

The Basic of NMR (Nuclear Magnetic Resonance)

Theint Theint

PHY 492 (Physics Seminar)

April 20th 2011

1. Introduction

Nuclear Magnetic Resonance (NMR) is a very powerful analytical method not only because both liquid and solid state sample can be studied but also because it is a nondestructive method. Other analytical methods, such as Mass Spectrometry, destroy the sample during the analysis therefore sample cannot be reused after the analysis. However sample in the NMR experience can be reused for other analytical methods. Additionally NMR analysis can yield various information such as structure, dynamic, and conformation of biological and chemical samples. Therefore many new applications of NMR are emerging rapidly nowadays and making it a more powerful tool than before. Recently, a professor from University of California, Davis came up with an unconventional idea of using NMR as explosive materials detector for the security check points at the airports (Tugman, 2011). If the research is successful, there will be no more hassle of throwing away our liquid bottles at the airport check points.



Figure 1. Pacific Northwest National Laboratory's high magnetic field (800 MHz, 18.8 T) NMR spectrometer. (Woodley, 2010)

1. Basic NMR Theories

Subatomic particles such as electrons, protons and neutrons can be imagined as spinning particles. In most cases, those spin are paired together and result in net spin 0. However in some cases, the nuclear have an overall spin. Generally the overall spin of nucleus can be divided into three main groups. The first one is spin 0 nuclei, which occur when the number of neutrons and protons are even. The second one is spin-half nuclei, which has odd total number of neutrons and protons. Lastly when both the numbers of neutrons and protons are both odd, the nuclei are called inter spin nuclei (Levitt, 2009).

2. Energy Level and Zeeman Splitting

Overall spin of the nuclei is very important – quantum mechanically, the nucleus of spin I will possibly have $2I+1$ orientations. In the absence of an external magnetic field, those orientations have equal energy. However when the external magnetic field is applied, the energy levels split. This phenomenon of shifting of the energy levels is known as Zeeman effect (A. Carrington, 1967). The perturbation in energy can be expressed as follow;

$$\Delta E = -\mu_0 \cdot \mathbf{B}_0$$

Where ΔE = energy difference

μ_0 = magnetic dipole moment

\mathbf{B}_0 = applied magnetic field

For example, in the presence of an external magnetic field (B_0), nuclei such as ^1H and ^{13}C split into two different energy states known as α and β (Fig.2). In NMR experiences, radio frequency (RF) was used to excite lower level spin to higher level spin and observe the absorption of the energies from different nuclei. Therefore differences in energy can also be calculated by using the energy of the applied radio frequency.

$$\Delta E = h\nu$$

Where h = plank's constant (6.626×10^{-34} J s)

ν = frequency of the photon = $\gamma \mathbf{B}_0$

The energy difference becomes,

$$\Delta E = \frac{h\gamma B_0}{2\pi}$$

Where γ = gyromagnetic ratio of a specific spin

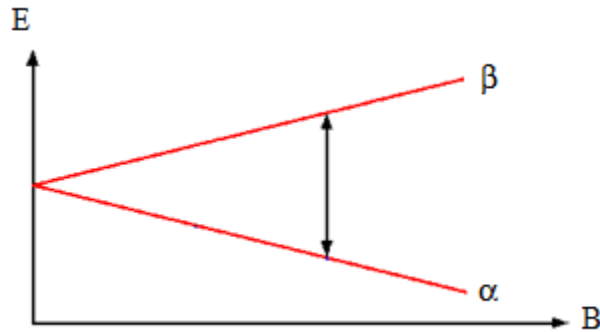


Figure 2. Energy splitting of nuclear spin states in the present of magnetic field.

It can be clearly seen that the difference in energy between the two spin states is proportional to the strength of external magnetic field.

When there is energy difference, the transition between different energies can be induced. A nucleus of low energy can be excited to the higher frequency by introducing with the electromagnetic radiation of proper energy. During NMR experiment, the electromagnetic radiation which has equal energy to that of the energy differences between two adjacent spin states. The nuclei from the lower spin state absorb energy and excited to the higher level. By sweeping the applied electromagnetic frequency, the graph of frequency versus absorbed energy can be generated. The transitions between spin states are govern by the selection rule. Selection rule states that the transition between two spin states is allowed only when the difference between the spin states is exactly one. It can be expressed as:

$$\Delta m = m(\text{inintial}) - m(\text{final}) = \pm 1$$

Ideally in a homogeneous system of one kind of nucleus, the NMR spectrum will show a single peak at a specific frequency. However in reality, the nucleus is influenced by the environment - some environments increase the energy separation and some lowers the energy separation (Levitt, 2009). These changes in energy can be related to frequency, and the

differences in frequencies are called chemical shifts. The chemical nature of an atom can be analyzed by look at the frequencies at which the spin transition occurs (Harris, 1983).

3. Nuclear Spin, and J-coupling

In NMR experiments, we observe the interaction of the nucleus respect to the external magnetic field and the electrons around it. We have known from quantum mechanics that the nucleus has spin property and those spin states are usually identify as nuclear spin quantum number(I). Even though many different spin states are presented in the nature, in NMR we focus on spin $\frac{1}{2}$ nuclei.

3.1 One Spin

When spin-half nuclei are placed in a magnetic field, it gives rises to two different energy levels known as spin up and spin down states which are often as m quantum numbers. $m = \frac{1}{2}$ state is denotes as α and described as spin up. $m = -\frac{1}{2}$ is denotes as β and sometimes described as spin down (Fig 2). The nuclei we are interested in are lower energy level α state. Due to the Boltzmann distribution, lower energy level (α) has slightly more nuclei than higher level (β). Radio frequency wave is used to excite lower energy spin to higher energy spin and the absorbed energy was translated to frequency versus absorption graph as NMR spectrum (Hornak, 1997), (Keeler, 2001).

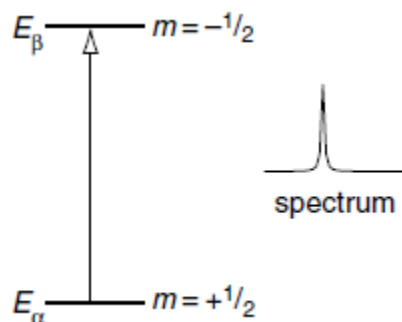


Figure 3. Energy diagram of a spin $\frac{1}{2}$ nucleus and frequency domain spectrum (Keeler, 2001).

3.2 Two Spin

If we only have one spin in our system, we will have two states $m = \frac{1}{2}$ and $m = -\frac{1}{2}$. If we have two spins in our system, each of them will have both α and β states and there are four possible combinations of their spin states, known as $\alpha_1\alpha_2$, $\alpha_1\beta_2$, $\beta_1\alpha_2$, and $\beta_1\beta_2$. these four possibilities correspond to the four energy levels. The energies states can be represented as in the following table:

Number	Spin states	Energy
1	$\alpha\alpha$	$+\frac{1}{2} V_{0,1} + \frac{1}{2} V_{0,2}$
2	$\alpha\beta$	$+\frac{1}{2} V_{0,1} - \frac{1}{2} V_{0,2}$
3	$\beta\alpha$	$-\frac{1}{2} V_{0,1} + \frac{1}{2} V_{0,2}$
4	$\beta\beta$	$-\frac{1}{2} V_{0,1} - \frac{1}{2} V_{0,2}$

The second column gives the spin states of the two spins, 1 and 2 respectively. The energy equation can be represented in the general form as follow:

$$E_{m_1 m_2} = m_1 V_{0,1} + m_2 V_{0,2} + m_1 m_2 J_{12}$$

Where m_1 and m_2 are the m values for spin 1 and 2 and $V_{0,1}$ and $V_{0,2}$ are Larmor frequencies of the spins. J_{12} arises from the J-coupling of the interaction between two nuclear spin due to the influence of bounding electrons. J-coupling is usually quoted in Hz. The J-coupling represents the great link between NMR and the chemistry. While the chemical shift indicates the local electronic environment, the J-coupling provides the direct spectral manifestation of the chemical bond. Two spins have measurable J-coupling if they are only a few chemical bonds away from each other. Therefore J-coupling is exclusively intramolecular property (Keeler, 2001).

If the two spins are of equal type, their gyromagnetic ratio will be equal and such kind of system is known as homonuclear. When the two spins are of different types, for example proton and carbon, such system will be described as hetronuclear.

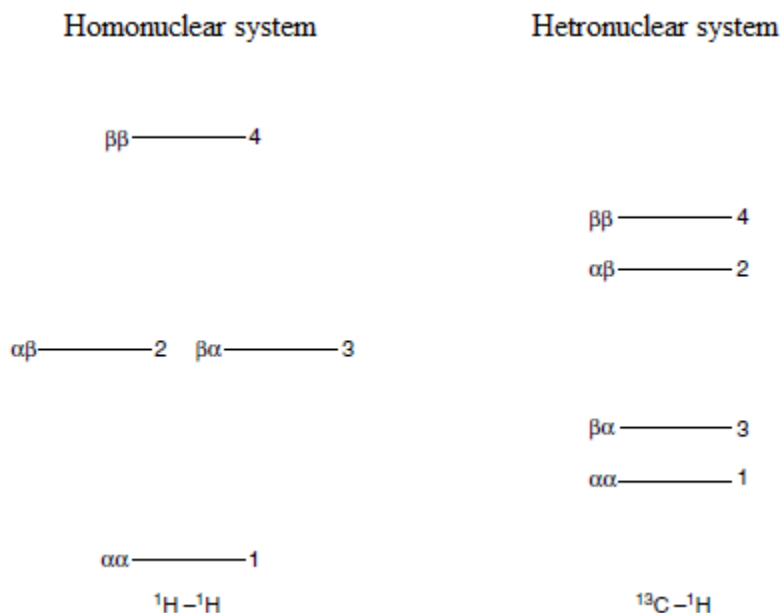


Figure 4. Energy diagram of homonuclear (protons) and hetronuclear (^1H and ^{13}C) systems (Keeler, 2001).

For a homonuclear system, Larmor frequencies are much greater than the J-couplings. In such case, the contribution of J-coupling to the overall energy becomes insignificant and the energies of the $\alpha\beta$ and $\beta\alpha$ states are very similar, yet very different from the other two states. For the hetronuclear system, Larmor frequencies of the spins are different and give rises to four different energy levels. The differences in the splitting of the energy levels for the two systems are described in the figure (4).

The energy levels for the two state systems (Hetronuclear) and corresponding schematic spectrum are shown in figure (5). In energy levels diagram on the left, the arrows show the allowed transitions and in the schematic spectrum on the right, it is assumed that the Larmor frequency of the spin 2 is greater in magnitude than that of spin 1. Therefore the J-coupling peak for spin 2 flipping appears at higher frequency in the spectrum. The distance between two split absorption lines is called the J coupling constant or the spin-spin splitting constant and is a measure of the magnetic interaction between two nuclei.

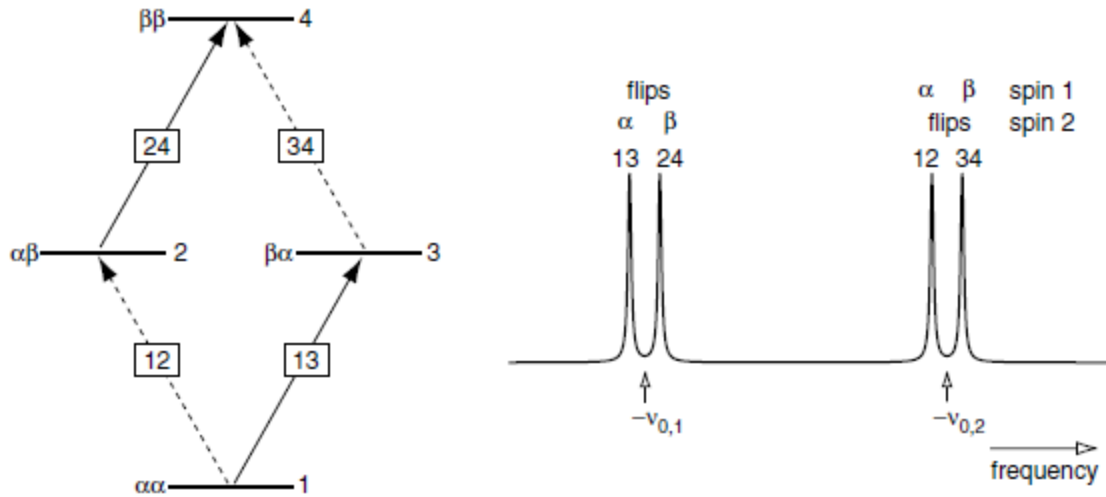


Figure 5. The energy levels for the two state systems and corresponding schematic spectrum (Keeler, 2001).

4. Chemical Shift

When an atom or a molecule is placed in a magnetic field, the electrons circulate about the direction of the applied magnetic field and cause a small magnetic field at the nucleus which opposes the externally applied field. Therefore the effective magnetic field at the nucleus is normally smaller than the applied field by a constant, which is usually noted as σ . This phenomenon is called shielding.

$$B_{\text{Effective}} = B_0 (1 - \sigma)$$

However in some molecules, such as benzene, the resonating π electrons in the benzene ring induced small magnetic field which is in the same direction as the applied field and hence increase the magnetic field experienced by the nuclei (Figure 6). This kind of phenomenon is called deshielding. In the following figure, the magnetic field (B_0) is applied in the positive Z direction, and the induced current in the ring is in the clockwise direction when look down from above (Hornak, 1997).

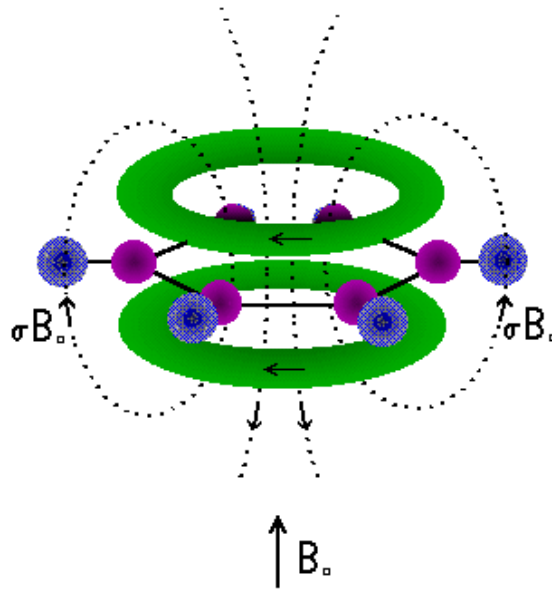


Figure 6. Effect of the changes in direction of induced magnetic field in benzene molecules (Hornak, 1997).

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The effective field at each nucleus directly related to the electron density and the chemical shift is the measuring of changes in the effective field for different nuclei in a molecule or a compound (NHM).

The appearances of the resonance frequency of the NMR signals depend on both the external magnetic field strength (B_0) and the applied radio frequency (RF). However bigger magnet can exert larger magnetic field to achieve higher frequency and yield higher resolution spectra. Depending on the strength of the magnet, the signal of the same frequency can show up at different locations on the spectra and it will be hard to compare one spectra acquired from different magnet. In order to overcome this problem, a standard compound was added to the spectrum as the reference. Normally TMS (tetramethyl silane,) was used as the standard, which appears as one sharp peak on the spectrum due to its high molecular symmetry (Figure 7). The difference in the resonance frequency and that of the reference peak was divided by the frequency of the magnet in order to yield the ultimate location of the signals. The result of this operation is known as Chemical shift (δ) and it can be expressed as follow:

$$\delta = \frac{|f_R - f_S|}{f_M}$$

Where f_R = frequency of the reference

f_S = frequency of the resonance frequency

f_M = frequency of the magnet

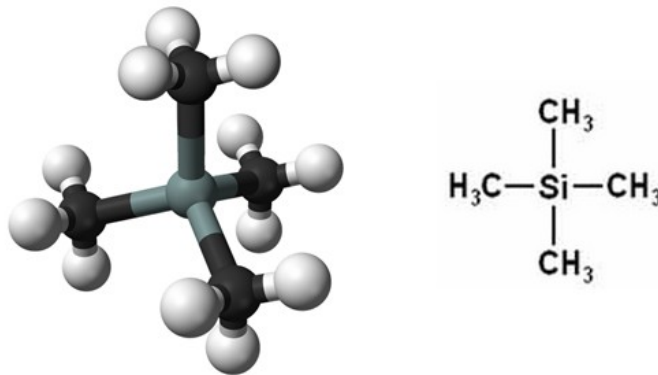


Figure 7. . Tetramethyl Silane.

5. Larmor Precession

5.1 Vector Model

The splitting of energy levels of a nucleus due to the applied magnetic field can also be represented by vector model by picturing the vectors as precessing around the external magnetic field. First magnetized nuclear spin vector is tipped an angle (α) to the external magnetic field, B_0 , by using RF pulse. When it is tipped away from the z axis, the spin vector rotate about the direction of the magnetic field sweeping out a cone with angle (α) Fig. 5. The vector is precessing about the z axis and the precession is called Larmor frequency, $\omega = \gamma B_0$. Therefore the energy difference for a spin $\frac{1}{2}$ nucleus in magnetic field is given by $\Delta E = \frac{h\nu B}{2\pi}$. If the RF pulse at the Larmor frequency is applied to the nucleus, the nuclear spin vector will be tipped away from the original vector position, direction of the main magnetic field, Z. The spin vector will continue to precess about the Z axis until it comes to rest at the original vector position along Z axis. During the precession, the nucleus will emit energy as Rf pulse. Emitted Rf pulses can later be translated to frequency domain for the analysis. Different nuclei experience different magnetic field. Hence they absorb different Larmor frequency and their emitted energy frequencies show up at different places on NMR spectrum (Keeler, 2001).

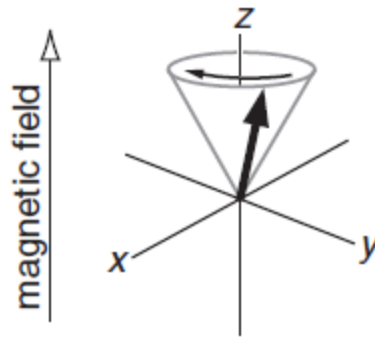


Figure 8. Larmor precession in vector model. The bulk magnetization is in the Z direction and the spin vector precesses about the Z axis (Keeler, 2001).

5.2 Quantum mechanical model

The Larmor precession can also be explained by the quantum mechanical model. For a spin $\frac{1}{2}$ particles, their spin up and spin down eigenstates can be represent by χ_+ and χ_- matrixes respectively. The two-element column matrixes can also be referred as spinor.

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\chi = a\chi_+ + b\chi_- = \begin{pmatrix} a \\ b \end{pmatrix}$$

When the spin $\frac{1}{2}$ particle in placed in uniform magnetic field of the z-direction,

$$\mathbf{B} = B_0 \hat{k}$$

Hamiltonian for the particle is

$$\mathbf{H} = -\gamma B_0 \mathbf{S}_z$$

In matrix form

$$\mathbf{H} = -\frac{\gamma B_0 \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The Hamiltonian returns the following energies (eigenstates)

$$E_+ = -\frac{\gamma B_0 \hbar}{2}$$

$$E_- = + \frac{\gamma B_0 \hbar}{2}$$

E_+ and E_- are the energies for the spin up and down states. Same as the classical results, the energy is lower for the spin up state, when the dipole moment is parallel to the applied magnetic field. Since the Hamiltonian is time-independent, the general solution can be written as follow;

$$\chi(t) = a\chi_+ e^{-iE_+t/\hbar} + b\chi_- e^{-iE_-t/\hbar}$$

Substituting E_+ and E_- values,

$$\chi(t) = \begin{pmatrix} a e^{\frac{i\gamma B_0 t}{2}} \\ b e^{\frac{-i\gamma B_0 t}{2}} \end{pmatrix}$$

At time $t=0$

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

$$|a|^2 + |b|^2 = 1$$

$|a|^2$ and $|b|^2$ are probability of finding the particles in the spin up and down states. Regardless of any condition, the total probability has to sum up to 1. We can write $a = \cos\left(\frac{\alpha}{2}\right)$ and $b = \sin\left(\frac{\alpha}{2}\right)$, in this way we can still keep the property of $|a|^2 + |b|^2 = 1$.

$$\chi(t) = \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ \sin\left(\frac{\alpha}{2}\right) e^{\frac{-i\gamma B_0 t}{2}} \end{pmatrix}$$

Expectation values of S can be calculated by using $\chi(t)$,

$$\begin{aligned} \langle \mathbf{S}_x \rangle &= \chi(t)^\dagger \mathbf{S}_x \chi(t) \\ &= \left(\cos\left(\frac{\alpha}{2}\right) e^{\frac{-i\gamma B_0 t}{2}} \quad \sin\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \right) \times \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ \sin\left(\frac{\alpha}{2}\right) e^{\frac{-i\gamma B_0 t}{2}} \end{pmatrix} \end{aligned}$$

$$\begin{aligned}
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \quad \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \right) \begin{pmatrix} \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \\ \cos\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \end{pmatrix} \\
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right) \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t} + \sin\left(\frac{\alpha}{2}\right) \cos\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t} \right) \\
&= \frac{\hbar}{2} \cos\left(\frac{\alpha}{2}\right) \sin\left(\frac{\alpha}{2}\right) (e^{-i\gamma B_0 t} + e^{i\gamma B_0 t})
\end{aligned}$$

Since $e^{ix} + e^{-ix} = 2\cos(x)$ and $\cos\left(\frac{x}{2}\right) \sin\left(\frac{x}{2}\right) = \frac{1}{2} \sin(x)$, the equation becomes,

$$\begin{aligned}
&= \frac{\hbar}{2} \sin(\alpha) \cos(\gamma B_0 t) \\
\langle S_y \rangle &= \chi(t)^\dagger S_y \chi(t) \\
&= \left(\cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \quad \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \right) x \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \\ \sin\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \end{pmatrix} \\
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right) e^{-i\gamma B_0 t/2} \quad \sin\left(\frac{\alpha}{2}\right) e^{i\gamma B_0 t/2} \right) \begin{pmatrix} \sin\left(\frac{\alpha}{2}\right) (-i) e^{-i\gamma B_0 t/2} \\ \cos\left(\frac{\alpha}{2}\right) (i) e^{i\gamma B_0 t/2} \end{pmatrix} \\
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right) \sin\left(\frac{\alpha}{2}\right) (-i) e^{-i\gamma B_0 t} + \sin\left(\frac{\alpha}{2}\right) \cos\left(\frac{\alpha}{2}\right) (i) e^{i\gamma B_0 t} \right) \\
&= \frac{i\hbar}{2} \cos\left(\frac{\alpha}{2}\right) \sin\left(\frac{\alpha}{2}\right) (-e^{-i\gamma B_0 t} + e^{i\gamma B_0 t})
\end{aligned}$$

Since $e^{ix} - e^{-ix} = 2i\sin(x)$ and $\cos\left(\frac{x}{2}\right) \sin\left(\frac{x}{2}\right) = \frac{1}{2} \sin(x)$,

$$\begin{aligned}
&= \frac{-\hbar}{2} \sin(\alpha) \sin(\gamma B_0 t) \\
\langle S_z \rangle &= \chi(t)^\dagger S_z \chi(t)
\end{aligned}$$

$$\begin{aligned}
&= \left(\cos\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} \quad \sin\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \right) \times \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ \sin\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} \end{pmatrix} \\
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right) e^{-\frac{i\gamma B_0 t}{2}} \quad \sin\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \right) \begin{pmatrix} \cos\left(\frac{\alpha}{2}\right) e^{\frac{i\gamma B_0 t}{2}} \\ \sin\left(\frac{\alpha}{2}\right) (-1) e^{-\frac{i\gamma B_0 t}{2}} \end{pmatrix} \\
&= \frac{\hbar}{2} \left(\cos\left(\frac{\alpha}{2}\right)^2 - \sin\left(\frac{\alpha}{2}\right)^2 \right)
\end{aligned}$$

Since $\cos\left(\frac{x}{2}\right)^2 - \sin\left(\frac{x}{2}\right)^2 = \cos(2x)$,

$$= \frac{\hbar}{2} \cos(\alpha)$$

$\langle S \rangle$ precesses about Z axis with angle α and its frequency is $\omega = \gamma B_0$. The frequency is known as Larmor frequency.

6. Conclusion

Some basic quantum mechanical and other related theories of Nuclear Magnetic Resonance Spectroscopy are explained in this paper. Above mentioned concepts are necessary in understanding the physic behind the NMR machine and the understanding of the machine comes play major part in designing new experimental methods using NMR and coming up with more interesting medium to study. It is good to be aware that the theory can go deeper in many aspects. However this paper covered the most important terms and concepts as well as offered well understanding of the theories at an undergraduate level.

References

1. A. Carrington, A. M. (1967). *Introduction To Magnetic Resonance*. Chapman and Hall.
2. Abragam, A. (1983). *Principles of Nuclear Magnetism*. Oxford University Press.
3. Bakhmutov, V. I. (2004). *Practical NMR relaxation for chemists*. John Wiley & Sons.
4. Freeman, R. (1997). *Spin choreography : basic steps in high resolution NMR*. Oxford: Oxford University Press.
5. Harris, R. (1983). *Nuclear Magnetic Resonance Spectroscopy*. Pitman.
6. Hornak, J. (1997). *The Basic of NMR* . Retrieved April 23, 2011, from www.cis.rit.edu: <http://www.cis.rit.edu/htbooks/nmr/bnmr.htm>
7. Keeler, J. (2001). *Understanding NMR Spectroscopy*. Retrieved Feb 22, 2011, from www-keeler.ch.cam.ac.uk: <http://www-keeler.ch.cam.ac.uk/lectures/Irvine/>
8. Levitt, M. H. (2009). *Spin Dynamics: Basics of Nuclear Magnetic Resonance*. Wiley .
9. Tugman, L. (2011, Feb 9). *Liquid scanner could make airport security checks easier*. Retrieved March 19, 2011, from CNN: <http://www.todaysthv.com/news/local/story.aspx?storyid=142752&catid=288>
10. Woodley, M. (2010). *Nuclear Magnetic Resonance*. Retrieved April 2, 2011, from [quincunx](http://www.quincunx.com/papers.html): <http://www.quincunx.com/papers.html>