17.6 Nuclear Magnetic Resonance

In nuclear magnetic resonance, spins are subject to a time-dependent magnetic field. This magnetic field has a time-independent z-component and a circularly polarized component representing a magnetic field rotating on the (x, y) plane. More concretely, we have

$$\mathbf{B}(t) = B_0\,\mathbf{z} + B_1\big(\mathbf{x}\cos\omega t - \mathbf{y}\sin\omega t\big). \tag{17.6.1}$$

Generally, the constant z-component $B_0 > 0$ is larger than B_1, the magnitude of the radio-frequency (RF) signal. Associated to the longitudinal magnetic field B_0, the Larmor angular frequency ω_0 is defined by

$$\omega_0 \equiv \gamma B_0. \tag{17.6.2}$$

The time-dependent part of the field points along the x-axis at $t = 0$ and is rotating with angular velocity $\omega > 0$ in the clockwise direction of the (x, y) plane. This corresponds to *negative* angular velocity about the positive z-axis. The spin Hamiltonian is

$$\hat{H}_S(t) \;=\; -\gamma\,\mathbf{B}(t)\cdot\hat{\mathbf{S}} \;=\; -\gamma\,[B_0\hat{S}_z + B_1(\cos\omega t\,\hat{S}_x - \sin\omega t\hat{S}_y)]. \tag{17.6.3}$$

This Hamiltonian is not only time dependent; the Hamiltonians at different times do not commute. This is therefore a nontrivial time-evolution problem.

We attempt to simplify the problem by considering a frame of reference that rotates just like the RF signal in the above magnetic field. To analyze this first imagine the case where the full magnetic field vanishes, and therefore $\hat{H}_S = 0$. With no magnetic field, spin states would simply be static; they do not precess. What should the Hamiltonian be in the frame rotating about the z-axis like the RF signal, with negative angular velocity of magnitude ω? It cannot be zero because in this frame the spin states are rotating with *positive* angular velocity ω about the z-direction. There must be a Hamiltonian that has that effect. The unitary operator $\mathcal{U}_\omega$ that generates this rotation is

$$\mathcal{U}_\omega(t) \;=\; \exp\Big(-\frac{i\omega t\hat{S}_z}{\hbar}\Big) \quad\Rightarrow\quad \hat{H}_{\mathcal{U}_\omega} = \omega\hat{S}_z, \tag{17.6.4}$$

with $\hat{H}_{\mathcal{U}_\omega}$ the associated time-independent Hamiltonian. The Hamiltonian $\hat{H}_{\mathcal{U}_\omega}$ governs the time evolution of the "rotating-frame" state $|\Psi_R, t\rangle$ when $\hat{H}_S = 0$.

To implement this concretely, we postulate that even when $\hat{H}_S \neq 0$ the state $|\Psi_R, t\rangle$ and the laboratory-frame state $|\Psi, t\rangle$ are related as follows:

$$\boxed{|\Psi_R, t\rangle \equiv \mathcal{U}_\omega(t)|\Psi, t\rangle.} \tag{17.6.5}$$

This relation is what we want when $\hat{H}_S = 0$: the state $|\Psi, t\rangle$ is then time independent, and $\square_\omega(t)$ alone generates the time evolution. Note that if we can find $|\Psi_R, t\rangle$, this relation determines $|\Psi, t\rangle$ since $\square_\omega$ is known. Moreover, at $t = 0$ the two states agree: $|\Psi_R, 0\rangle = |\Psi, 0\rangle$.

We now use (17.6.5) to find the full rotating-frame Hamiltonian $\hat{H}_R$ when $\hat{H}_S \neq 0$. Indeed, this relation is rewritten as

$$|\Psi_R, t\rangle = \mathcal{U}_\omega(t)|\Psi, t\rangle = \mathcal{U}_\omega(t)\mathcal{U}_S(t)|\Psi, 0\rangle = \mathcal{U}_\omega(t)\mathcal{U}_S(t)|\Psi_R, 0\rangle, \tag{17.6.6}$$

with $\square_S(t)$ the unitary operator generating the time evolution associated with $\hat{H}_S(t)$. Since the Hamiltonian associated to an arbitrary unitary time-evolution operator $\square$ is $i\hbar(\partial_t\square)\square^\dagger$ (see (16.2.10)), we have

$$\hat{H}_R(t) = i\hbar\,\partial_t(\mathcal{U}_\omega\,\mathcal{U}_S)\,\mathcal{U}_S^\dagger\,\mathcal{U}_\omega^\dagger = i\hbar\,(\partial_t\mathcal{U}_\omega)\mathcal{U}_\omega^\dagger + \mathcal{U}_\omega\; i\hbar\,(\partial_t\mathcal{U}_S)\mathcal{U}_S^\dagger\,\mathcal{U}_\omega^\dagger. \tag{17.6.7}$$

This means we have shown that

$$\hat{H}_R = \hat{H}_{\mathcal{U}_\omega} + \mathcal{U}_\omega\,\hat{H}_S\,\mathcal{U}_\omega^\dagger. \tag{17.6.8}$$

This is a nice result: when $\hat{H}_S = 0$, it gives the expected $\hat{H}_{\square_\omega}$, and when $\hat{H}_S \neq 0$, the rotating-frame Hamiltonian receives an extra contribution.

We now check that $\hat{H}_R$ is much simpler than $\hat{H}_S$; it is in fact time independent. Using the expressions for $\hat{H}_{\square_\omega}$ and $\square_\omega$ from (17.6.4) and the formula for $\hat{H}_S$, we find that

$$\begin{aligned}\hat{H}_R &= \omega\hat{S}_z - \gamma\, e^{-\frac{i\omega t\hat{S}_z}{\hbar}}\Big(B_0\hat{S}_z + B_1\big(\cos\omega t\,\hat{S}_x - \sin\omega t\hat{S}_y\big)\Big)e^{\frac{i\omega t\hat{S}_z}{\hbar}}\\ &= (-\gamma B_0 + \omega)\hat{S}_z - \gamma B_1\hat{M}(t),\end{aligned} \tag{17.6.9}$$

where we defined

$$\hat{M}(t) \equiv e^{-\frac{i\omega t\hat{S}_z}{\hbar}}(\cos\omega t\,\hat{S}_x - \sin\omega t\hat{S}_y)e^{\frac{i\omega t\hat{S}_z}{\hbar}}. \tag{17.6.10}$$

We show that $\hat{M}(t)$ is time independent by calculating the time derivative of $\hat{M}$:

$$\partial_t\hat{M} = e^{-\frac{i\omega t\hat{S}_z}{\hbar}}\Big(-\tfrac{i\omega}{\hbar}\,[\hat{S}_z, \cos\omega t\,\hat{S}_x - \sin\omega t\,\hat{S}_y] + \big(-\omega\sin\omega t\,\hat{S}_x - \omega\cos\omega t\,\hat{S}_y\big)\Big)e^{\frac{i\omega t\hat{S}_z}{\hbar}}.$$

The commutator arises from differentiation of the exponentials in $\hat{M}$ and the other terms from differentiation of the expression within the exponentials in $\hat{M}$. Evaluating the commutators, we find a complete cancellation: $\partial_t \hat{M} = 0$. Since $\hat{M}$ is time independent, we can evaluate it at any time. The simplest time is $t = 0$, giving

$$\hat{M}(t) = \hat{S}_x. \tag{17.6.11}$$

As a result, the rotating-frame Hamiltonian $\hat{H}_R$ of (17.6.9) becomes

$$\hat{H}_R = (-\gamma B_0 + \omega)\hat{S}_z - \gamma B_1 \hat{S}_x. \tag{17.6.12}$$

The time independence of $\hat{H}_R$ means that the time evolution of $|\Psi_R, t\rangle$ is easily calculated. A little rewriting allows us to read an effective magnetic field $\mathbf{B}_R$ associated with $\hat{H}_R$:

$$\hat{H}_R = -\gamma\Big[B_1\hat{S}_x + \Big(B_0 - \frac{\omega}{\gamma}\Big)\hat{S}_z\Big] = -\gamma\Big[B_1\hat{S}_x + B_0\Big(1 - \frac{\omega}{\omega_0}\Big)\hat{S}_z\Big], \tag{17.6.13}$$

using $\omega_0 = \gamma B_0$ for the Larmor frequency associated with the constant component of the field. We thus have

$$\boxed{\hat{H}_R = -\gamma\, \mathbf{B}_R \cdot \hat{\mathbf{S}} \quad \Rightarrow \quad \mathbf{B}_R = B_1 \mathbf{x} + B_0\Big(1 - \frac{\omega}{\omega_0}\Big)\mathbf{z}.} \tag{17.6.14}$$

Note that the RF signal contributes to the effective magnetic field a component B_1 pointing along the x-axis. The longitudinal effective magnetic field is also changed: the initial value B_0 is now multiplied by an ω-dependent factor.

The full solution for the state is obtained beginning with (17.6.5) and (17.6.4):

$$|\Psi, t\rangle = \mathcal{U}_\omega^\dagger(t)|\Psi_R, t\rangle = \exp\Big[\frac{i\omega t\hat{S}_z}{\hbar}\Big]|\Psi_R, t\rangle. \tag{17.6.15}$$

Since $\hat{H}_R$ is time independent, the time evolution of $|\Psi_R, t\rangle$ is easily taken into account:

$$|\Psi, t\rangle = \exp\Big[\frac{i\omega t\hat{S}_z}{\hbar}\Big]\exp\Big[-i\frac{(-\gamma \mathbf{B}_R \cdot \hat{\mathbf{S}})\, t}{\hbar}\Big]|\Psi_R, 0\rangle. \tag{17.6.16}$$

Recalling that $|\Psi_R, 0\rangle = |\Psi, 0\rangle$, we finally get

$$\boxed{|\Psi, t\rangle = \exp\left[\frac{i\omega t \hat{S}_z}{\hbar}\right] \exp\left[i\frac{\gamma \mathbf{B}_R \cdot \hat{\mathbf{S}}\, t}{\hbar}\right] |\Psi, 0\rangle.} \tag{17.6.17}$$

This is the complete solution to the time evolution of an arbitrary spin state in a longitudinal plus transverse RF magnetic field.

Exercise 17.10. *Verify that for $B_1 = 0$ the above solution reduces to the one describing precession about the z-axis.*

In the applications to be discussed below, we always find that the magnitude of the RF signal is far smaller than the magnitude of the longitudinal magnetic field:

$$B_1 \ll B_0. \tag{17.6.18}$$

Now consider the evolution of a spin that initially points in the positive z-direction. We look at two cases:

1. $\omega \ll \omega_0$. In this case the effective magnetic field (17.6.14) in the rotating frame is approximately given by

$$\mathbf{B}_R \simeq B_0 \mathbf{z} + B_1 \mathbf{x}. \tag{17.6.19}$$

   This is a field mostly along the z-axis but tipped a little toward the x-axis. The right most exponential in (17.6.17) makes the spin precess rapidly about the direction of $\mathbf{B}_R$. Since $|\mathbf{B}_R| \sim B_0$, the angular rate of precession is pretty much ω_0. The next exponential in (17.6.17) induces a rotation about the z-axis with smaller angular velocity ω.

2. $\omega = \omega_0$. This is a resonance condition, with the RF frequency set equal to the longitudinal Larmor frequency. This condition makes the longitudinal component of the effective magnetic field in the rotating frame vanish. Indeed, equation (17.6.14) gives

$$\mathbf{B}_R = B_1 \mathbf{x}. \tag{17.6.20}$$

   In this case the rightmost exponential in (17.6.17) makes the spin precess about the x-axis. As a result, with $\gamma B_1 > 0$, the spin that points initially along the z-axis will rotate toward the positive y-axis with angular velocity $\omega_1 = \gamma B_1$. If we set the RF signal to last a time T such that

$$\omega_1 T = \frac{\pi}{2}, \tag{17.6.21}$$

the state $|\Psi_R, T\rangle$ will point along the y-axis. The effect of the other exponential in (17.6.17) is just to rotate the spin about the z-axis. We then have

$$|\Psi, t\rangle = \exp\left[\frac{i\omega_0 t\hat{S}_z}{\hbar}\right]|\Psi_R, t\rangle, \quad t < T, \tag{17.6.22}$$

and if the RF pulse turns off after time T,

$$|\Psi, t\rangle = \exp\left[\frac{i\omega_0 t\hat{S}_z}{\hbar}\right]|\Psi_R, T\rangle, \quad t > T. \tag{17.6.23}$$

The state $|\Psi, t\rangle$ can be visualized as a spin that is slowly rotating with angular velocity ω_1 from the z-axis toward the y-axis while rapidly rotating around the z-axis with angular velocity ω_0. As a result the tip of the spin vector is performing a spiral motion on the surface of a hemisphere. By the time the polar angle reaches $\pi/2$, the RF signal turns off, and the spin now just rotates on the (x, y) plane. This is called a 90° pulse. The motion of the tip of the spin state is sketched in figure 17.3.

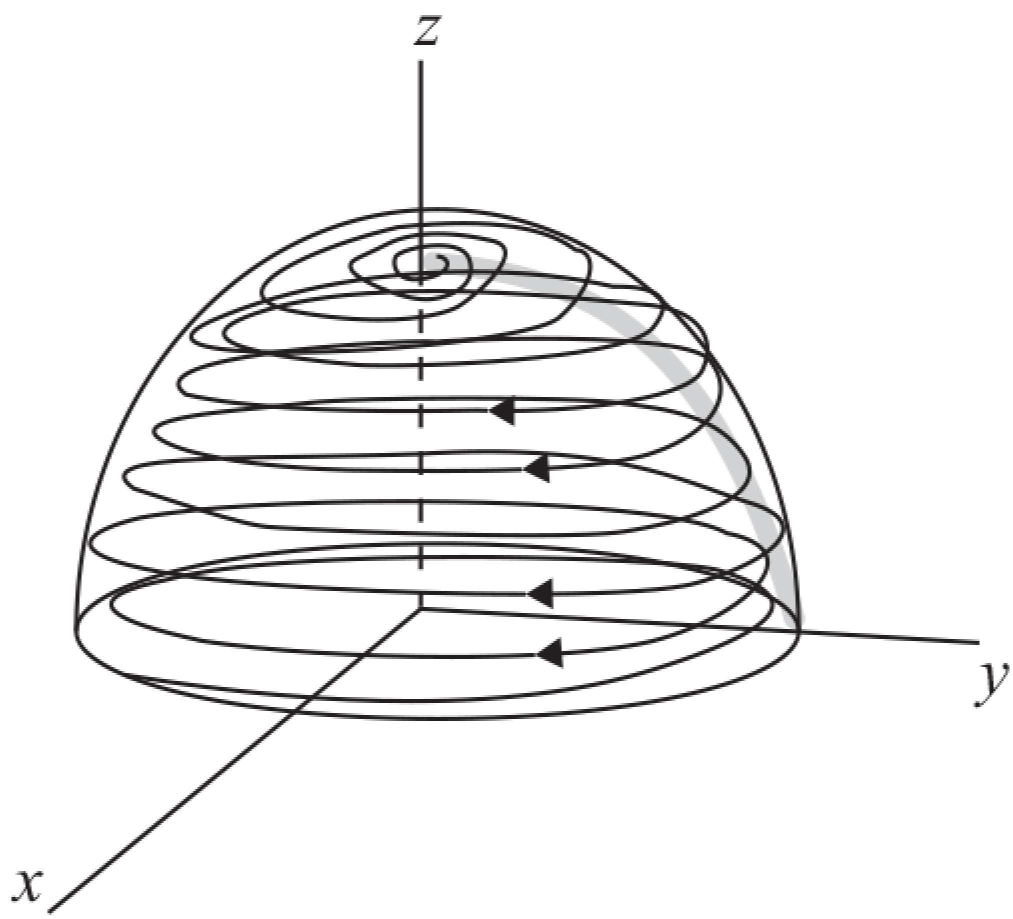

Figure 17.3
The time evolution of a spin state, initially pointing along the positive z-axis at $t = 0$ and subject to a 90° RF pulse. The tip of the vector representing the spin follows a spiral trajectory resulting from the composition of a slow rotation about the x-axis and a fast rotation about the z-axis.

The value of the longitudinal magnetic field B_0 in experimental setups is of the order of a few tesla. We have defined the Larmor angular frequency $\omega_0 = \gamma B_0$. It follows that the Larmor *frequency* f_0 is given by $f_0 = \frac{\omega_0}{2\pi} = \frac{\gamma}{2\pi} B_0$. From the results in exercise 17.9, we find that

$$\left| \frac{\gamma_e}{2\pi} \right| = 28.0\,\mathrm{GHz/T}, \quad \left| \frac{\gamma_p}{2\pi} \right| = 42.6\,\mathrm{MHz/T}. \tag{17.6.24}$$

For a magnetic field of two tesla, the proton precesses with a frequency of about 85 MHz.

Magnetic resonance imaging (MRI) This technology was developed in the late 1970s using earlier research on nuclear magnetic resonance by Felix Bloch and by Edward Purcell, working at MIT's Radiation

Laboratory. In 1952 Bloch and Purcell received the Nobel Prize in Physics for this work. Magnetic resonance imaging has advantages over X-rays: it allows one to distinguish various soft tissues and does not involve radiation.

The human body is mostly composed of water molecules (H_2O). We thus have many hydrogen atoms, whose nuclei are protons and are the main players through their magnetic dipole moments. The MRI machine produces a large and constant magnetic field B_0 along the axis of the machine, a direction we choose to call the z-direction. Despite the disordering effects of body temperature, there is a net alignment of nuclear spins along B_0. This *longitudinal magnetization* puts a large number of spins in play.

We apply a 90° pulse so we get the spins to rotate with Larmor frequency ω_0 in the (x, y) plane. These rotating dipoles produce an oscillating magnetic field, and this signal is picked up by a receiver. The magnitude of the signal is proportional to the proton density. This is the first piece of information and allows differentiation of tissues.

The above signal from the rotation of the spins decays with a time constant T_2 that is typically much smaller than a second. This decay is attributed to interactions between the spins that quickly dampen their rotation. A T_2-weighted image allows doctors to detect the abnormal accumulation of fluids (edema).

There is another time constant T_1, of order one second, that controls the time needed to regain the longitudinal magnetization. This effect is due to the spins interacting with the rest of the lattice of atoms. White matter, gray matter, and cerebrospinal fluids have about the same proton density but are distinguished by different T_1 constants. The constants T_1 and T_2 are in fact associated with processes of decoherence. Such processes can be studied phenomenologically using the Lindblad equation, as we will do in section 22.6.

MRIs commonly include the use of contrast agents, which are substances that shorten the time constant T_1 and are usually administered by injection into the bloodstream. The contrast agent (gadolinium) can accumulate at organs or locations where information is valuable. For a number of substances, one can use the MRI apparatus to determine their

(T_1, T_2) constants and build a table of data. This table can then be used as an aid to evaluating the results of other MRIs.

The typical MRI machine has a B_0 of about two tesla or twenty thousand gauss. This requires a superconducting magnet with liquid helium cooling. For people with claustrophobia there are “open” MRI scanners that work with lower magnetic fields. In addition, the machines are equipped with a number of *gradient* magnets, each of about two hundred gauss. They change locally the value of B_0 and provide spatial resolution by making the Larmor frequency spatially dependent. One can then attain spatial resolutions of about half a millimeter! MRIs are considered safe, as there is no evidence of biological harm caused by very large static magnetic fields.