5– Chapter 2 in QM Lingo

In this chapter, we will see how we can perturb our spins using a $\vec{B}_1(t)$ field, as we did in Chapter 2. We will, however, write our equations in terms of the quantum mechanical operators and observables presented in the previous chapter.

5.1 Rotation Operators

The nuclear angular momentum operators we defined in the previous chapter can be used to define rotation operators:

$$\begin{aligned} \hat{R}_x(\beta) &= exp\{-i\beta\hat{I}_x\} \\ \hat{R}_y(\beta) &= exp\{-i\beta\hat{I}_y\} \\ \hat{R}_z(\beta) &= exp\{-i\beta\hat{I}_z\} \end{aligned} \tag{5.1}$$

where β is the rotation angle. The operators above represent a positive rotation. For example, $\hat{R}_x(\beta)$ is a positive rotation about the x-axis through an angle β. As before, the convention we will use is a counter-clockwise rotation. The inverse rotation is

through an angle of $-\beta$, such that

$$\hat{R}_x(\beta)\hat{R}_x(-\beta) = \hat{1}, \tag{5.2}$$

and likewise for the other two.

Since we used the angular momentum operators to define the rotation operators, a rotation operator and angular momemtum operator about the same axis commute, i.e.

$$\hat{R}_x(\beta)\hat{I}_x = \hat{I}_x\hat{R}_x(\beta). \tag{5.3}$$

As a consequence,

$$\hat{R}_x(\beta)\hat{I}_x\hat{R}_x(-\beta) = \hat{I}_x. \tag{5.4}$$

since

$$\begin{aligned} \hat{R}_x(\beta)\hat{I}_x\hat{R}_x(-\beta) &= \hat{I}_x\hat{R}_x(\beta)\hat{R}_x(-\beta) \\ &= \hat{I}_x\hat{1} \end{aligned} \tag{5.5}$$

This corresponds to the classical picture that the rotation of a vector, which lies along a given axis, about that same axis does nothing.

If a rotation operator is applied to an angular

momentum vector which lies along a different axis to the axis of rotation then

$$\hat{R}_x(\beta)\hat{I}_y\hat{R}_x(-\beta) = \hat{I}_y cos(\beta) + \hat{I}_z sin(\beta) \tag{5.6}$$

or in general for any three operators obeying the cyclic commutation rule

$$[\hat{A}, \hat{B}] = i\hat{C} \tag{5.7}$$

then

$$exp(-i\theta\hat{A})\hat{B}exp(i\theta\hat{A}) = \hat{B}cos\theta + \hat{C}sin\theta \tag{5.8}$$

which can be interpreted as a rotation of operator $\hat{B}$ towards the operator $\hat{C}$ around the axis $\hat{A}$.

To prove this relation (and practice manipulating operators), we can show that

$$\hat{R}_z(\beta)\hat{I}_x\hat{R}_z(-\beta) = \hat{I}_x cos(\beta) + \hat{I}_y sin(\beta) \tag{5.9}$$

starting from the definition of the lowering operator:

$$\hat{I}^- = \hat{I}_x - i\hat{I}_y \tag{5.10}$$

The commutation relation

$$[\hat{I}_z, \hat{I}^-] \quad = \quad [\hat{I}_z, \hat{I}_x] - i[\hat{I}_z, \hat{I}_y]$$

$$
\begin{aligned}
&= i\hat{I}_y - i(-i\hat{I}_x) \\
&= -\hat{I}^- \qquad (5.11)
\end{aligned}
$$

Therefore

$$\hat{I}_z\hat{I}^- = \hat{I}^-\hat{I}_z - \hat{I}^- = \hat{I}^-(\hat{I}_z - \hat{1}) \qquad (5.12)$$

Multiplying both sides of the equation by $\hat{I}_z$, we get

$$
\begin{aligned}
\hat{I}_z\hat{I}_z\hat{I}^- &= \hat{I}_z\hat{I}^-(\hat{I}_z - \hat{1}) \\
\hat{I}_z^2\hat{I}^- &= \hat{I}^-(\hat{I}_z - \hat{1})(\hat{I}_z - \hat{1}) \\
&= \hat{I}^-(\hat{I}_z - \hat{1})^2 \qquad (5.13)
\end{aligned}
$$

Repeating this n times gives

$$\hat{I}_z^n\hat{I}^- = \hat{I}^-(\hat{I}_z - \hat{1})^n \qquad (5.14)$$

We can use this now to rewrite

$$exp\{-i\beta\hat{I}_z\}\hat{I}^- = \sum_{n=0}^{\infty} \frac{(-i\beta)^n}{n!}\hat{I}_z^n\hat{I}^-, \qquad (5.15)$$

where we have expanded the exponential term as a

sum, as

$$\begin{aligned} exp\{-i\beta\hat{I}_z\}\hat{I}^- &= \sum_{n=0}^{\infty} \frac{(-i\beta)^n}{n!} \hat{I}^- (\hat{I}_z - \hat{1})^n \\ &= \hat{I}^- \sum_{n=0}^{\infty} \frac{(-i\beta)^n}{n!} (\hat{I}_z - \hat{1})^n \\ &= \hat{I}^- exp\{-i\beta(\hat{I}_z - \hat{1})\} \\ &= \hat{I}^- exp\{-i\beta\hat{I}_z\} exp\{i\beta\hat{1}\} \\ &= \hat{I}^- exp\{-i\beta\hat{I}_z\} e^{i\beta}\hat{1} \\ &= e^{i\beta}\hat{I}^- exp\{-i\beta\hat{I}_z\}. \end{aligned} \tag{5.16}$$

Finally, multiplying the last equation from the right by $exp\{i\beta\hat{I}_z\}$, we get

$$exp\{-i\beta\hat{I}_z\}\hat{I}^- exp\{i\beta\hat{I}_z\} = e^{i\beta}\hat{I}^-. \tag{5.17}$$

We can derive a similar equation for the raising operator $\hat{I}^+$,

$$exp\{-i\beta\hat{I}_z\}\hat{I}^+ exp\{i\beta\hat{I}_z\} = e^{-i\beta}\hat{I}^+. \tag{5.18}$$

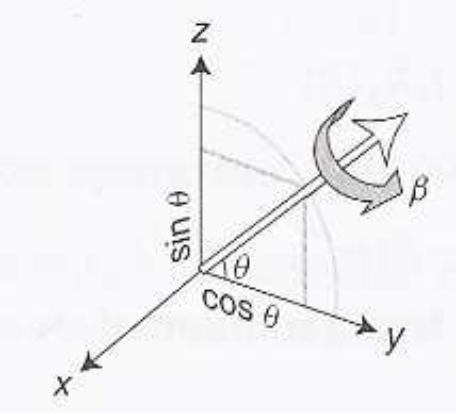
Adding equation 5.17 and 5.18, we get

$$\begin{aligned} exp\{-i\beta\hat{I}_z\}\hat{I}_x exp\{i\beta\hat{I}_z\} &= \frac{1}{2}\left[e^{i\beta}\hat{I}^- + e^{-i\beta}\hat{I}^+\right] \\ &= \hat{I}_x cos\beta + \hat{I}_y sin\beta \end{aligned} \tag{5.19}$$

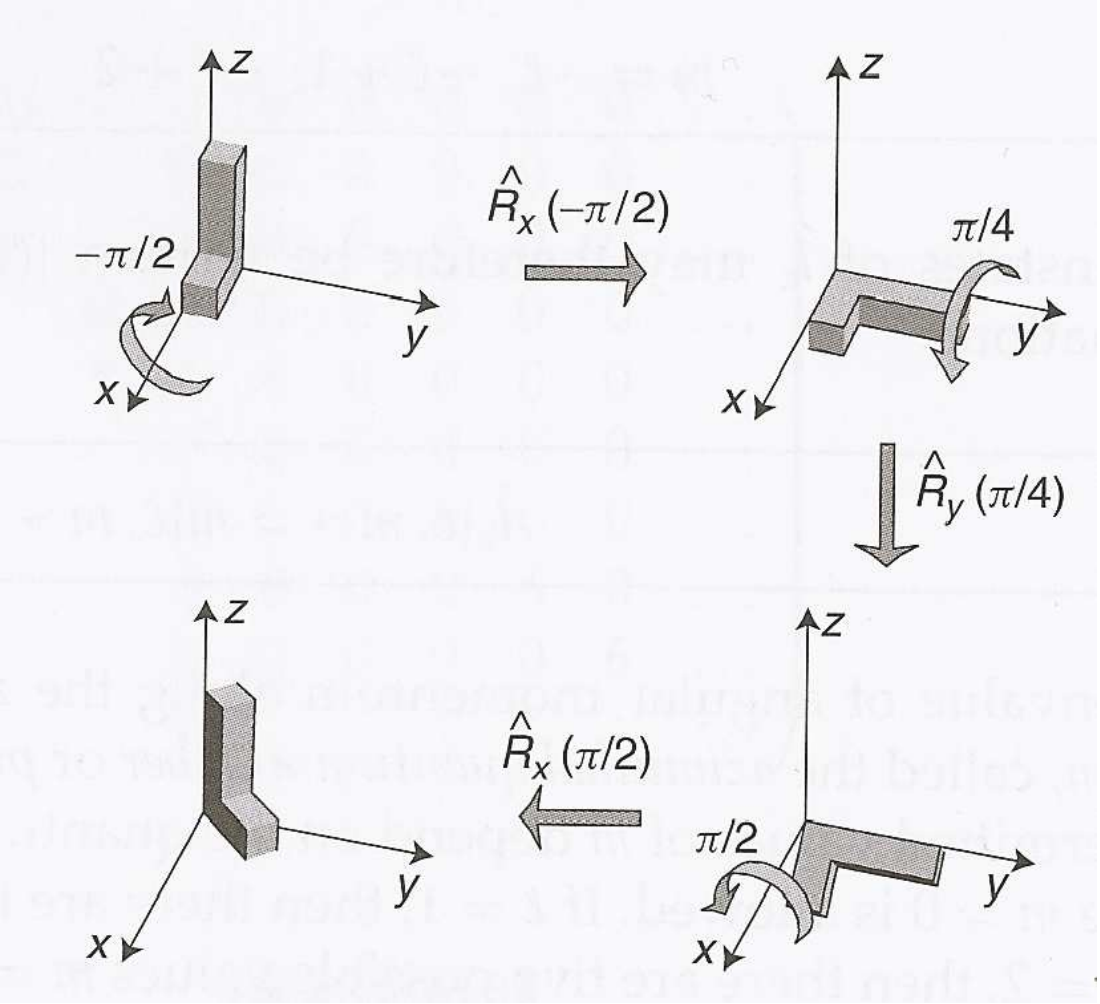
Another important property of rotation operators is:

$$\hat{R}_x(\theta)\hat{R}_y(\beta)\hat{R}_x(-\theta) = exp\{-i\beta\left(\hat{I}_y cos(\theta) + \hat{I}_z sin(\theta)\right)\} \tag{5.20}$$

The graphical representation of this operator is given as



Example: $\beta = \pi/4$, $\theta = \pi/2$



(Source of both pictures: M.H. Levitt, Spin Dynamics). This is equivalent to a single rotation $\hat{R}_z(\pi/4)$.

As with the nuclear angular momentum operators, we can also write the rotation operators in matrix form. Let's look at an example for spin 1/2: $\hat{R}_x(\beta) = exp\{-i\beta\hat{I}_x\}$. We can expand the exponential function as a series and rearrange the

terms such that

$$\begin{aligned} exp\{-i\beta\hat{I}_x\} &= \hat{1} - \frac{1}{2!}\left(\frac{\beta}{2}\right)^2 (2\hat{I}_x)^2 \\ &+ \frac{1}{4!}\left(\frac{\beta}{2}\right)^4 (2\hat{I}_x)^4 + ... \\ &- i\{\left(\frac{\beta}{2}\right)(2\hat{I}_x) - \frac{1}{3!}\left(\frac{\beta}{2}\right)^3 (2\hat{I}_x)^3 + ...\} \end{aligned} \tag{5.21}$$

Given the definition of (I_x) from the previous chapter, we can calculate

$$\{2(I_x)\}^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = (1) \tag{5.22}$$

Therefore the terms in the expansion above can be simplified to

$$\begin{aligned} \{2(I_x)\}^n &= (1) \\ \{2(I_x)\}^m &= 2(I_x)\{2(I_x)\}^n = \{2(I_x)\}(1) \end{aligned} \tag{5.23}$$

where n are even numbers and m are odd numbers,

such that

$$\begin{aligned} exp\{-i\beta(I_x)\} &= (1)\{1 - \frac{1}{2!}\left(\frac{\beta}{2}\right)^2 + \frac{1}{4!}\left(\frac{\beta}{2}\right)^4 + ...\} \\ &- i2(I_x)\{\left(\frac{\beta}{2}\right) - \frac{1}{3!}\left(\frac{\beta}{2}\right)^3 + ...\} \end{aligned} \tag{5.24}$$

in matrix form.

The first term in the { } is the series expansion of a cosine function, whereas the { } is the series expansion of a sine function. Therefore,

$$(R_x(\beta)) = exp\{-i\beta(I_x)\} = (1)cos(\frac{\beta}{2}) - i2(I_x)sin(\frac{\beta}{2}) \tag{5.25}$$

Writing this out explicitly in matrix form:

$$(R_x(\beta)) = \begin{pmatrix} cos(\frac{\beta}{2}) & -isin(\frac{\beta}{2}) \\ -isin(\frac{\beta}{2}) & cos(\frac{\beta}{2}) \end{pmatrix} \tag{5.26}$$

One can repeat a similar derivation for the other two

rotation operators. The final result is

$$(R_y(\beta)) = \begin{pmatrix} cos(\frac{\beta}{2}) & -sin(\frac{\beta}{2}) \\ sin(\frac{\beta}{2}) & cos(\frac{\beta}{2}) \end{pmatrix} \tag{5.27}$$

$$(R_z(\beta)) = \begin{pmatrix} exp\{\frac{-i\beta}{2}\} & 0 \\ 0 & exp\{\frac{i\beta}{2}\} \end{pmatrix} \tag{5.28}$$

5.2 Applying a Pulse

Let us now apply a pulse such that the magnetization vector lies along the x-axis (as we did in Chapter 2). The total local field felt by the spins is given by

$$\vec{B}(t) = B_0\vec{e_z} + \vec{B}_1(t). \tag{5.29}$$

Recall from Chapter 2 that we define $\vec{B}_1(t)$ as

$$\vec{B}_1(t) = B_1 cos(\omega_{rf}t)\vec{e}_x + B_1 sin(\omega_{rf}t)\vec{e}_y. \tag{5.30}$$

Using the time-dependent Schrödinger equation

$$\begin{aligned} \frac{-\hbar}{i}\frac{\partial\psi}{\partial t} &= \hat{\mathcal{H}}\psi \\ &= E\psi \\ &= -\vec{\mu}\cdot\vec{B}(t)\psi \end{aligned}$$

$$\frac{-\hbar}{i}\frac{\partial\psi}{\partial t} = -\gamma\hbar \quad \{ \quad B_0\hat{I}_z + \quad B_1(\hat{I}_x cos(\omega_{rf}t) + \hat{I}_y sin(\omega_{rf}t))\}\psi. \tag{5.31}$$

Using the definition in equation 5.9, we see that we can rewrite this as

$$\frac{-\hbar}{i}\frac{\partial\psi}{\partial t} = -\gamma\hbar \quad \{ \quad B_0\hat{I}_z + \quad B_1(\hat{R}_z(\omega_{rf}t)\hat{I}_x\hat{R}_z(-\omega_{rf}t))\}\psi. \tag{5.32}$$

The first term in the equation above is the spin Hamiltonian of each spin interacting with the external magnetic field. This interaction is called the nuclear *Zeeman interaction* - therefore we will denote the Zeeman Hamiltonian as

$$\hat{\mathcal{H}}_Z = -\gamma\hbar B_0\hat{I}_z. \tag{5.33}$$

where the subscript is a capital Z. We will see in the next chapter that although this interaction is important and always present, it is not very informative in terms of the molecules we want to

study using NMR.

The second term is the time-dependent rf Hamiltonian, $\hat{\mathcal{H}}_{rf}(t)$.

5.3 Rotating Frame

At this point, we still have a time-dependent total Hamiltonian given by

$$\hat{\mathcal{H}}_{ext}(t) = \hat{\mathcal{H}}_Z + \hat{\mathcal{H}}_{rf}(t) \tag{5.34}$$

where *ext* stands for external.

Close inspection of the time-dependent part in equation 5.32 gives us an idea. If we could define our wavefunction in the rotating frame as a rotation operator operating on the laboratory frame wavefunction

$$\widetilde{\psi} = \hat{R}_z(-\omega_{rf}t)\psi \tag{5.35}$$

where the tilde denotes that we are in the rotating frame. The choice of $\hat{R}_z(-\omega_{rf}t)$ here is important and can be rationalised if we look at the time-dependent Schrödinger equation for the rotating frame wavefunction

$$\frac{-\hbar}{i}\frac{\partial\widetilde{\psi}}{\partial t} = \frac{-\hbar}{i}\frac{\partial}{\partial t}\{\hat{R}_z(-\omega_{rf}t)\psi\}$$

$$= \frac{-\hbar}{i}\left(\{\frac{\partial \hat{R}_z(-\omega_{rf}t)}{\partial t}\}\psi + \hat{R}_z(-\omega_{rf}t)\{\frac{\partial \psi}{\partial t}\}\right) \tag{5.36}$$

Given the definition for the rotation operator given in equation 5.1, the time derivative works out to be

$$\begin{aligned}
\{\frac{\partial \hat{R}_z(-\omega_{rf}t)}{\partial t}\} &= \frac{\partial}{\partial t} exp\{i\omega_{rf}t\hat{I}_z\} \\
&= \frac{\partial(i\omega_{rf}t\hat{I}_z)}{\partial t} exp\{i\omega_{rf}t\hat{I}_z\} \\
&= i\omega_{rf}\hat{I}_z exp\{i\omega_{rf}t\hat{I}_z\} \\
&= i\omega_{rf}\hat{I}_z\hat{R}_z(-\omega_{rf}t) \qquad (5.37)
\end{aligned}$$

Therefore equation 5.36 can be rewritten as

$$\begin{aligned}
\frac{-\hbar}{i}\frac{\partial\widetilde{\psi}}{\partial t} &= \\
\frac{-\hbar}{i}\left(i\omega_{rf}\hat{I}_z\hat{R}_z(-\omega_{rf}t)\psi + \hat{R}_z(-\omega_{rf}t)\{\frac{\partial\psi}{\partial t}\}\right) & \\
\frac{-\hbar}{i}\left(i\omega_{rf}\hat{I}_z\hat{R}_z(-\omega_{rf}t)\psi + \frac{-i}{\hbar}\hat{R}_z(-\omega_{rf}t)\left(\hat{\mathcal{H}}_{ext}\psi\right)\right) & \\
\left(-\hbar\omega_{rf}\hat{I}_z\hat{R}_z(-\omega_{rf}t) + \hat{R}_z(-\omega_{rf}t)\hat{\mathcal{H}}_{ext}\right)\psi & \\
\left(-\hbar\omega_{rf}\hat{I}_z\hat{R}_z(-\omega_{rf}t) + \hat{R}_z(-\omega_{rf}t)\hat{\mathcal{H}}_{ext}\right)\hat{R}_z(\omega_{rf}t)\widetilde{\psi} &
\end{aligned} \tag{5.38}$$

or

$$\frac{-\hbar}{i}\frac{\partial\widetilde{\psi}}{\partial t} = \widetilde{\mathcal{H}}\widetilde{\psi} \tag{5.39}$$

where

$$\widetilde{\mathcal{H}} = \hat{R}_z(-\omega_{rf}t)\hat{\mathcal{H}}_{ext}\hat{R}_z(\omega_{rf}t) - \hbar\omega_{rf}\hat{I}_z \tag{5.40}$$

5.4 Rotating Frame Hamiltonian

Let us examine more closely the two cases for $\widetilde{\mathcal{H}}$.

Zeeman term only

This means that

$$\hat{\mathcal{H}}_{ext} = \hat{\mathcal{H}}_Z = -\gamma\hbar B_0\hat{I}_z \tag{5.41}$$

or in physical terms, that we are looking at a system undergoing precession in the rotating frame.

In this case, the rotating frame Hamiltonian is

$$\widetilde{\mathcal{H}} = \hat{R}_z(-\omega_{rf}t)\left(-\gamma\hbar B_0\hat{I}_z\right)\hat{R}_z(\omega_{rf}t) - \hbar\omega_{rf}\hat{I}_z \tag{5.42}$$

As we saw before when a rotation operator and the angular momemtum operator are along the same axis, the rotation operator has no effect. Therefore,

$$\widetilde{\mathcal{H}} \quad = \quad -\gamma\hbar B_0\hat{I}_z - \hbar\omega_{rf}\hat{I}_z$$

$$
\begin{aligned}
&= \omega_0 \hbar \hat{I}_z - \hbar \omega_{rf} \hat{I}_z \\
&= (\omega_0 - \omega_{rf})\, \hbar \hat{I}_z \\
&= \Omega \hbar \hat{I}_z. \qquad (5.43)
\end{aligned}
$$

where ω_0 is the Larmor frequency. This is the same Ω we saw in Chapter 2.

RF Pulse

In this case

$$
\begin{aligned}
\hat{\mathcal{H}}_{ext} &= \hat{\mathcal{H}}_Z + \hat{\mathcal{H}}_{rf}(t) \\
&= \omega_0 \hbar \hat{I}_z - \gamma \hbar B_1 (\hat{R}_z(\omega_{rf} t) \hat{I}_x \hat{R}_z(-\omega_{rf} t)) \qquad (5.44)
\end{aligned}
$$

In the rotating frame, the first term is like the one we saw in the previous section and the second will have terms of $\hat{R}_z(-\theta)\hat{R}_z(\theta)$ to the left of I_x and terms in $\hat{R}_z(\theta)\hat{R}_z(-\theta)$ to the right, where $\theta = \omega_{rf} t$. So it would appear that we could simplify the equation of the rotating frame Hamiltonian to

$$
\begin{aligned}
\widetilde{\mathcal{H}} &= \Omega \hbar \hat{I}_z + (-\gamma B_1) \hbar \hat{I}_x \\
&= \Omega \hbar \hat{I}_z + \omega_{nut} \hbar \hat{I}_x, \qquad (5.45)
\end{aligned}
$$

where ω_{nut} is the nutation frequency of our rf pulse.

This is a valid equation if the phase of the pulse ϕ_p is 0. It is possible to generate pulses with non-zero phase. In this case, the rotation operators remain in the form

$$\begin{aligned}\widetilde{\mathcal{H}} &= \Omega\hbar\hat{I}_z + (-\gamma B_1)\hbar\hat{R}_z(\phi_p)\hat{I}_x R_z(-\phi_p) \\ &= \Omega\hbar\hat{I}_z + \omega_{nut}\hbar\hat{R}_z(\phi_p)\hat{I}_x R_z(-\phi_p) \\ &= \Omega\hbar\hat{I}_z + \omega_{nut}\hbar\left(\hat{I}_x cos(\phi_p) + \hat{I}_y sin(\phi_p)\right).\end{aligned} \tag{5.46}$$

since

$$\begin{aligned}\hat{\mathcal{H}}_{ext} &= \omega_0\hbar\hat{I}_z \\ &- \gamma\hbar B_1(\hat{R}_z(\omega_{rf}t + \phi_p)\hat{I}_x\hat{R}_z(-\omega_{rf}t - \phi_p)).\end{aligned} \tag{5.47}$$