives the system of equations:

$$\begin{cases} \dot{a} = i\frac{\gamma}{2}\left(B_0 a + B_{\text{rf}}e^{i\omega t}b\right) = \frac{i}{2}\left(\Omega e^{i\omega t}b + \omega_0 a\right) \\ \dot{b} = -i\frac{\gamma}{2}\left(B_0 b - B_{\text{rf}}e^{-i\omega t}a\right) = \frac{i}{2}\left(\Omega e^{-i\omega t}a - \omega_0 b\right) \end{cases} \tag{15}$$

where $\Omega = \gamma B_{\text{rf}}$ is related to the strength of the RF field. To solve for $a(t)$ and $b(t)$, we can differentiate with respect to time to decouple the system and imposing the initial conditions, $a(0) = a_0$ and $b(0) = b_0$, we have

$$a(t) = \left\{a_0\cos(\omega' t/2) + \frac{i}{\omega'}[a_0(\omega_0 - \omega) + b_0\Omega]\sin(\omega' t/2)\right\}e^{i\omega t/2} \tag{16}$$

$$b(t) = \left\{b_0\cos(\omega' t/2) + \frac{i}{\omega'}[b_0(\omega - \omega_0) + a_0\Omega]\sin(\omega' t/2)\right\}e^{-i\omega t/2} \tag{17}$$

where $\omega' = \sqrt{(\omega - \omega_0)^2 + \Omega^2}$. If a particle is initially in the spin up state ($a_0 = 1$, $b_0 = 0$), the probability of transition into the down state would be

$$b(t) = \frac{i}{\omega'}\Omega \sin(\omega' t/2) e^{-i\omega t/2} \longrightarrow P_\downarrow(t) = |b(t)|^2 = \frac{\Omega^2}{(\omega - \omega_0)^2 + \Omega^2} \sin^2(\omega' t/2) \tag{18}$$

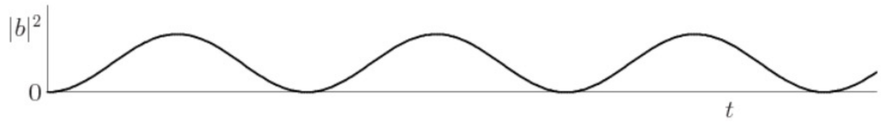

Figure 2: The oscillatory probability of transitioning from spin up to spin down.

Equation 18 is plotted in Figure 2, shows that initially, the probability of transition is zero, but over time, there is an oscillation between the particle being with certainty in the spin down state, and certainty of being in the spin up state. The frequency at which this probability flips is called the Rabi frequency $\omega'/2$.

The coefficient in front of the $\sin^2(\omega' t/2)$ determines how the perturbing RF frequency affects the spin of the spin-1/2 particle. This coefficient is called the resonance factor

$$P(\omega) = \frac{\Omega^2}{(\omega - \omega_0)^2 + \Omega^2} \tag{19}$$

which has a peak at the Larmor frequency.

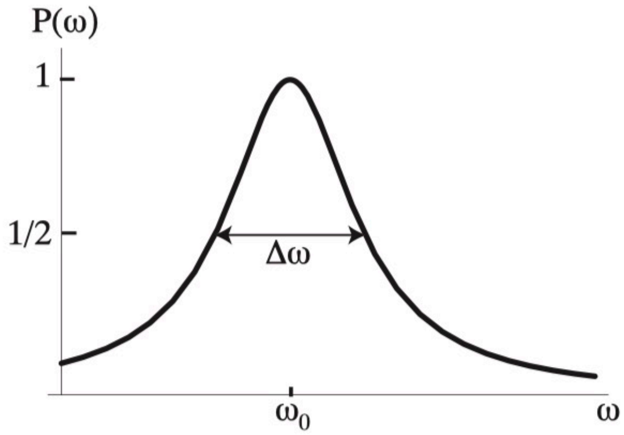

Figure 3: The resonance curve having a maximum at the Larmor frequency ω_0

Thus, for the perturbing RF field to have the maximum effect, its frequency ω must equal the spin-1/2 particle's Larmor frequency ω_0. Additionally we can find the FWHM of the peak by

$$P = \frac{1}{2} \Longrightarrow (\omega - \omega_0)^2 = \Omega^2 \Longrightarrow \omega = \omega_0 \pm \Omega, \text{ so that } \Delta\omega = \omega_+ - \omega_- = 2\Omega = 2\gamma B_{\text{rf}}. \tag{20}$$

Thus, for this resonant frequency to be accurately determined through experiment, the peak of the resonance curve must be narrow, meaning that the perturbing RF magnetic field must be very weak compared to the primary magnetic field, $B_{\text{rf}} << B_0$.