

# Chapter2: Quantum Control and NMR spectroscopy

In last chapter, we talked about electron and its orbitals. Then we talked about spin of an electron, and showed how spin of an electron can be coupled to orbital angular momentum to give the fine structure of hydrogen. We then talked about coupling of the electron and orbital angular momentum to nuclear spin and studied hyperfine structure. In this chapter, we will entirely focus on the spin of nucleus and study methods to control and observe nuclear spin using magnetic fields. This brings us to the subject of NMR (Nuclear magnetic resonance) Spectroscopy, the focus of this chapter.

## 1 Nuclear Spin

Many atomic nuclei like  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  have the property that they behave like little bar magnets. They respond to magnetic fields. This property arises due to intrinsic angular momentum called spin. They are like little tops spinning around their axis. We studied all this in last chapter. Let recapitulate a bit.

You are familiar with earth spinning on its axis. This gives earth a angular momentum. Now imagine our earth was charged. Then spinning will give earth a magnetic moment. Imagine a loop of wire carrying current (circulating charge), then it has a magnetic moment  $M = IA$ , where  $I$  is the current and  $A$  area of the loop, from your basic physics. Now imagine a charge  $q$  going around in a loop of radius  $r$ , with angular velocity  $\omega$ . Then it makes  $\frac{\omega}{2\pi}$  rotations per sec. The current is then  $\frac{q\omega}{2\pi}$  and its magnetic moment is  $M = \frac{q\omega\pi r^2}{2\pi} = \frac{q}{2m}(mvr)$  where  $l = mvr$  is the angular momentum. Then  $M = \frac{q}{2m}L$ , the ratio  $\gamma = \frac{q}{2m}$  is called the gyromagnetic ratio, it relates angular momentum to magnetic moment.

Now suppose we have our charged spinning earth and we apply a magnetic field  $B = (B_x, B_y, B_z)$ , then  $M = (m_x, m_y, m_z) = \gamma(l_x, l_y, l_z)$  will experience a torque. This torque is  $M \times B$ , and changes the angular momentum as

$$\dot{L} = M \times B.$$

Relating  $M = \gamma L$ , we have,

$$\dot{M} = \gamma M \times B = -\gamma(B_z\Omega_z + B_x\Omega_y + B_y\Omega_x)M, \quad (1)$$

where  $\Omega_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$ ,  $\Omega_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}$  and  $\Omega_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$  are generator of rotation. For reasons that will become clear as we go on denote  $\omega_0 = -\gamma B_z$  and  $u = -\gamma B_x$  and  $v = -\gamma B_y$  and we get,

$$\dot{M} = (\omega_0 \Omega_z + u \Omega_x + v \Omega_y) M,$$

Note  $M(t) = \Theta M(0)$  where

$$\dot{\Theta} = (\omega_0 \Omega_z + u \Omega_x + v \Omega_y) \Theta, \quad \Theta(0) = I$$

Then  $\Theta \in SO(3)$ .  $M$  rotates in  $B$ . It precesses around  $B$ .

What concerns us is spin of a atomic nuclie. Many atomic nuclie like hydrogen, carbon, nitrogen have spin  $\frac{1}{2}$ . This gives the nucleus a angular momentum and hence magnetic moment. However because of quantum mechanics this angular momentum is quantized. If we measure its value in say  $z$  direction, we will only find two values  $\frac{\hbar}{2}$  and  $-\frac{\hbar}{2}$ , spinning up and spinning down. The state of the nucleus is then written as a two dimensional vector which is  $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$  when spinning up and  $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$  when spinning down. In general the state is defined by a two dimensional complex vector  $\psi = \begin{bmatrix} a \\ b \end{bmatrix}$ . For the spinning earth, we saw that its magnetic moment precesses in a magnetic field given by Eq. (1). The two dimesnional vector will also precess in a magnetic field with equation given by

$$\dot{\psi} = i\gamma(B_z \sigma_z + B_x \sigma_x + B_y \sigma_y) \psi = -i(\omega_0 \sigma_z + u \sigma_x + v \sigma_y) \psi, \quad (2)$$

where in Eq. (1), we have replaced the generator of rotations in real three dimensions  $\Omega_x, \Omega_y, \Omega_z$  with  $-i\sigma_x, -i\sigma_y, -i\sigma_z$  generator of rotations in complex two dimensions.

The evolution of  $\psi$  a two dimensional complex vector is given by  $\psi(t) = U\psi(0)$ , where

$$\dot{U} = -i(\omega_0 \sigma_z + u \sigma_x + v \sigma_y) U, \quad (3)$$

where  $U$  is in  $SU(2)$ .

In practice, in a NMR experiment, we have very large number of atoms of order  $10^{23}$  and each atom/nucleus has a spin state defined by a vector  $\psi_k$ , each  $\psi_k$  sees same magnetic field and hence evolves according to equation

$$\dot{\psi}_k = -i(\omega_0 \sigma_z + u \sigma_x + v \sigma_y) \psi_k, \quad (4)$$

We can form an average subspace spanned by these  $\psi_k$  as  $\rho = \frac{1}{N} \sum \psi_k \psi_k^\dagger$ .  $\rho$  is called the density matrix. Then  $\rho$  evolves as

$$\dot{\rho} = [-i(\omega_0\sigma_z + u\sigma_x + v\sigma_y), \rho] \quad (5)$$

$\rho$  is a two dimensional Hermitian matrix and can be written as

$\rho = \frac{1}{2}I + l_x\sigma_x + l_y\sigma_y + l_z\sigma_z$ , where  $L = (l_x, l_y, l_z)'$  represents average  $(x, y, z)$  angular momentum of the of the ensemble. To see this remember for a spinor  $\psi$

$$\langle L_z \rangle = \langle \psi | L_z | \psi \rangle = \langle \psi | \sigma_z | \psi \rangle \quad (6)$$

Then for a ensemble we have

$$\langle L_z \rangle = \frac{1}{N} \sum_k \langle \psi_k | \sigma_z | \psi_k \rangle = \frac{1}{N} \sum_k tr(\sigma_z | \psi_k \rangle \langle \psi_k |) = tr(\sigma_z \rho) = l_z \quad (7)$$

This average or classical angular momentum evolves as

$$\dot{L} = (\omega_0\Omega_z + u\Omega_x + v\Omega_y)L, \quad (8)$$

and denoting  $M = \gamma L$  we have the same Eq. (1). These are called Bloch equations. Thus we see how evolution of spin state of individual nuclei evolves as two dimensional complex vector and how the average angular momentum and magnetic moment of the spin ensemble evolves as a three dimensional Bloch vector.

Lets think of an ensemble in which all spins are up. Then all  $\psi_k = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$  and  $\rho = \frac{1}{2}I + \sigma_z$ . Thus  $l_z = 1$  and we have an ensemble with net z angular momentum 1.

Lets think of an ensemble in which all spins are down. Then all  $\psi_k = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$  and  $\rho = \frac{1}{2}I - \sigma_z$ . This  $l_z = -1$  and we have an ensemble with net z angular momentum -1.

Lets think of an ensemble in which all spins are  $\psi_k = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$  and  $\rho = \frac{1}{2}I + \sigma_x$ . This  $l_x = 1$  and we have an ensemble with net x angular momentum 1.

Now lets understand the basic NMR experiment. In an NMR experiment we have spins in a strong magnetic field along say z direction of order 10 – 20 Tesla. Earths magnetic field is around  $10^{-5}$  tesla. In this magnetic field, up spins have lower energy than down spins and so in thermal equilibrium, we have more spins up. The ratio of up to down spins is given by Boltzmann distribution and is  $\exp(\frac{\Delta E}{kT})$  where  $\Delta E = \mu \cdot B$  is energy difference between down and up spins, which is small, as magnetic moment  $\mu$  of a nuclear spin is small. Thus at room temperature at such high fields, only 1 in  $10^5$  spins preferentially points up. Thus

$\rho = \frac{1}{2}I + \alpha\sigma_z$ , where  $\alpha \sim 10^{-5}$ , none the less the sample has a net angular momentum along z and hence has a net magnetic moment along z direction. Thus in Eq. (1) we start

with  $M = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$ . Now we turn on x and y magnetic fields and rotate this vector to  $(1, 0, 0)'$ .

How this is done will be discussed shortly. But imagine we have rotated  $M$  to  $(1, 0, 0)'$  and we switch off  $u, v$  in Eq. (1). Then  $M$  just rotates around  $B_0$  and we have an evolution  $M(t) = (\cos \omega_0 t, \sin \omega_0 t, 0)$ . This rotating magnetic moment will induce an emf in a nearby coil with a frequency  $\omega_0$  and hence we can measure  $\omega_0$ . At fields of 14 tesla the  $\omega_0$  for hydrogen is 600 MHz, for carbon is 150 MHz, and for nitrogen is 60 MHz. Thus frequency of the induced emf tells us about chemical composition of the sample. This NMR can tell us about composition of the sample. Now we come to the question of how we use  $u, v$  to rotate  $M$  from  $(0, 0, 1)$  to  $(1, 0, 0)$ .

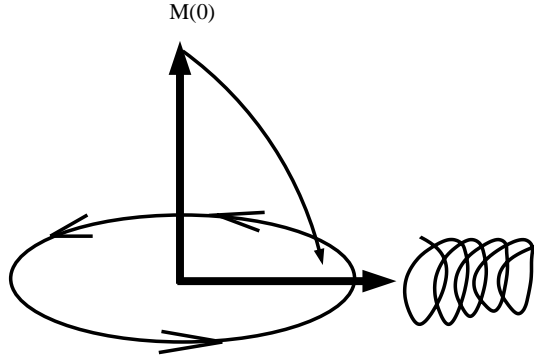


Figure 1: Figure shows how the magnetic moment  $M(0)$  along  $z$  direction is rotated to transverse plain and it then rotates around  $z$  field and induces a EMF in the coil.

In Eq. (1),  $B_0$  is much larger than  $B_x, B_y$  which are actually produced by rf-coil. To give an idea if  $\omega_0$  is 600 MHz, then  $u, v$  are only around 60 kHz. Around  $10^5$  times smaller. Then we ask how can such small  $u, v$  effect a change in  $M(0)$ . Beacuse suppose we choose  $u = 1$  and  $v = 0$ . Then since  $\omega_0$  is  $10^5$  times  $u$ . The Eq. (1) essentially is rotating around  $z$  axis. The figure 2 below

shows how the magnetic moment  $M(0)$  along  $z$  direction just rotates around an axis with a small tilt of  $z$  axis when we apply a constant control  $u$ . Then a constant control  $u$  will not rotates  $M(0)$  to transverse plain as desired, because  $u$  is too small compared to  $\omega_0$ . What works and is used is instead a oscillatory control input,  $(u, v) = (A \cos \omega_0 t, A \sin \omega_0 t)$ , with frequency same as  $\omega_0$ . To understand how this control works, Eq. (1)

$$\dot{X} = (\omega_0 \Omega_z + A \cos \omega_0 t \Omega_x + A \sin \omega_0 t \Omega_y) X, \quad A \ll \omega_0$$

we can write the above equation as

$$\dot{X} = (\omega_0 \Omega_z + A \exp(\omega_0 t \Omega_z) \Omega_x \exp(-\omega_0 t \Omega_z)) X,$$

Lets make a change of cordinates  $Y = \exp(-\omega_0 t \Omega_z) X$ , then

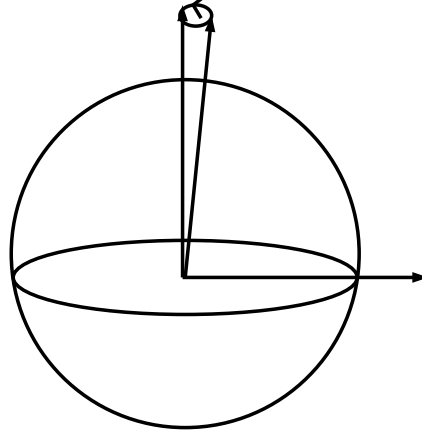


Figure 2: Figure shows how the magnetic moment  $M(0)$  along  $z$  direction just rotates around an axis with a small tilt of  $z$  axis when we apply a constant control  $u$ .

$$\dot{Y} = A\Omega_x Y,$$

this is great as  $\omega_0$  has disappeared and  $Y$  starting from  $Y(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$  rotates to  $Y(T) =$

$$\begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} \text{ at } T = \frac{\pi}{2A}.$$

Then  $X(T) = \exp(\omega_0 T \Omega_z) Y(T)$ , a vector on the equator. Thus we have been able to bring the Bloch vector in Eq. (1) to equator by use of an oscillatory controls. This is the first lesson in quantum control. The controls we apply are much weaker compared to drift in the system so constant control laws donot work. We need oscillatory controls. We need to excite the system on resonance.

## 1.1 Rotating Wave Approximation

In practice what we have is the system

$$\dot{X} = (\omega_0 \Omega_z + A \cos \omega_0 t \Omega_x) X, \quad A \ll \omega_0,$$

i.e, we only apply rf-field along X axis. We can write the above as

$$\dot{X} = (\omega_0 \Omega_z + \frac{A}{2} \exp(\omega_0 t \Omega_z) \Omega_x \exp(-\omega_0 t \Omega_z) + \frac{A}{2} \exp(-\omega_0 t \Omega_z) \Omega_x \exp(\omega_0 t \Omega_z)) X,$$

Lets make a change of cordinates  $Y = \exp(-\omega_0 t \Omega_z) X$ , then

$$\dot{Y} = \left( \frac{A}{2} \Omega_x + \frac{A}{2} \underbrace{\exp(-2\omega_0 t \Omega_z) \Omega_x \exp(2\omega_0 t \Omega_z)}_{\text{fast oscillating}} \right) Y,$$

We neglect the fast oscillating term as it oscillated much faster compared to rate at which it evolves  $\omega_0 \gg A$ . This is called rotating wave approximation. Then we have

$$\dot{Y} = \frac{A}{2} \Omega_x Y,$$

this is great as  $\omega_0$  has disappeared and  $Y$  starting from  $Y(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$  rotates to  $Y(T) =$

$$\begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} \text{ at } T = \frac{\pi}{A}.$$

Then  $X(T) = \exp(\omega_0 T \Omega_z) Y(T)$ , a vector on the equator. Thus we have been able to bring the Bloch vector in Eq. (1) to equator by use of an oscillatory controls.

We said at  $B_0$  of 14 T we have for hydrogen  $\omega_0 = 600$  MHz. This is not strictly true. Hydrogen nucleus has electrons around it. These moving/hovering electrons produce local magnetic fields and change the field from  $B_0$  to  $B_0(1 - \sigma_0)$  and hence  $\omega_0$  changes from to  $\omega_0(1 - \sigma_0) = \omega_0 + \Delta\omega$ . This  $\sigma_0$  is of order few parts per million, i.e.  $10^{-6}$  and hence when  $\omega_0 = 600$  Mhz we have  $\Delta\omega$  of order few kHz. This  $\sigma_0$  also called chemical shift is characteristic of a electronic environment of nucleus. We talked about it in this first chapter. We can measure  $\Delta\omega$ , when we measure frequencies in our EMF. For example in Ethanol molecule we have three hydrogen, each with different chemical environment and hence three different  $\Delta\omega$ . When we find three different  $\Delta\omega$  is our experiment at certain specific values, then we know we have a fingerprint spectrum of Ethanol. This way chemical shifts help us identify the molecules. Not only does NMR give information about the chemical composition but also the chemical shifts can identify compounds.

Now how do we rotate  $M$  to equator when we have many  $\Delta\omega$ .

To understand how control works now, consider Eq. (1)

$$\dot{X} = ((\omega_0 + \Delta\omega)\Omega_z + A \cos(\omega_0 t + \phi)\Omega_x + A \sin(\omega_0 t + \phi)\Omega_y) X, \quad A \ll \omega_0$$

Lets as before make a change of cordinates  $Y = \exp(-\omega_0 t \Omega_z) X$ , then

$$\dot{Y} = (\Delta\omega \Omega_z + A \cos \phi \Omega_x + A \sin \phi \Omega_y) Y,$$

this is great as before  $\omega_0$  has disappeared but  $\Delta\omega$  stays and we have to now choose  $A$  and

$\phi$  as functions to time so that  $Y(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$  rotates to  $Y(T) = \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}$ .

This is an important control problem because we want our control to work for all  $\Delta\omega$  in a given range. Size of  $\Delta\omega$  and  $A$  are comparable. This problem is called broadband

control. We now astudy this problem in stages. We first study how to rotate  $Y(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$

to  $Y(T) = \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}$ . This is called broadband inversion.

In summary, we learnt about single spin  $\frac{1}{2}$  whose state is a 2 dimensional complex vector evolving as

$$\dot{\psi} = -i(\underbrace{\omega_0\sigma_z}_{H_0} + u \underbrace{\sigma_x}_{H_1} + v \underbrace{\sigma_y}_{H_2})\psi, \quad (9)$$

As we saw this equation evolves as  $\psi(t) = U(t)\psi(0)$ , where  $U(t) \in SU(2)$ .

This is the simplest example of a quantum control system, where  $H_0$  is the drift Hamiltonian and  $H_1, H_2$  are control Hamiltonians.

## 1.2 Broadband Inversion (Chirp or Adiabatic following)

Let

$$\Omega_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad \Omega_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \quad \Omega_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

denote generator of rotations around  $x, y, z$  axis respectively. A x-rotation by flip angle  $\theta$  is  $\exp(\theta\Omega_x)$ . To fix ideas, we start be talking about single spin  $\frac{1}{2}$ .

Given the Bloch equations in rotating frame,

$$\dot{X} = (\omega_0\Omega_z + A \cos \phi \Omega_x + A \sin \phi \Omega_y)X,$$

where  $X$  is the magnetization vector and  $\omega_0$  the offset. The chirp pulse has instantaneous frequency  $\dot{\phi} = \omega = -C + at$  where  $a$  is the sweep rate and phase  $\phi(t) = -Ct + \frac{at^2}{2}$ . The frequency  $\omega$  is swept from  $[-C, C]$ , in time  $T = \frac{2C}{a}$  with offsets  $\omega_0$  in the range  $[-B, B]$ . See Fig. 3a.

In the interaction frame of the chirp phase,  $\phi(t)$ , we have  $Y(t) = \exp(-\phi(t)\Omega_z)X(t)$ , evolve as

$$\dot{Y} = ((\omega_0 - \omega)\Omega_z + A\Omega_x)Y = \omega_{\text{eff}} (\cos \theta(t) \Omega_z + \sin \theta(t) \Omega_y)Y, \quad (10)$$

where effective field strength  $\omega_{\text{eff}} = \sqrt{(\omega_0 - \omega(t))^2 + A^2}$  and  $\tan \theta(t) = \frac{A}{\omega_0 - \omega(t)}$ . See Fig. 3b.

Now in interaction frame of  $\theta$  where  $Z = \exp(-\theta(t)\Omega_y)Y$ , we have

$$\dot{Z} = (\omega_{\text{eff}}\Omega_z - \dot{\theta}\Omega_y)Z.$$

If  $\omega_{\text{eff}} \gg \dot{\theta}$ , which is true when sweep rate and rf-field strength satisfy  $a \ll A^2$ . Recall  $\tilde{\omega} = \sqrt{A^2 + (\omega_0 + C - at)^2}$ , and  $\tan \theta(t) = \frac{A}{(\omega_0 + C - at)}$ . This gives

$$\dot{\theta}(t) = \frac{Aa}{A^2 + (\omega_0 + C - at)^2}. \quad (11)$$

Largest value of  $\dot{\theta}$  is  $\frac{a}{A}$  and smallest value of  $\tilde{\omega} = A$ , then  $\omega_{\text{eff}} \gg \dot{\theta}$  when  $a \ll A^2$ .

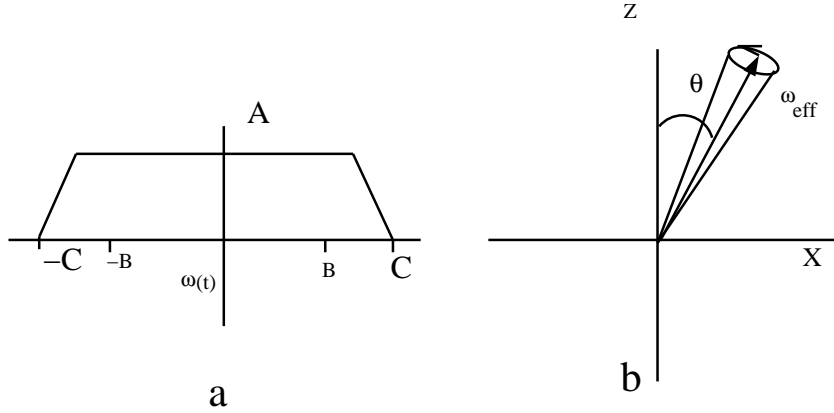


Figure 3: Fig. a shows the amplitude  $A$  of the chirp pulse as function of sweep frequency  $\omega(t)$  as it is swept from  $-C$  to  $C$ . Fig b shows how  $Y(t)$  in Eq. (31) follows the effective field as  $\theta$  goes from 0 to  $\pi$ .

Until now we talked about broadband

### 1.3 Broadband Excitation

In section, we present the theory of broadband excitation.

Let

$$\Omega_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad \Omega_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \quad \Omega_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

denote generator of rotations around  $x, y, z$  axis respectively. A x-rotation by flip angle  $\theta$  is  $\exp(\theta\Omega_x)$ .



We consider the problem of broadband excitation. Consider the evolution of the Bloch vector  $X$  of a spin  $\frac{1}{2}$  in a rotating frame, rotating around  $z$  axis at Larmor frequency.

$$\frac{dX}{dt} = (\omega\Omega_z + A(t)\cos\theta(t)\Omega_x + A(t)\sin\theta(t)\Omega_y)X, \quad (12)$$

where  $A(t)$  and  $\theta(t)$  are amplitude and phase of rf-pulse and we normalize the chemical shift in the range  $\omega \in [-1, 1]$ . In what follows, we choose phase  $\sin\theta(t) = 0$  and let

$$\frac{dX}{dt} = (\omega\Omega_z + u(t)\Omega_x)X, \quad (13)$$

for  $t \in [0, T]$ .

Going into the interaction frame of chemical shift, using  $Y(t) = \exp(-\omega(t - \frac{T}{2})\Omega_z)X(t)$ , we obtain,

$$\frac{dY}{dt} = u(t)(\cos\omega(t - \frac{T}{2})\Omega_x - \sin\omega(t - \frac{T}{2})\Omega_y)Y; \quad Y(0) = \exp(\omega\Omega_z\frac{T}{2})X(0). \quad (14)$$

We design  $u(t)$ , such that for all  $\omega$ , we have

$$\int_0^T u(t)\cos\omega(t - \frac{T}{2})dt \sim \frac{\pi}{2}, \quad \int_0^T u(t)\sin\omega(t - \frac{T}{2})dt = 0. \quad (15)$$

Divide  $[0, T]$  in intervals of step,  $\Delta t$ , over which  $u(t)$  is constant. Call them  $\{u_{-M}, \dots, u_{-k}, \dots, u_0\}$  over  $[0, \frac{T}{2}]$  and  $\{u_0, \dots, u_k, \dots, u_M\}$  over  $[\frac{T}{2}, T]$ .

$$\int_0^T u(t)\cos\omega(t - \frac{T}{2}) \sim (u_0 + \sum_{k=-M}^M u_k \cos(\omega k \Delta t))\Delta t, \quad (16)$$

where write  $\Delta t = \frac{\pi}{N}$  and choose  $u_k = u_{-k}$ . This insures that sine equation above is automatically satisfied. Then we get

$$\int_0^T u(t)\cos\omega(t - \frac{T}{2}) \sim 2 \sum_{k=0}^M u_k \cos(\omega k \Delta t)\Delta t = 2 \sum_{k=0}^M u_k \cos(kx)\Delta t, \quad (17)$$

where for  $x \in [-\frac{\pi}{N}, \frac{\pi}{N}]$ , we have  $2 \sum_{k=0}^M u_k \cos(kx)\Delta t \sim \theta$  and 0 for  $x$  outside this range. This is a Fourier series, and we get the Fourier coefficients as,

$$u_0 = \frac{\theta}{2\pi}; \quad u_k = \frac{2\theta \sin(\frac{k\pi}{N})}{\pi \frac{2k\pi}{N}}. \quad (18)$$

For  $\theta = \frac{\pi}{2}$ , we get,

$$u_0 = \frac{1}{4}; \quad u_k = \frac{\sin(\frac{k\pi}{N})}{\frac{2k\pi}{N}}. \quad (19)$$

In Eq. (14), using small flip angle  $\theta$ , we approximate,

$$Y(T) \sim \exp\left(\int_0^T u(t) \cos \omega(t - \frac{T}{2}) \Omega_x\right) Y(0). \quad (20)$$

Starting from the initial state  $X(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$ , we have from Eq. 14,

$$X(T) \sim \exp\left(\frac{\omega T}{2} \Omega_z\right) \exp\left(\int_0^T u(t) \cos \omega(t - \frac{T}{2}) \Omega_x\right) \exp\left(\frac{\omega T}{2} \Omega_z\right) X(0) \sim \exp\left(\frac{\omega T}{2} \Omega_z\right) \exp\left(\frac{\pi}{2} \Omega_x\right) X(0). \quad (21)$$

This state is dephased on the Bloch sphere equator. We show how using a double adiabatic sweep, we can refocus the phase. Let  $\Theta(\omega)$  be the rotation for a adiabatic inversion of a spin. We can use Euler angle decomposition to write,

$$\Theta(\omega) = \exp(\alpha(\omega) \Omega_z) \exp(\pi \Omega_x) \exp(\beta(\omega) \Omega_z). \quad (22)$$

The center rotation should be  $\pi$  for  $\Theta(\omega)$  to do inversion of  $\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \rightarrow \begin{bmatrix} 0 \\ 0 \\ -1 \end{bmatrix}$ .

We can use this to refocus the forward free evolution. Observe

$$\Delta(\omega, \frac{T}{2}) = \exp\left(-\frac{\omega T}{2} \Omega_z\right) = \Theta(\omega) \exp\left(\frac{\omega T}{2} \Omega_z\right) \Theta(\omega). \quad (23)$$

Then

$$\Delta(\omega, \frac{T}{2}) X(T) = \Theta(\omega) \exp\left(\frac{\omega T}{2} \Omega_z\right) \Theta(\omega) X(T) \sim \exp\left(\frac{\pi}{2} \Omega_x\right) X(0), \quad (24)$$

which is a broadband excitation.

The pulse sequence consists of a sequence of x-phase pulses, which produce the evolution

$$U(\omega, \theta) = \exp\left(\frac{\omega T}{2} \Omega_z\right) \exp(\theta \Omega_x) \exp\left(\frac{\omega T}{2} \Omega_z\right) \quad (25)$$

where  $\theta = \frac{\pi}{2}$ , as described above, followed by a double sweep rotation  $\Delta(\omega, \frac{T}{2})$ . From Eq. (19) this requires a peak amplitude of  $u(t) \sim \frac{1}{2}$ . We now show how we can accomplish the

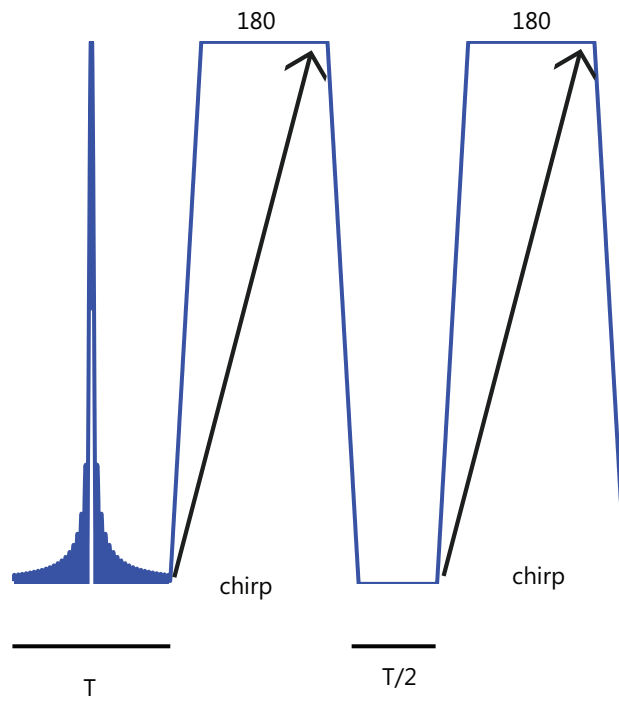


Figure 4: The figure shows the amplitude of the basic pulse sequence with a double sweep that performs broadband excitation as in Eq. (24).

above with lower peak amplitude, using multiple sweeps. If peak amplitude is  $\frac{1}{4} \leq u < \frac{1}{2}$ , we can prepare  $U(\omega, \frac{\pi}{4})$  and combine two such rotations with two double sweeps as follows

$$U_1 = \Delta(\omega, \frac{T}{2}) U(\omega, \frac{\pi}{4}) \Delta(\omega, T) U(\omega, \frac{\pi}{4}). \quad (26)$$

In general, if  $\frac{1}{2n} \leq u < \frac{1}{2(n-1)}$ , then we can produce a broadband excitation as

$$U_1 = \Delta(\omega, \frac{T}{2}) U(\omega, \frac{\pi}{2n}) \left( \Delta(\omega, T) U(\omega, \frac{\pi}{2n}) \right)^{n-1}. \quad (27)$$

When  $n = 3$ , we do three double sweeps.

Thus we can produce broadband excitation for arbitrary small rf-amplitude or viceversa, for a given rf-amplitude, we can cover arbitrary large bandwidths.

We talked about broadband excitations. Now we discuss broadband  $\frac{\pi}{2}$  rotations. This is simply obtained from above by an initial double sweep. Thus

$$U_1 = \Delta(\omega, \frac{T}{2}) U(\omega, \frac{\pi}{2}) \Delta(\omega, \frac{T}{2}), \quad (28)$$

is a  $\frac{\pi}{2}$  rotation around  $x$  axis.

If peak amplitude is  $\frac{1}{4} \leq u < \frac{1}{2}$  we can prepare  $U(\omega, \frac{\pi}{4})$  and combine two such rotations with three double sweeps as follows

$$U_1 = \Delta(\omega, \frac{T}{2}) U(\omega, \frac{\pi}{4}) \Delta(\omega, T) U(\omega, \frac{\pi}{4}) \Delta(\omega, \frac{T}{2}), \quad (29)$$

to get a broadband  $\frac{\pi}{2}$  rotation around  $x$  axis.

In general, if  $\frac{1}{2n} \leq u < \frac{1}{2(n-1)}$ , then we can produce a broadband  $\frac{\pi}{2}$ ,  $x$  rotation as

$$U_1 = \Delta(\omega, \frac{T}{2}) U(\omega, \frac{\pi}{2n}) \left( \Delta(\omega, T) U(\omega, \frac{\pi}{2n}) \right)^{n-1} \Delta(\omega, \frac{T}{2}). \quad (30)$$

## 2 Simulations

We normalize  $\omega$  in Eq. (12), to take values in the range  $[-1, 1]$ . We choose time  $\frac{T}{2} = M\pi$ , where we choose  $M = 10$  and  $N = 20$  in  $\Delta t = \frac{\pi}{N}$  in Eq. (16). Choosing  $\theta = \frac{\pi}{2}$  and coefficients  $u_k$  as in Eq. (19), we get the value of the Eq. (17) as a function of bandwidth as shown in left panel of Fig. 5. This is a decent approximation to  $\frac{\pi}{2}$  over the entire bandwidth. The right panel of Fig. 5, shows the excitation profile i.e., the  $-y$  coordinate of the bloch vector after application of the pulse in Eq. (24), where we assume that adiabatic inversion is ideal. The peak rf-amplitude  $A \sim \frac{1}{2}$ .

Next, we implement the non-ideal adiabatic sweep, by sweeping from  $[-1.5, 1.5]$  in 150 units of time with amplitude  $A$ . The shape of chirp is as in Fig. 4, with peak amplitude

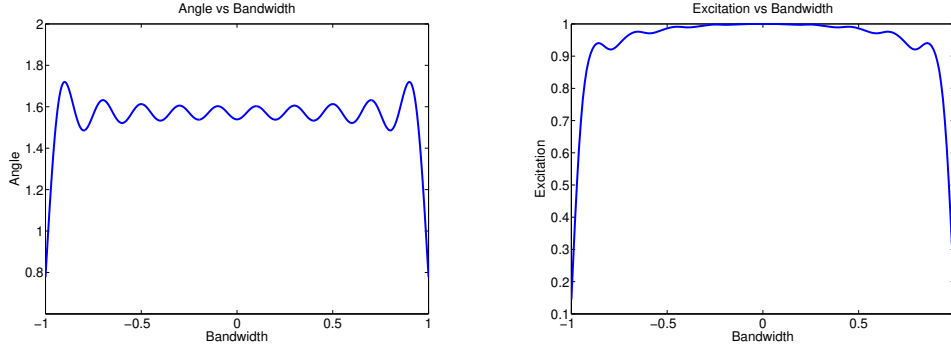


Figure 5: Left panel shows value of the Eq. (17) as a function of bandwidth when we choose  $T = 20\pi$  and  $\Delta = \frac{\pi}{20}$ . The right panel shows the excitation profile i.e., the  $-y$  coordinate of the Bloch vector after application of the pulse in Eq. (24), with  $u_k$  as in Eq. (19) and we assume that adiabatic inversion is ideal. This shows that approximation in Eq. (20) works well. The peak rf-amplitude  $A \sim \frac{1}{2}$ .

of chirp when we sweep between  $[-1, 1]$ . This gives a sweep rate  $\frac{1}{50} \ll A^2$ , where  $A = \frac{1}{2}$ . The resulting excitation profile of Eq. (24) is shown in Fig. 6 A, where we show the  $-y$  coordinate of the Bloch vector. For  $A = 10$  kHz, this pulse takes 3.82 ms, and excites a bandwidth of  $[-20, 20]$  kHz.

Next, we simulate the excitation with reduced amplitude  $A = \frac{1}{4}$ , as in Eq. (26). This requires to perform double sweep twice, as in Eq. (26). Adiabatic sweep is implemented as above by sweeping  $[-1.5, 1.5]$  in 300 units of time. This gives a sweep rate  $\frac{1}{100} \ll A^2$ , where  $A = \frac{1}{4}$ . The resulting excitation profile of Eq. (26) is shown in Fig. 6 B, where we show the  $-y$  coordinate of the Bloch vector. For  $A = 10$  kHz, this pulse takes 6.41 ms, and excites a bandwidth of  $[-40, 40]$  kHz.

Next, we simulate the excitation with reduced amplitude  $A = \frac{1}{6}$ , as in Eq. (27) for  $n = 3$ . This requires to perform double sweep thrice as in Eq. (27). Adiabatic sweep is implemented as above by sweeping  $[-1.5, 1.5]$  in 800 units of time. This gives a sweep rate  $\frac{3}{800} \ll A^2$ , where  $A = \frac{1}{6}$ . The resulting excitation profile of Eq. (27) is shown in Fig. 6 C, where we show the  $-y$  coordinate of the Bloch vector. For  $A = 10$  kHz, this pulse takes 14.32 ms, and excites a bandwidth of  $[-60, 60]$  kHz.

Next, we simulate the broadband  $x$  rotation as in Eq. (28), with peak amplitude  $A = \frac{1}{2}$ . This requires to perform double sweep twice as in Eq. (28). Adiabatic sweep is implemented as above by sweeping  $[-1.5, 1.5]$  in 150 units of time. This gives a sweep rate  $\frac{1}{50} \ll A^2$ , where  $A = \frac{1}{2}$ . The resulting excitation profile of Eq. (28) is shown in Fig. 7 A, where we show the  $z$  coordinate of the Bloch vector starting from initial  $y = 1$ . For  $A = 10$  kHz, this pulse takes 6.66 ms, and excites a bandwidth of  $[-20, 20]$  kHz.

Next, we simulate the broadband  $x$  rotation as in Eq. (29), with peak amplitude  $A = \frac{1}{4}$ . This requires to perform double sweep thrice as in Eq. (29). Adiabatic sweep is implemented by sweeping  $[-1.5, 1.5]$  in 300 units of time. This gives a sweep rate  $\frac{1}{100} \ll A^2$ , where  $A = \frac{1}{4}$ . The resulting excitation profile of Eq. (29) is shown in Fig. 7 B, where we show the  $z$  coordinate of the Bloch vector starting from initial  $y = 1$ . For  $A = 10$  kHz, this pulse takes 9.0049 ms, and excites a bandwidth of  $[-40, 40]$  kHz.

Next, we simulate the broadband  $x$  rotation as in Eq. (30), with peak amplitude  $A = \frac{1}{6}$  and  $n = 3$ . This requires to perform double sweep four times as in Eq. (30). Adiabatic sweep is implemented by sweeping  $[-1.5, 1.5]$  in 800 units of time. This gives a sweep rate  $\frac{3}{800} \ll A^2$ , where  $A = \frac{1}{6}$ . The resulting excitation profile of Eq. (30) is shown in Fig. 7 C, where we show the  $z$  coordinate of the Bloch vector starting from initial  $y = 1$ . For  $A = 10$  kHz, this pulse takes 18.66 ms, and excites a bandwidth of  $[-60, 60]$  kHz.

### 3 Chirp Excitation

We now look at another method of broadband excitation. We present the theory of chirp excitation.

Let

$$\Omega_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}, \quad \Omega_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}, \quad \Omega_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

denote generator of rotations around  $x, y, z$  axis respectively. A  $x$ -rotation by flip angle  $\theta$  is  $\exp(\theta\Omega_x)$ .

A chirp excitation pulse is understood as concatenation of three rotations

$$\underbrace{\exp(\theta_0\Omega_y)}_{III} \underbrace{\exp(\alpha\Omega_x)}_{II} \underbrace{\exp(\theta_0\Omega_y)}_I,$$

which satisfy  $\cos \alpha = \tan^2 \theta_0$ . Lets see how.

Given the Bloch equation,

$$\dot{X} = (\omega_0\Omega_z + \omega_1 \cos \phi \Omega_x + \omega_1 \sin \phi \Omega_y)X,$$

where  $X$  is the magnetization vector, the chirp pulse has instantaneous frequency  $\dot{\phi} = \omega = -A + at$  where  $a$  is the sweep rate and phase  $\phi(t) = -At + \frac{at^2}{2}$ . The frequency  $\omega$  is swept from  $[-A, A]$ , in time  $T = \frac{2A}{a}$  with offsets  $\omega_0$  in the range  $[-B, B]$ .

In the interaction frame of the chirp phase,  $\phi(t)$ , we have  $Y(t) = \exp(-\phi(t)\Omega_z)X(t)$ , evolve as

$$\dot{Y} = ((\omega_0 - \omega)\Omega_z + \omega_1\Omega_x)Y = \omega_{\text{eff}} (\cos \theta(t) \Omega_z + \sin \theta(t) \Omega_y)Y, \quad (31)$$

where effective field strength  $\omega_{\text{eff}} = \sqrt{(\omega_0 - \omega(t))^2 + \omega_1^2}$  and  $\tan \theta(t) = \frac{\omega_1}{\omega_0 - \omega(t)}$ .

The three stages of the chirp excitation are understood in this frame.

The first rotation, *I*, arises as frequency of the chirp pulse  $\omega$  is swept from a large negative offset  $-A$  to  $\omega - \omega_0 = -\omega_1 \cot \theta_0$  ( $1 < \cot \theta_0 < 2$ , see below). As a result, the initial magnetization follows the effective field and is transferred to

$$\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \rightarrow \begin{bmatrix} \sin \theta_0 \\ 0 \\ \cos \theta_0 \end{bmatrix}.$$

During the phase *II* of the pulse the frequency  $\omega - \omega_0$  is swept over the range  $[-\omega_1 \cot \theta_0, \omega_1 \cot \theta_0]$  in time  $\frac{\alpha}{\omega_1}$  and for  $\cot \theta_0$  not very larger than 1, we can approximate the evolution in this phase II as

$$\sim \exp\left(\int_0^{\alpha/\omega_1} (\omega_0 - \omega)\Omega_z + \omega_1\Omega_x\right) dt = \exp(\alpha\Omega_x).$$

This produces the evolution

$$\begin{bmatrix} \sin \theta_0 \\ 0 \\ \cos \theta_0 \end{bmatrix} \rightarrow \begin{bmatrix} \sin \theta_0 \\ -\cos \theta_0 \sin \alpha \\ \cos \theta_0 \cos \alpha \end{bmatrix}.$$

Finally, during phase *III*, the frequency is swept from  $\omega_1 \cot \theta_0$  to a large positive offset  $A$  in time  $t_f$ . This produces the transformation

$$\exp\left(-\underbrace{\int \omega_{\text{eff}}(t) dt}_{\Phi(\omega_0)} \Omega_z\right) \exp(\theta_0 \Omega_y) \begin{bmatrix} \sin \theta_0 \\ -\cos \theta_0 \sin \alpha \\ \cos \theta_0 \cos \alpha \end{bmatrix}. \quad (32)$$

To see this, observe, given

$$\dot{Y} = \omega_{\text{eff}} (\cos \theta \Omega_z + \sin \theta \Omega_y)Y,$$

in the interaction frame of  $\theta$  where  $Z = \exp(-\theta(t)\Omega_y)Y$ , we have,

$$\dot{Z} = (\omega_{\text{eff}}\Omega_z - \dot{\theta}\Omega_y)Z.$$

If  $\omega_{\text{eff}} \gg \dot{\theta}$ , which is true in phase III of the pulse, where  $a \ll \omega_{\text{eff}}^2$ , as will be shown below. Then in the interaction frame of  $W = \exp(-\int_0^t \omega_{\text{eff}}(t) dt \Omega_z)Z$ , we average  $W(t)$  to *I*. Therefore the evolution of the Bloch equation for the chirp pulse takes the form

$$\begin{aligned}
Y(t_f) &= \exp(\theta(t_f)\Omega_y)Z(t_f) \\
&= \exp(\theta(t_f)\Omega_y) \exp\left(\int_0^{t_f} \omega_{\text{eff}} dt \Omega_z\right) \underbrace{\exp(-\theta(0)\Omega_y) Y(0)}_{Z_0}, \\
Y(t_f) &= \exp(\pi \Omega_y) \exp\left(\underbrace{\int_0^{t_f} \omega_{\text{eff}} dt \Omega_z}_{\Phi(\omega_0)}\right) \exp(-\theta(0)\Omega_y)Y(0), \tag{33}
\end{aligned}$$

where 0 marks beginning of phase III and  $\theta(0) = \pi - \theta_0$ , and  $\theta(t_f) = \pi$ . See Fig. 8 left panel. Then this gives Eq. (32).

Now for this to be an excitation, the  $z$  coordinate should vanish, which means,

$$\frac{\cos \theta_0 \cos \alpha}{\sin \theta_0} = \tan \theta_0. \tag{34}$$

$$\tan^2 \theta_0 = \cos \alpha. \tag{35}$$

For example, when  $\cot^2 \theta_0 = 2$ , we have  $\cos \alpha = \frac{1}{2}$ , i.e,  $\alpha = 1.0472$ . Thus phase *II* is traversed in time  $\alpha\omega_1^{-1} = 1.0472\omega_1^{-1}$ . The frequency swept in this time is  $2\omega_1 \cot \theta_0 = 2\omega_1\sqrt{2}$ . The sweep rate is  $a = \frac{2\sqrt{2}}{1.0472}\omega_1^2 = 2.7\omega_1^2$ . The smallest effective field in phase *I* and *III* is  $\omega_{\text{eff}}^2 = \omega_1^2(1 + \cot^2 \theta_0) = 3\omega_1^2$  in phase *I* and *III*. Therefore, in phase *I* and *III*, we have  $a \leq \omega_{\text{eff}}^2$  and adiabatic approximation is valid. In nutshell sweep rate  $a = 2.7\omega_1^2$ .

For another example, when  $\cot^2 \theta_0 = 3$ , we have  $\cos \alpha = \frac{1}{3}$ , i.e,  $\alpha = 1.23$ . Thus phase *II* is traversed in time  $\alpha\omega_1^{-1} = 1.23\omega_1^{-1}$ . The frequency swept in this time is  $2\omega_1 \cot \theta_0 = 2\omega_1\sqrt{3}$ . The sweep rate is  $a = \frac{2\sqrt{3}}{1.23}\omega_1^2 = 2.81\omega_1^2$ . The smallest effective field in phase *I* and *III* is  $\omega_{\text{eff}}^2 = \omega_1^2(1 + \cot^2 \theta_0) = 4\omega_1^2$  in phase *I* and *III*. Therefore, in phase *I* and *III*, we have  $a \leq \omega_{\text{eff}}^2$  and adiabatic approximation is valid.

In remaining paper we take  $a = 2.7\omega_1^2$ . The chirp excitation doesn't produce a uniform excitation phase for all offsets.

To understand this refer to Figure 9, where offsets vary from  $[-B, B]$  and we sweep from  $[-A, A]$  at rate  $a$ . It takes  $T_0$  units of time to sweep from  $-A$  to  $-B$  and  $T_1$  units of time to sweep from  $-B$  to  $A$ . Let  $T = T_0 + T_1$  be total time. It takes  $t_1$  units of time to sweep from  $\omega(t) - \omega_0 = 0$  to  $\omega(t) - \omega_0 = \omega_1 \cot \theta_0$ . Then the phase  $\Phi$  accumulated in Eq. 32 for the offset  $-B$  is  $\Phi(-B) = \int_{t_1}^{T_1} \omega_{\text{eff}}(t) dt$  and for offset  $-B + \Delta\omega = -B + a\Delta$  is  $\Phi(-B + a\Delta) = \int_{t_1}^{T_1 - \Delta} \omega_{\text{eff}}(t) dt$ .

Note when  $(\omega_0 - \omega(t)) \gg \omega_1$ , we approximate,

$$\omega_{\text{eff}} = \sqrt{(\omega_0 - \omega(t))^2 + \omega_1^2} \sim (\omega_0 - \omega(t)) + \frac{\omega_1^2}{2(\omega_0 - \omega(t))}.$$



The difference of the phases is

$$\int_{T_1-\Delta}^{T_1} \omega_{\text{eff}}(t) dt \sim \int_{T_1-\Delta}^{T_1} \left( at + \frac{\omega_1^2}{2at} \right) dt = \frac{a}{2}(T_1^2 - (T_1 - \Delta)^2) + \frac{\omega_1^2}{2a} \ln \frac{T_1}{T_1 - \Delta}. \quad (36)$$

$$= \frac{a}{2}(-\Delta^2 + 2T_1\Delta) + \frac{\omega_1^2}{2a} \ln \frac{T_1}{T_1 - \Delta}. \quad (37)$$

We can refocus this phase by following the chirp excitation pulse with a chirp  $\pi$  pulse at twice the sweep rate  $2a$  and rf-field strength  $\omega_2^2 \gg 2a$ . To understand this, consider again the Bloch equation

$$\dot{X} = (\omega_0 \Omega_z + \omega_2 \cos \phi \Omega_x + \omega_2 \sin \phi \Omega_y) X,$$

where the chirp frequency  $\dot{\phi} = \omega = -A + 2at$  is swept from  $[-A, A]$ .

In the interaction field of the chirp phase,  $\phi(t)$ , we have  $Y(t) = \exp(-\phi(t)\Omega_z)X(t)$ , and

$$\dot{Y} = ((\omega_0 - \omega)\Omega_z + \omega_2 \Omega_x) Y = \omega_{\text{eff}} (\cos \theta \Omega_z + \sin \theta \Omega_y) Y,$$

where effective field strength  $\omega_{\text{eff}} = \sqrt{(\omega_0 - \omega(t))^2 + \omega_2^2}$  and  $\tan \theta = \frac{\omega_2}{\omega_0 - \omega}$ .

Now in interaction frame of  $\theta$  where  $Z = \exp(-\theta(t)\Omega_y)Y$ , we have

$$\dot{Z} = (\omega_{\text{eff}} \Omega_z - \dot{\theta} \Omega_y) Z.$$

If  $\omega_{\text{eff}} \gg \dot{\theta}$ , which is true when rf-field strength  $\omega_2^2 \gg 2a$ , in the interaction frame of  $W = \exp(-\int_0^t \omega_{\text{eff}} dt \Omega_z)Z$ , we average  $W(t)$  to  $I$ . Therefore the evolution of the Bloch equation for the chirp pulse takes the form

$$X(t) = \exp(\phi(t) \Omega_z) \exp(\theta(t) \Omega_y) \exp\left(\underbrace{\int_0^t \omega_{\text{eff}} dt \Omega_z}_{\Phi_1(\omega_0)}\right) X(0), \quad (38)$$

where  $\phi(0) = \phi(T) = 0$  and  $\theta(0) = 0$  and  $\theta(T) = \pi$  and now we can again evaluate  $\Phi_1(-B) - \Phi_1(-B + a\Delta)$ . Observe

$$\begin{aligned}
\Phi_1(-B) &= \int_0^{\frac{T_0}{2}} \sqrt{(2at)^2 + \omega_2^2} dt + \int_0^{\frac{T_1}{2}} \sqrt{(2at)^2 + \omega_2^2} dt. \\
\Phi_1(-B + a\Delta) &= \int_0^{\frac{T_0+\Delta}{2}} \sqrt{(2at)^2 + \omega_2^2} dt + \int_0^{\frac{T_1-\Delta}{2}} \sqrt{(2at)^2 + \omega_2^2} dt. \\
\Phi_1(-B) - \Phi_1(-B + a\Delta) &= \int_{\frac{T_1-\Delta}{2}}^{\frac{T_1}{2}} \sqrt{(2at)^2 + \omega_2^2} dt - \int_{\frac{T_0}{2}}^{\frac{T_0+\Delta}{2}} \sqrt{(2at)^2 + \omega_2^2} dt. \\
\int_{\frac{T_1-\Delta}{2}}^{\frac{T_1}{2}} \sqrt{(2at)^2 + \omega_2^2} dt &\sim \frac{a}{4}(T_1^2 - (T_1 - \Delta)^2) + \frac{\omega_2^2}{4a} \ln \frac{T_1}{T_1 - \Delta}. \\
\Phi_1(-B) - \Phi_1(-B + a\Delta) &\sim \frac{a}{4}(-2\Delta^2 + 2(T_1 - T_0)\Delta) + \frac{\omega_2^2}{4a} \ln \frac{T_1 T_0}{(T_1 - \Delta)(T_0 + \Delta)}.
\end{aligned}$$

Now if we combine the phase due to chirp excitation excitation pulse and the chirp  $\pi$  pulse we get

$$\begin{aligned}
\{\Phi_1(-B + a\Delta) - \Phi_1(-B)\} - \{\Phi(-B + a\Delta) - \Phi(-B)\} &= \frac{a(T_1 + T_0)\Delta}{2} - \frac{\omega_2^2}{4a} \ln \frac{T_1 T_0}{(T_1 - \Delta)(T_0 + \Delta)} \\
&+ \frac{\omega_1^2}{2a} \ln \frac{T_1}{T_1 - \Delta}.
\end{aligned}$$

If chirp  $\pi$  pulse is followed by free evolution for  $\frac{T}{2}$  where  $T = T_1 + T_0$ , it refocuses the phase  $\frac{a(T_1+T_0)\Delta}{2} = \frac{T\Delta\omega}{2}$ . See Fig. 10A. The only phase dispersion that is left is

$$\frac{\omega_2^2}{4a} \ln \frac{(T_1 - \Delta)(T_0 + \Delta)}{T_1 T_0} + \frac{\omega_1^2}{2a} \ln \frac{T_1}{T_1 - \Delta}. \quad (39)$$

For  $a\Delta = 2B$ , the other extreme of the spectrum, the above expression simplifies to

$$\frac{\omega_1^2}{2a} \ln \frac{1 + \frac{B}{A}}{1 - \frac{B}{A}}. \quad (40)$$

As described before for  $a = 2.7\omega_1^2$  and when  $\frac{B}{A} \ll 1$  say  $\frac{B}{A} = 1/3$ , this dispersion is small around  $7^\circ$ .

The factor  $\frac{\omega_2^2}{4a} \ln \frac{(T_1-\Delta)(T_0+\Delta)}{T_1 T_0}$  in Eq. (39) can be cancelled by introducing a  $\pi$  pulse of amplitude  $\frac{\omega_2}{\sqrt{2}}$ , and sweep rate  $a$ , following  $\frac{\pi}{2}$  chirp pulse and then a delay of  $\frac{T}{2}$ , and finally the  $\pi$  pulse of amplitude  $\omega_2$  and sweep rate  $2a$ . See Fig. 10B. Then all phase dispersion cancel except the one in Eq. (40). We can make this dispersion small by  $\frac{B}{A} \ll 1$ .

## 4 Coupling

Until now we talked about single spin  $\frac{1}{2}$ . How to excite them with rf-field. How to detect them and read their frequencies. Now we talk about two spin coupled to each other, Like two magnets talking to each other. To make this happen we first enter into few generalities.

Now as a general rule, we can have a quantum system  $A$  of dimension  $n_1$ , which means its state is a  $n_1$  dimensional complex vector evolving as

$$\dot{\psi} = -iH\psi,$$

where  $H$  is a  $n_1 \times n_1$  Hermitian matrix, such that  $\psi(t) = U(t)\psi(0) = \exp(-iHt)\psi(0)$ , where  $-iH$  is skew Hermitian and  $U(t) \in SU(n)$ .

If we have a quantum system  $A$  of dim  $n_1$  and a quantum system  $B$  of dim  $n_2$ , then when we bring the two systems together and make them interact, we get a a quantum system of dim  $n_1 \times n_2$ , whose state is a complex vector in a vector space of size  $n_1 n_2$ , spanned by a basis of the form  $e_i \otimes f_j$  where  $e_i$  are basis for space  $A$  and  $f_j$  are basis for space  $B$ . A state  $\psi$  that can be written as  $\psi_a \otimes \psi_b$  is called a separable state, else it has the form  $\psi = \sum_{ij} \alpha_{ij} e_i \otimes f_j$  and is called an entangled state.

The hamiltonian for the joint system

$$H = \sum H_a^i \otimes H_b^j,$$

where  $H_a^i$  are Hamiltonians for system  $A$  and  $H_b^j$  are Hamiltonians for system  $B$ . Hamiltonians of the form  $H_a \otimes I$  and  $I \otimes H_b$  are called local Hamiltonians, beacuse if we have a seprable space  $\psi_a \otimes \psi_b$  and we evolve it under  $H_a \otimes I$ , then

$$\exp(-iH_a \otimes I) = \exp(-iH_a) \otimes I$$

and

$$\exp(-iH_a \otimes I)\psi_a \otimes \psi_b = (\exp(-iH_a)\psi_a) \otimes \psi_b$$

The Hamiltonian only evoves  $A$  part of the subsystem. Similarly

$$\exp(-iI \otimes H_b)\psi_a \otimes \psi_b = \psi_a \otimes (\exp(-iH_b)\psi_b).$$

On the other hand if we have a Hamiltonian of the form  $H_a \otimes H_b$ , we call it an interaction Hamiltonian.

Then Hamiltonians for the joint system are of the general form

$$\{H_a \otimes I, I \otimes H_b, H_a \otimes H_b\}.$$

If we count dimensions there are  $n_1^2 - 1$  (traceless Hermitian) Hamiltonians of the form  $H_a \otimes I$  and  $n_2^2 - 1$  of form  $I \otimes H_b$  and  $(n_1^2 - 1)(n_2^2 - 1)$  of form  $H_a \otimes H_b$  and if we count them all we get total of  $(n_1 n_2)^2 - 1$  which is indeed the dimension of Hamiltonians for a  $n_1 n_2$  dimensional space.

To make all this concrete consider again spin  $\frac{1}{2}$ . Its state space is 2 dimensional complex space with basis  $|0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$  and  $|1\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$ . They are up-down states of spin. Like classical bits, a spin  $\frac{1}{2}$  is called a quantum bit or qubit. However unlike a classical bit we can evolve our spin and prepare a state

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle).$$

This is called a superposition of 0 and 1. Now lets consider 2 spin  $\frac{1}{2}$ . Then the basis of our state space are

$$\begin{aligned} |00\rangle &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \\ |01\rangle &= \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \\ |10\rangle &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} \\ |11\rangle &= \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \end{aligned}$$

Two spin  $\frac{1}{2}$  are called coupled qubits. The Hamiltonians for the coupled qubit system are of the following kind

$$\{ -i\sigma_x \otimes I, -i\sigma_y \otimes I, -i\sigma_z \otimes I, -iI \otimes \sigma_x, -iI \otimes \sigma_y, -iI \otimes \sigma_z, -i\sigma_x \otimes \sigma_x, -i\sigma_x \otimes \sigma_y, -i\sigma_x \otimes \sigma_z, -i\sigma_y \otimes \sigma_x, -i\sigma_y \otimes \sigma_y, -i\sigma_y \otimes \sigma_z, -i\sigma_z \otimes \sigma_x, -i\sigma_z \otimes \sigma_y, -i\sigma_z \otimes \sigma_z \}$$

They are 15 in all of these  $\sigma_\alpha \otimes I$  and  $I \otimes \sigma_\beta$  are local Hamiltonians and  $\sigma_\alpha \otimes \sigma_\beta$  are interaction Hamiltonians where  $\alpha, \beta \in \{x, y, z\}$ .

Now suppose we start in the state  $|00\rangle$  and evolve this state under Hamiltonian  $-i\sigma_x \otimes I$  for time  $\pi$  then we get

$$\exp(-i\sigma_y \otimes I\pi) \left( \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) = (\exp(-i\pi\sigma_y) \begin{bmatrix} 1 \\ 0 \end{bmatrix}) \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

Now direct calculation shows that

$$\exp(-i\theta\sigma_y) = \cos \frac{\theta}{2} I - 2i \sin \frac{\theta}{2} \sigma_y = \begin{bmatrix} \cos \frac{\theta}{2} & -\sin \frac{\theta}{2} \\ \sin \frac{\theta}{2} & \cos \frac{\theta}{2} \end{bmatrix}$$

Then

$$\exp(-i\sigma_y \otimes I\pi) \left( \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) = \left( \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) = |10\rangle$$

Thus by evolving the system under the given Hamiltonian we invert the state of the first spin. We have built an inverter. This is like an inverter in boolean/computer circuits but now done on a qubit. We say we have built an inverter gate.

Now in quantum mechanics we do not distinguish between state vector  $\psi$  and  $\exp(i\alpha)\psi$ , they differ by a so called global phase and are considered the same state. Therefore, we can also invert by

$$\exp(-i\sigma_x \otimes I\pi) \left( \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \right) = (-i \begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix}) = -i|10\rangle$$

which is the same as  $|10\rangle$ .

Now can we do something more interesting. Can we say evolve an Hamiltonian that will swap the state of two spins. Such that

$$|10\rangle \rightarrow |01\rangle, \quad |01\rangle \rightarrow |10\rangle$$

To do this we have to make the qubits interact using an interaction Hamiltonian.

Lets evolve under the hamiltonian

$$U = \exp(-i\pi(\sigma_x \otimes \sigma_x + \sigma_y \otimes \sigma_y))$$

$$\sigma_x \otimes \sigma_x + \sigma_y \otimes \sigma_y = \frac{1}{4} \left( \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} + \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \right) = \frac{1}{2} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

$$U = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

Then

$$\begin{aligned} U|01\rangle &= U\left(\begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 0 \\ 1 \end{bmatrix}\right) = -i \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} = |10\rangle \\ U|10\rangle &= U\left(\begin{bmatrix} 0 \\ 1 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix}\right) = -i \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} = |01\rangle \\ U|00\rangle &= |00\rangle \\ U|11\rangle &= |11\rangle \end{aligned}$$

We have built a SWAP gate. Another interesting gate is so called C-NOT gate. It inverts the state of the second qubit conditioned on the state of first qubit. If the state of first qubit is 0 we don't do anything else we invert.

$$|00\rangle \rightarrow |00\rangle, \quad |01\rangle \rightarrow |01\rangle, \quad |10\rangle \rightarrow |11\rangle, \quad |11\rangle \rightarrow |10\rangle$$

Let

$$U = \exp(-i\pi(\frac{I}{2} - \sigma_z) \otimes \sigma_x) = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \end{bmatrix}$$

Then check we have built a CNOT gate.

Now we can generalize all this. We can have say n qubits. The state space is  $2^n$  dimensional. The state

$$|000\dots 0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix} \otimes \dots \otimes \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

is all qubits in state zero. We can evolve a Hamiltonian  $\sigma_x \otimes I \dots \otimes I$ , which is a local Hamiltonian that will only evolve the first qubit. Similarly a hamiltonian of the form

$\sigma_x \otimes \sigma_x \otimes I \cdots \otimes I$ , will make first two qubits interact and do a two qubit operation. So we can evolve Hamiltonians and do single qubit and two qubit operations. Now we can do any Boolean operation on  $n$  qubits and we have built a quantum computer. We can do operations as in classical computer but at the same time generate superpositions and do more powerful things we cannot do in classical computers. This allows us to do things we cannot do on a classical computer. Like we can factor very large integers in polynomial time. This is not possible on classical computers else we will break all existing crypto-systems which rely on the fact that it is hard to factor large integers.

Next we ask physically how do we get these Hamiltonians that we use to evolve our system. We saw for a single spin, when we put the spin in a magnetic field we get the evolution in Eq. (9), we then have our Hamiltonians, one drift  $H_0$  and two control  $H_1$  and  $H_2$ .

Interaction Hamiltonians arise because spins have magnetic moments and magnets interact. For example two magnetic moments in space  $\mu_1$  and  $\mu_2$  have hamiltonian (energy) as

$$H = \frac{\mu_0}{4\pi r^3}(\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \hat{r})(\mu_2 \cdot \hat{r}))$$

where  $r$  is the distance between moments and  $\hat{r}$  is the unit vector connecting them.

Once again consider two qubits (spin  $\frac{1}{2}$ ) and consider the evolution of the state vector  $\psi$  as

$$\dot{\psi} = -i\{u_1 \underbrace{\sigma_x \otimes I}_{H_1} + u_2 \underbrace{\sigma_y \otimes I}_{H_2} + u_3 \underbrace{I \otimes \sigma_x}_{H_3} + u_4 \underbrace{I \otimes \sigma_y}_{H_4} + J \underbrace{\sigma_z \otimes \sigma_z}_{H_0}\} \psi \quad (41)$$

Observe  $\psi(t) = U(t)\psi(0)$ , where  $U(t) \in SU(4)$ . Can we produce any unitary transformation on  $\psi$ . This is same as asking, is my system

$$\dot{U} = -i\{u_1 \sigma_x \otimes I + u_2 \sigma_y \otimes I + u_3 I \otimes \sigma_x + u_4 I \otimes \sigma_y + J \underbrace{\sigma_z \otimes \sigma_z}_{H_0}\} U \quad (42)$$

controllable. Observe we have four control Hamiltonians, which are local Hamiltonians. The first two rotate qubit 1 and last two rotate qubit 2. The drift hamiltonian is a interaction Hamiltonian and arises from spin-spin interaction. The local Hamiltonians are produced by applying magnetic fields to the spins. Now to answer controllability question we have to use lie brackets.

By calculations like  $[-i\sigma_x \otimes I, -i\sigma_y \otimes I] = -i\sigma_z \otimes I$  we can show that brackets of  $H_1, H_2, H_3, H_4$  generate all local Hamiltonians

$$\{-i\sigma_x \otimes I, -i\sigma_y \otimes I, -i\sigma_z \otimes I, -iI \otimes \sigma_x, -iI \otimes \sigma_y, -iI \otimes \sigma_z\}$$

Now we can take brackets with drift and find we generate all the interaction generators,

$$\{-i\sigma_x \otimes \sigma_x, -i\sigma_x \otimes \sigma_y, -i\sigma_x \otimes \sigma_z, -i\sigma_y \otimes \sigma_x, -i\sigma_y \otimes \sigma_y, -i\sigma_y \otimes \sigma_z, -i\sigma_z \otimes \sigma_x, -i\sigma_z \otimes \sigma_y, -i\sigma_z \otimes \sigma_z\}$$

In taking Lie brackets we used the following identities

$$[A \otimes B, C \otimes D] = [A, C] \otimes BD + CA \otimes [B, D]$$

and

$$\begin{aligned}\sigma_x \sigma_y &= -\sigma_y \sigma_x = \frac{i}{2} \sigma_z \\ \sigma_y \sigma_z &= -\sigma_z \sigma_y = \frac{i}{2} \sigma_x \\ \sigma_z \sigma_x &= -\sigma_x \sigma_z = \frac{i}{2} \sigma_y\end{aligned}$$

For example,

$$[-i\sigma_z \otimes \sigma_z, -i\sigma_x \otimes I] = [-i\sigma_z, -i\sigma_x] \otimes \sigma_z + (-i\sigma_x - i\sigma_z) \otimes [\sigma_z, I] = -i\sigma_y \otimes \sigma_z$$

$$[-i\sigma_z \otimes \sigma_z, -i\sigma_x \otimes \sigma_x] = [-i\sigma_z, -i\sigma_x] \otimes \sigma_z \sigma_x + (\sigma_x \sigma_z) \otimes [-i\sigma_z, -i\sigma_x] = \frac{1}{2}(\sigma_y \otimes \sigma_y - \sigma_y \otimes \sigma_y)$$

The Lie algebra  $\mathfrak{g} = su(4)$  is 15 dimensional and spanned by

$$\mathfrak{g} = \{-i\sigma_x \otimes I, -i\sigma_y \otimes I, -i\sigma_z \otimes I, -iI \otimes \sigma_x, -iI \otimes \sigma_y, -iI \otimes \sigma_z, -i\sigma_x \otimes \sigma_x, -i\sigma_x \otimes \sigma_y, -i\sigma_x \otimes \sigma_z, -i\sigma_y \otimes \sigma_x, -i\sigma_y \otimes \sigma_y, -i\sigma_y \otimes \sigma_z, -i\sigma_z \otimes \sigma_x, -i\sigma_z \otimes \sigma_y, -i\sigma_z \otimes \sigma_z\}$$

This vector space  $\mathfrak{g}$  has two orthogonal subspaces

$$\mathfrak{k} = \{-i\sigma_x \otimes I, -i\sigma_y \otimes I, -i\sigma_z \otimes I, -iI \otimes \sigma_x, -iI \otimes \sigma_y, -iI \otimes \sigma_z\}$$

the local generators and the interaction generators

$$\mathfrak{p} = \{-i\sigma_x \otimes \sigma_x, -i\sigma_x \otimes \sigma_y, -i\sigma_x \otimes \sigma_z, -i\sigma_y \otimes \sigma_x, -i\sigma_y \otimes \sigma_y, -i\sigma_y \otimes \sigma_z, -i\sigma_z \otimes \sigma_x, -i\sigma_z \otimes \sigma_y, -i\sigma_z \otimes \sigma_z\}$$

$\mathfrak{k}$  is 6 dimensional and  $\mathfrak{p}$  is 9 dimensional and in total 15 dimensions. You should check that following commutations relations hold



$$[\mathfrak{k}, \mathfrak{k}] \subset \mathfrak{k}, \quad [\mathfrak{p}, \mathfrak{k}] \subset \mathfrak{p}, \quad [\mathfrak{p}, \mathfrak{p}] \subset \mathfrak{k} \quad (43)$$

In general decomposition of a Lie algebras  $\mathfrak{g}$ , into a direct sum of two vector subspaces

$$\mathfrak{g} = \mathfrak{p} \oplus \mathfrak{k}$$

such that Eqs. 43 are true, is called a Cartan decomposition.

Now coming back to Eq. 41, we have shown controllability. We can generate any  $U \in SU(4)$

We introduce a notation used in NMR literature.

Given two spins or qubits, we call the first one  $I$  and second one  $S$ . Then the hamiltonian  $\sigma_x \otimes I$  is written as  $I_x$  and  $I \otimes \sigma_x$  as  $S_x$  and

$$\sigma_x \otimes \sigma_x = (\sigma_x \otimes I)(I \otimes \sigma_x) = I_x S_x$$

In this notation

$$\mathfrak{g} = \{-iI_x, -iI_y, -iI_z, -iS_x, -iS_y, -iS_z, \\ -iI_x S_x, -iI_x S_y, -iI_x S_z, -iI_y S_x, -iI_y S_y, -iI_y S_z, -iI_z S_x, -iI_z S_y, -iI_z S_z\}$$

## 4.1 Polarization Transfer

We talked about basic NMR experiment on spin  $\frac{1}{2}$ . It can be done on spin  $^1\text{H}$  or  $^{13}\text{C}$ . The experiment on  $^1\text{H}$  is more sensitive than  $^{13}\text{C}$  as it has larger  $\gamma$  and hence larger thermal polarization. However if we have coupling between  $^1\text{H}$  and  $^{13}\text{C}$  then we can transfer polarization from  $^1\text{H}$  to  $^{13}\text{C}$ . To understand what we mean. Suppose we start with a sample with all  $^1\text{H}$  in state  $|0\rangle$  and half of  $^{13}\text{C}$  in state  $|0\rangle$  and remaining half of  $^{13}\text{C}$  in state  $|1\rangle$ . This approximates the case where  $^1\text{H}$  are highly polarized and  $^{13}\text{C}$  are poorly polarized. Then half of my ensemble is  $|00\rangle$  and half in  $|01\rangle$ . If we have coupling between the spins the first do a CNOT gate based on  $^{13}\text{C}$ , that makes the ensemble half  $|00\rangle$  and half  $|11\rangle$ . Now do a CNOT gate based on  $^1\text{H}$ , that makes the ensemble half  $|00\rangle$  and half  $|10\rangle$ . See what we have achieved is we have an ensemble where all  $^{13}\text{C}$  are polarized while  $^1\text{H}$  is unpolarized. This way we have been able to transfer Polarization from  $^1\text{H}$  to  $^{13}\text{C}$  and then can do a much sensitive detection of  $^{13}\text{C}$ .

## 4.2 Coherence Transfer and 2D NMR

We talked about chemical shifts and how using an NMR experiment when we observe fid whose Fourier transform gives location of frequencies present and hence chemical shifts. In

a big molecule when we do experiment on  $^1\text{H}$  we can have many many chemical shifts and peaks in fourier transform have finite widths due to decaying nature of FID then these peaks overlap and we cannot resolve the frequencies. Fig. A shows molecule with few chemical shifts well separated and easily resolved. Fig. B shows molecule with many chemical shifts overlapping and not easily resolved.

How do we resolve these overlapping chemical shifts. We again make use of coupling between the spins. Agin think we have  $^1\text{H}$  coupled to  $^{13}\text{C}$ . When we do a experiment on  $^1\text{H}$  then we measure the frequency  $\omega_H$ . Now suppose we do an experiment where we measure the pair  $(\omega_H, \omega_C)$ . Then when we plot all  $(\omega_H, \omega_C)$  in two dimensions. This has more resolution as everythings gets spread out in 2D comapred to crowded 1D. Then the challenge is how to generate the joint frquency information  $(\omega_H, \omega_C)$ . The basic idea istems from the polarization transfer experiment. We transfer polarization from  $^1\text{H}$  to  $^{13}\text{C}$  but we arranhe matters so that the polarization of  $^1\text{H}$  is propotional to  $\cos \omega_H t_1$  where  $\omega_H$  is the frequency of interest and  $t_1$  is an auxillary time variable. After this we can do a standard experiment on  $^{13}\text{C}$  and detect a signal of the form  $M(0) \cos \omega_C t_2$ , where now  $M(0) \propto \cos \omega_H t_1$  and  $t_2$  is real time. Then we have a signal of the form  $\cos \omega_H t_1 \cos \omega_C t_2$  where we can repeat this experiment many times by incrementing  $t_1$  and build a genuine 2D signal  $s(t_1, t_2) = \cos \omega_H t_1 \cos \omega_C t_2$  whose 2D fourier transforms gives peaks at  $(\omega_H, \omega_C)$ .

Now how do we arrange matters so that the polarization of  $^1\text{H}$  is propotional to  $\cos \omega_H t_1$ . lets say we start with  $^1\text{H}$ , with all spins  $|0\rangle$  when we give a  $\frac{\pi}{2}$  pulse we create the state  $\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$ . Then it evolves under natural precession (chemical shifts) to  $\frac{1}{\sqrt{2}}(\exp(-j\frac{\omega_H}{2}t_1)|0\rangle + \exp(j\frac{\omega_H}{2}t_1)|1\rangle)$  which can be written as  $\frac{\cos \frac{\omega_H}{2}t_1}{\sqrt{2}}(|0\rangle + |1\rangle) + i\frac{\sin \frac{\omega_H}{2}t_1}{\sqrt{2}}(|0\rangle - |1\rangle)$ . We again give a  $\frac{\pi}{2}$  pulse we create the state  $\cos \frac{\omega_H}{2}t_1|0\rangle + i\frac{\sin \frac{\omega_H}{2}t_1}{\sqrt{2}}(|0\rangle - |1\rangle)$ . The resulting polarization  $\cos^2 \frac{\omega_H t_1}{2} = \frac{1}{2}(1 + \cos \omega_H t_1)$  is the polarization that is then transferred. The remianing part has no polarization.

## 5 Decoupling

In 2D NMR experiment when we let spins evlove we donot want coupling between the spins to be active. Therefore we have to decouple the spins. This is done with a decoupling pulse sequence. Suppose we want to evolve spin  $I$ . Given the Hamiltonian

$$H = \underbrace{\omega_I I_z + \omega_S S_z + J I_z S_z}_{H_o} + A(t)(I_x + S_x)$$

Then since  $|\omega_I - \omega_S| \gg A \gg J$ , we can produce evolution  $\exp(-i\pi S_x)$ , then

$$\exp(-iH_0 \frac{\Delta t}{2}) \exp(-i\pi S_x) \exp(-iH_0 \frac{\Delta t}{2}) \exp(i\pi S_x) = \exp(-i\omega_I I_z \Delta t).$$

## 6 Problems

1. Consider the Bloch Eq.

$$\dot{X} = (\omega_0\Omega_z + u\Omega_x + v\Omega_y)X,$$

Simulate the evolution with on-resonance control  $(u, v) = A(\cos \omega_0 t, \sin \omega_0 t)$ , with  $A = 1$ ,  $\omega_0 = 10^5$  and  $X(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$ . Simulate for time  $T = \frac{\pi}{2}$  and  $T = \pi$  and plot trajectories. Repeat with a constant control  $(u, v) = A(1, 0)$ .

2. Consider the Bloch Eq.

$$\dot{X} = (\omega_0\Omega_z + u\Omega_x)X,$$

Simulate the evolution with on-resonance control  $u = A \cos \omega_0 t$ , with  $A = 1$ ,  $\omega_0 = 10^5$  and  $X(0) = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$ . Simulate for time  $T = \pi$  and  $T = 2\pi$  and plot trajectories. Repeat with a constant control  $u = A$ .

3. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

Simulate the adiabatic inversion with  $A = 1$ ,  $\omega \in [-5, 5]$  by sweeping from  $[-15, 15]$  with  $a = \frac{1}{30} \leq A^2 = 1$ . Plot  $X_3(\omega)$  for  $\omega \in [-5, 5]$ .

4. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

Simulate the adiabatic inversion with  $A = 1$ ,  $\omega \in [-5, 5]$  by sweeping from  $[-6, 6]$  with tapered ends and  $a = \frac{1}{30} \leq A^2 = 1$ . Plot  $X_3(\omega)$  for  $\omega \in [-5, 5]$ .

5. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

Implement broadband excitation pulse using method of double sweep with  $A = 1$ ,  $\omega \in [-3, 3]$ . Plot  $X_2(\omega)$  for  $\omega \in [-3, 3]$ .

6. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

with  $A = 1$ ,  $\omega \in [-3, 3]$ , implement band-selective excitation pulse using with excitation in range  $[-.5, .5]$  using method of double sweep with  $A = 1$ ,  $\omega \in [-3, 3]$ . Plot  $X_2(\omega)$  for  $\omega \in [-3, 3]$ .

7. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

Implement chirp excitation with  $A = 1$ ,  $\omega \in [-50, 50]$  with one refocusing (the two pulse sequence). Plot  $X_1(\omega)$  and  $X_2(\omega)$  for  $\omega \in [-50, 50]$ .

8. Consider the Bloch Eq.

$$\dot{X} = (\omega\Omega_z + A \cos \phi(t)\Omega_x + A \sin \phi(t)\Omega_y)X,$$

Implement chirp excitation with  $A = 1$ ,  $\omega \in [-50, 50]$  with double refocusing (the three pulse sequence). Plot  $X_1(\omega)$  and  $X_2(\omega)$  for  $\omega \in [-50, 50]$ .

9. Consider the coupling hamiltonian of two spin system

$$H = \omega_I I_z + \omega_S S_z + J I_z S_z + A(t)(I_x + S_x)$$

with  $\omega_I = 10^5$  and  $\omega_S = 2 \times 10^5$  and  $J = 10^{-3}$  and  $A = 1$ , design a pulse sequence to implement a CNOT gate based on spin I. Simulate starting from initial state  $|01\rangle$ .

10. In above implement polarization transfer from  $I$  to  $S$ . Simulate starting from initial states  $|01\rangle$ . and  $|00\rangle$ .

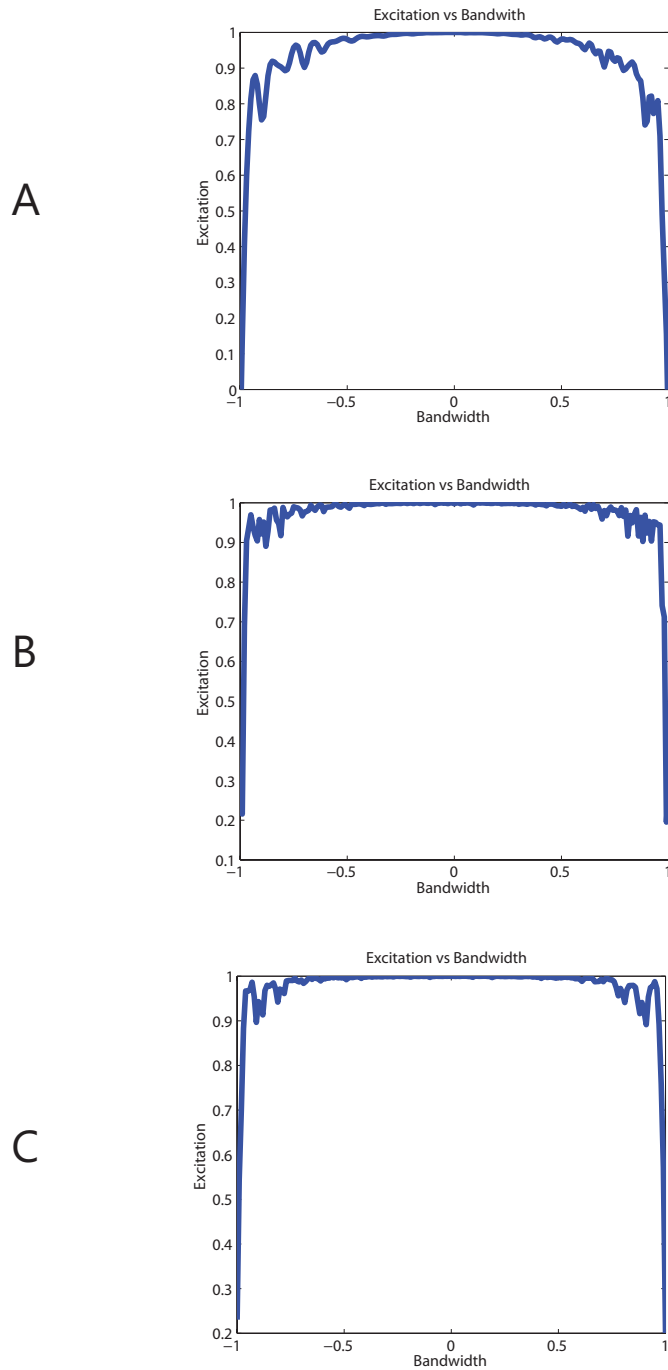


Figure 6: Fig. A shows the simulations of excitation profile (the  $-y$  coordinate of Bloch vector) for the basic excitation pulse in Eq. (24) with peak amplitude  $A = \frac{1}{2}$ . Fig. B shows the simulations of excitation profile for the excitation pulse in Eq. (26) with peak amplitude  $A = \frac{1}{4}$ . Fig. C shows the simulations of excitation profile for the basic excitation pulse in Eq. (27) with  $n = 3$ , with peak amplitude  $A \frac{2\Omega}{6} \frac{1}{6}$ .

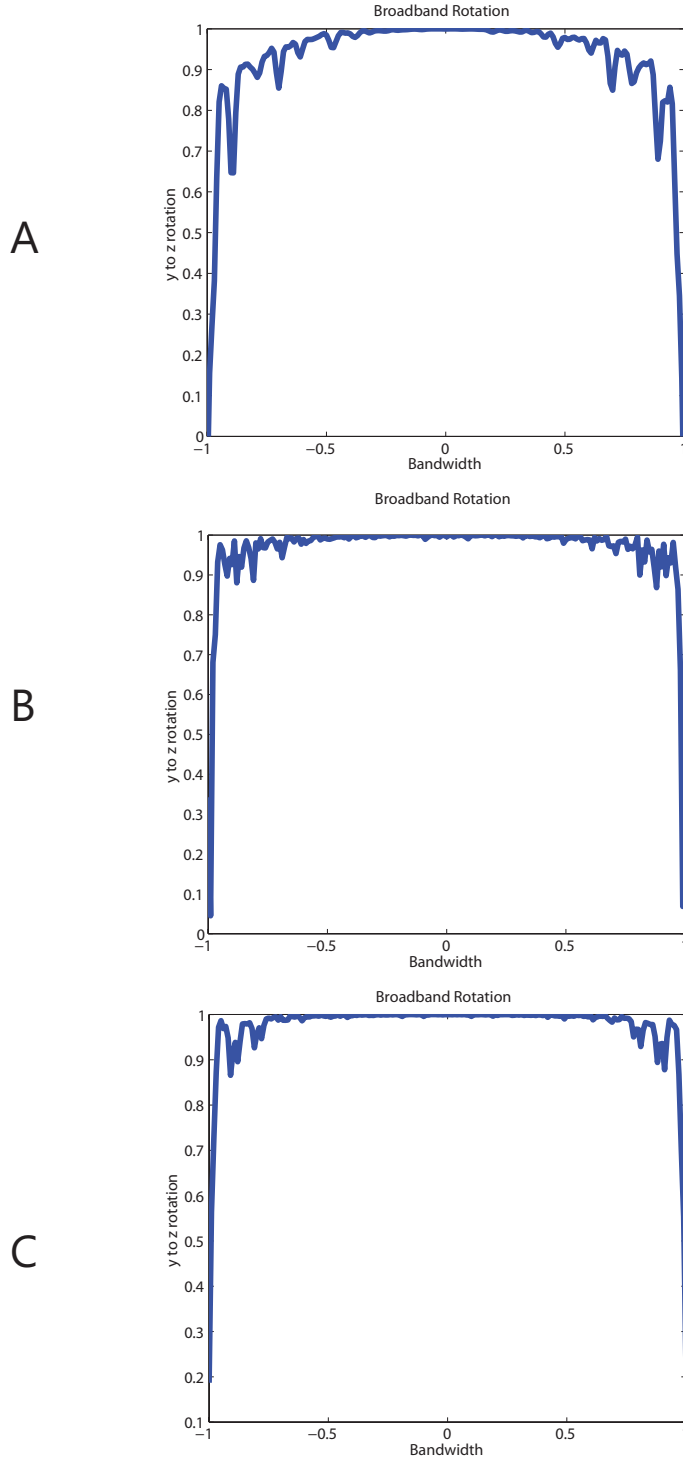


Figure 7: Fig. A shows the simulations of the  $y$  to  $z$  rotation profile (the  $z$  coordinate of Bloch vector) for the broadband  $x$  rotation pulse in Eq. (28) with peak amplitude  $A = \frac{1}{2}$ . Fig. B shows the simulations of the rotation profile for the broadband  $x$  rotation pulse in Eq. (29) with peak amplitude  $A = \frac{1}{4}$ . Fig. C shows the simulations of the rotation profile for the broadband  $x$  rotation pulse in Eq. (30) with  $n = 3$ , with peak amplitude  $A = \frac{1}{6}$ .

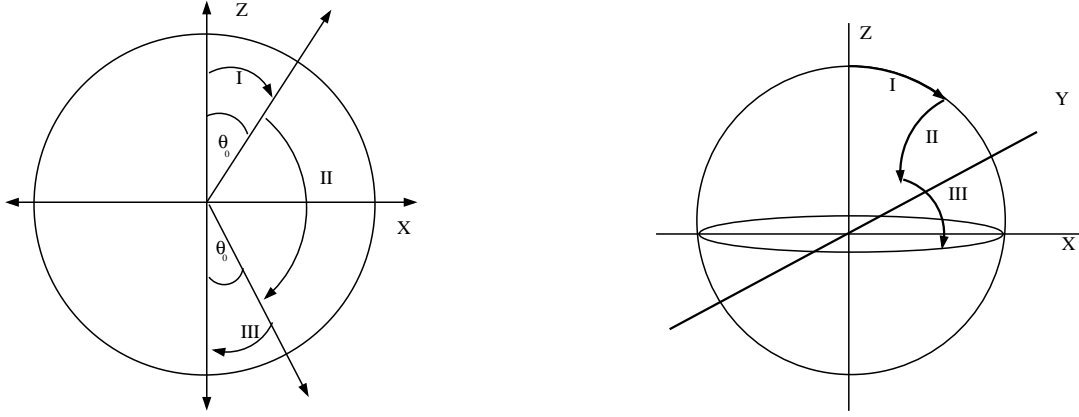


Figure 8: The *left panel* shows the effective field for the chirp excitation. The effective field starts along  $z$  axis and after phase I is rotated by  $\theta_0$ . After phase II, it makes angle of  $\theta_0$  with  $-z$  axis and finally at end of phase III ends up at the  $-z$  axis. The *right panel* shows how magnetization initially along  $z$  axis evolves in three stages in frame of phase  $\phi(t)$  as in Eq. (31). It is rotated along  $y$  axis in phase I by angle  $\theta_0$  and then along  $x$  axis by angle  $\alpha$  in phase II and finally along  $y$  axis by  $\theta_0$  in phase III.

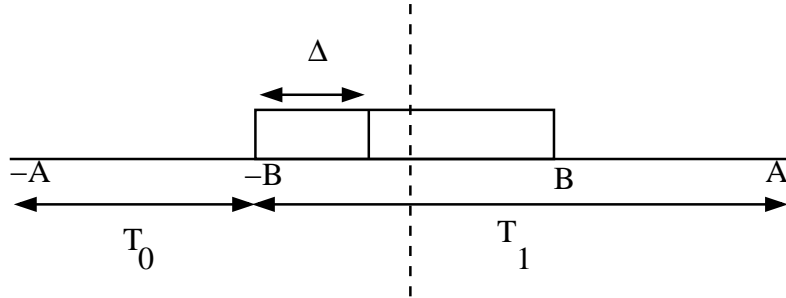


Figure 9: The figure shows the offsets in range  $[-B, B]$  and the sweep of chirp from  $[-A, A]$ .  $T_1$  is the time it takes to sweep from  $-B$  to  $A$  and  $T_0$  is the time to sweep from  $-A$  to  $-B$ . Also shown is a offset that takes  $\Delta$  time to reach from  $-B$ , at sweep rate  $a$ .

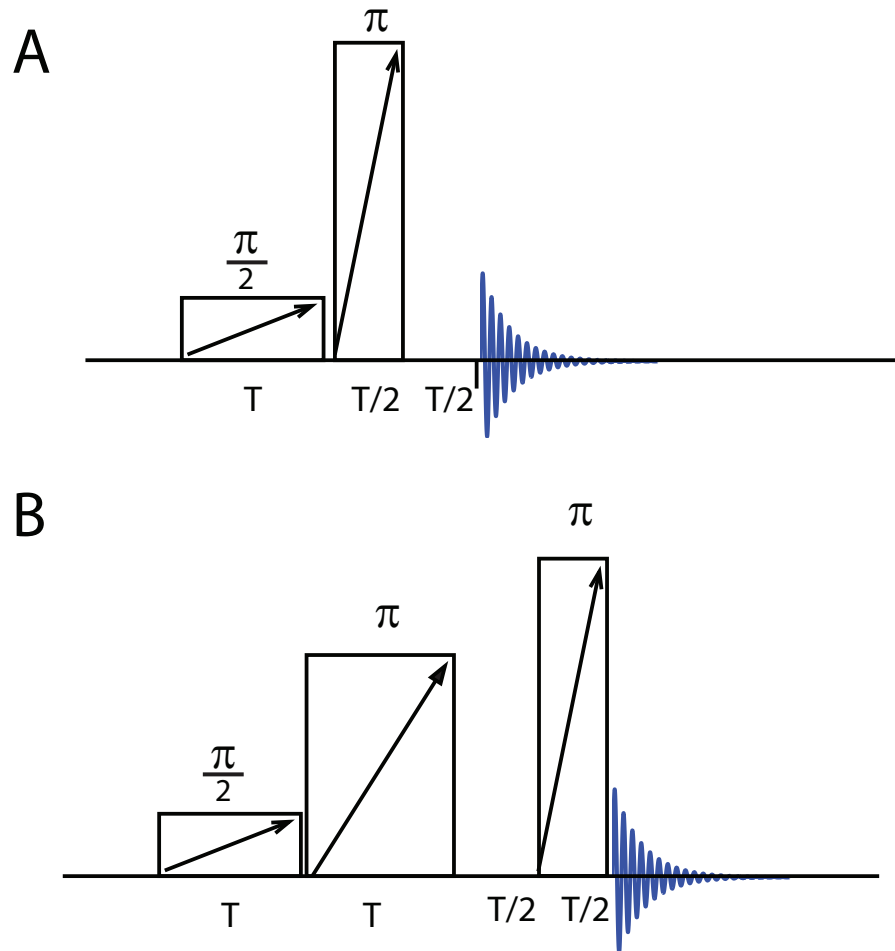


Figure 10: Fig. A shows the pulse sequence with a  $\frac{\pi}{2}$  excitation pulse of duration  $T$  followed by a  $\pi$  inversion pulse of duration  $\frac{T}{2}$  at twice the sweep rate and finally a free evolution for time  $\frac{T}{2}$ . Fig. B shows the pulse sequence with a  $\frac{\pi}{2}$  excitation pulse of duration  $T$  followed by a  $\pi$  inversion pulse of duration  $T$  both at same sweep rate and finally a free evolution for time  $\frac{T}{2}$  followed by a  $\pi$  inversion pulse of duration  $\frac{T}{2}$  at twice the chirp rate. The ratio of amplitude of last  $\pi$  pulse to center  $\pi$  pulse is  $\sqrt{2}$ .



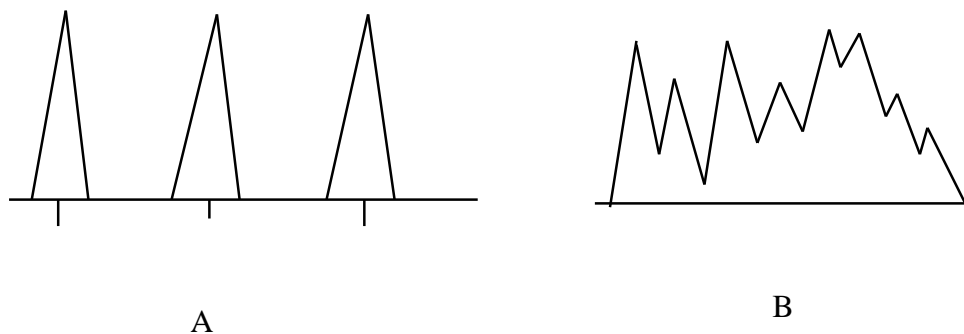


Figure 11: Fig. A shows spectrum of a molecule with few chemical shifts well separated and easily resolved. Fig. B shows molecule with many chemical shifts overlapping and not easily resolved.

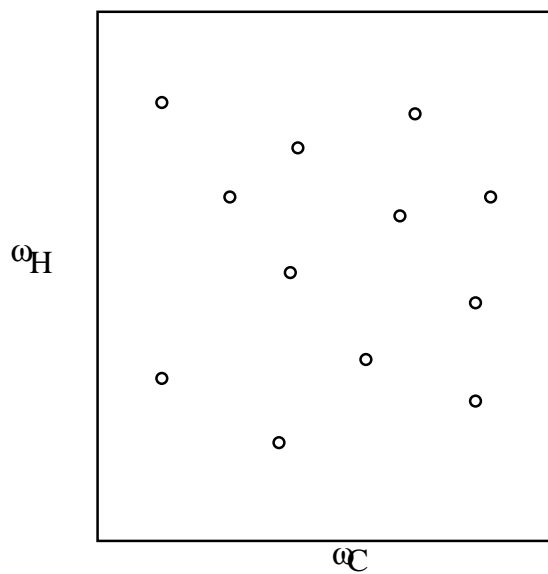


Figure 12: Fig. shows a 2D spectrum with joint frequency  $(\omega_H, \omega_C)$ . See peaks are well resolved as there is more room/space.