NMR Simulations using Python

Open ended lab submission

P-441/442 Report

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Abstract

Nuclear Magnetic Resonance or NMR was simulated using Python packages. We studied both the microscopic or Quantum picture and the macroscopic or the Classical picture. In microscopic scale, we saw the behaviour of magnetic moment with applied time dependent r.f field, while in macroscopic scale, we saw the overall magnetisation with changing r.f field, varying the parameters involved. NMR has huge applications in analyzing nuclear properties of matter.

Contents

Introduction

Nuclei have an intrinsic property which is magnetic moment μ, which is linearly proportional to angular momentum,

$$\mu = \gamma |P| = \gamma \hbar \sqrt{l(l+1)}$$

where, γ is gyromagnetic ratio which is a characteristic of a nucleus. The vector form of magnetic moment,

$$\vec{\mu} = \gamma \vec{P}$$

The orientation of magnetic moment is quantized. Here we will only talk about spin-half particles. So they have two orientations of μ.

Initially, in absence of magnetic field, the orientations share one degenerate energy state. As we apply magnetic field, the energy levels splits into two states, up-spin and down-spin.

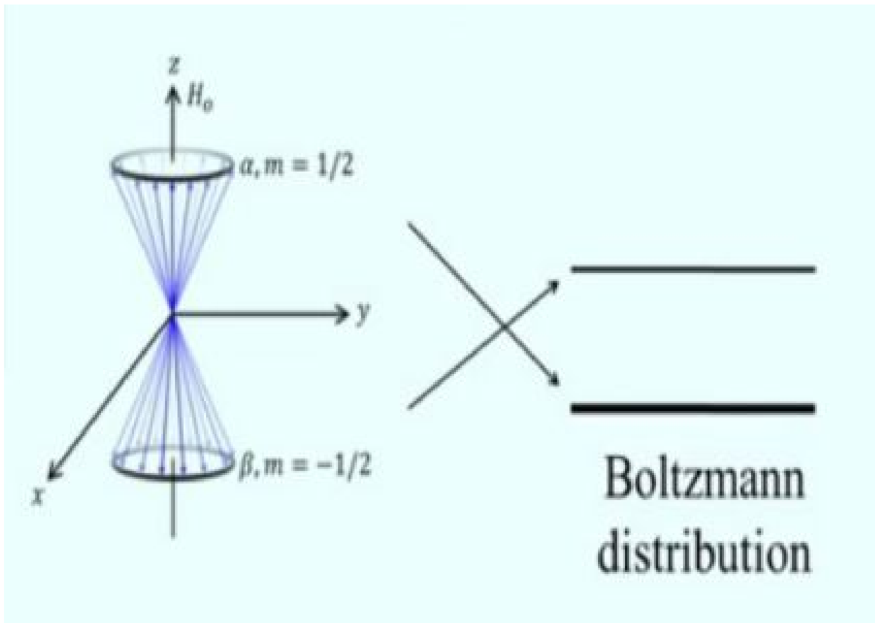

Figure 1.1: Spliting of the degenarate level

Quantum picture-
Spin probabilities

2.1 Theory

Say we apply a constant magnetic field H_0 to a nucleon, which is along Z direction. This is shown in the picture below. Now we apply a time varying

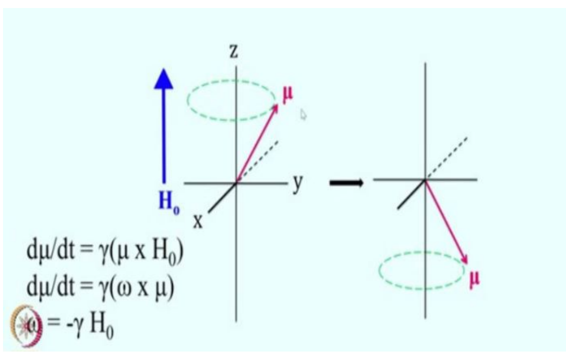

Figure 2.1: Magnetic moment under influence of H_0

radio frequency along x direction, with amplitude H_1. So the magnetic field takes the form,

$$H = H_0\hat{z} + H_1 cos(\omega t)\hat{x} \tag{2.1}$$

The condition is that $H_0 >> H_1$. The z component of H is responsible for the breaking of degeneracy of spin state into up-spin and down-spin, with energy gap $\Delta E \propto H_0$. This Zeeman effect. The small R.F. is responsible for transitions between up-state and down-state.

Now we consider the time dependent Schrodinger equation,

$$i\hbar\frac{d\psi(t)}{dt} = \hat{\mathcal{H}}\psi(t) \tag{2.2}$$

Here, $\psi(t)$ is the quantum state and $\hat{\mathcal{H}}$ is the Hamiltonian operator. In this simulation experiment, we only worked with spin half particles. So, we can consider $\psi(t)$ as a 2×1 matrix.

$$\psi(t) = \begin{bmatrix} a(t) \\ b(t) \end{bmatrix} \tag{2.3}$$

a(t) and b(t) are time dependent probability amplitude of spin up and spin down state respectively. The corresponding probabilities are

$$P_a = |a(t)|^2$$

$$P_b = |b(t)|^2$$

Now, the Hamiltonian operator for a spin is given by,

$$\hat{\mathcal{H}}(t) = -\vec{\mu}.\vec{H}(t)$$

where $\vec{\mu}$ = -g$\mu_B \hat{s}$, μ_B is the Bohr magneton, $\hat{s}$ is the spin operator. Putting the values of magnetic field and magnetic moment in the Hamiltonian, we get

$$\hat{\mathcal{H}}(t) = g\mu_B \hat{s}_z H_0 + g\mu_B \hat{s}_x H_1 cos(\omega t) \tag{2.4}$$

$$\frac{\hat{\mathcal{H}}(t)}{\hbar} = \omega_0 \hat{s}_z + \omega_1 \hat{s}_x cos(\omega t) \tag{2.5}$$

where $\omega_0 = g\mu_B H_0/\hbar$ and $\omega_1 = g\mu_B H_1/\hbar$. $\hat{s}_x$ and $\hat{s}_z$ are the Pauli matrices, we know the values. We can put all the values in the equation 2.2, to get

$$\begin{bmatrix} \dot{a} \\ \dot{b} \end{bmatrix} = -\frac{i}{2} \begin{bmatrix} \omega_0 & \omega_1 cos(\omega t) \\ \omega_1 cos(\omega t) & -\omega_0 \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} \tag{2.6}$$

Here we have two differential equations- for a and b. Now if we consider a and b to be complex, say $a = a_r + ia_i$ and $b = b_r + ib_i$, then we get four differential equations for each of a_r, a_i, b_r and b_i. Therefore,

$$\dot{a_r} = +\frac{1}{2}[\omega_0 a_i + \omega_1 cos(\omega t) b_i] \tag{2.7}$$

$$\dot{a_i} = -\frac{1}{2}[\omega_0 a_r + \omega_1 cos(\omega t) b_r] \tag{2.8}$$

$$\dot{b_r} = -\frac{1}{2}[\omega_0 b_i - \omega_1 cos(\omega t) a_i] \tag{2.9}$$

$$\dot{b_i} = +\frac{1}{2}[\omega_0 b_r - \omega_1 cos(\omega t) a_r] \tag{2.10}$$

2.2 Python simulation

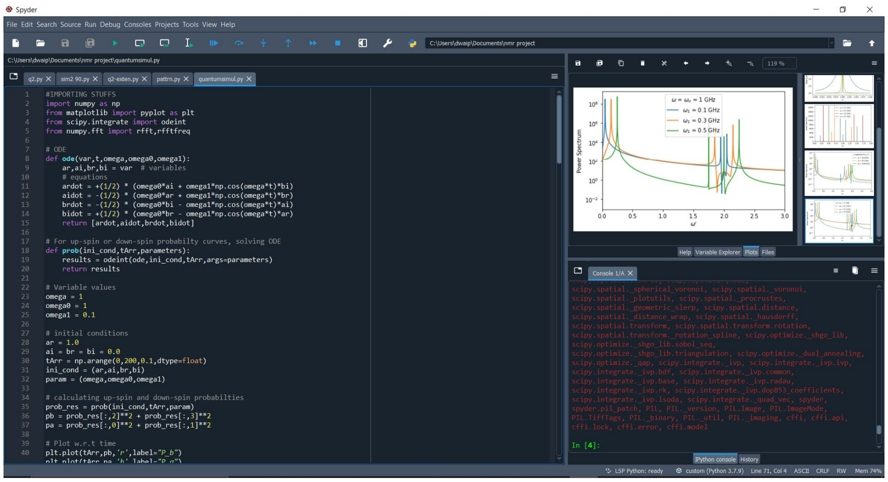

Figure 2.2: Working in Spyder (Python 3.8)

Now, this differential equations were solved using python. The plots we got and the analysis is discussed in this section.
The original code is provided in the references[2]

Before starting the simulation, we set the initial conditions. At t=0, $a_r = 1$ and $a_i = b_i = b_r = 0$, that means initially the magnetic moment is in spin up state. The R.F initiates flipping of the states[3] from spin up to spin down. Solving the differential equations and finding the probabilities Pa and Pb gives the plot with respect to time,

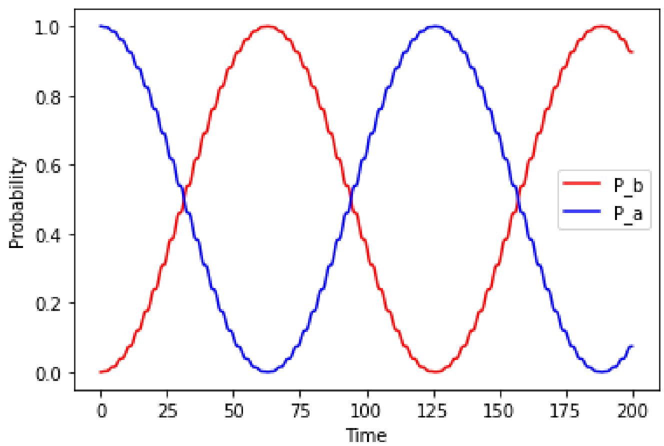

Figure 2.3: Probabilities of up spin and down spin with time. The conditions: $\omega = \omega_0 = 1$ and $\omega_1 = 0.1$

The flipping occurs at a certain frequency which is seen by the flipping probability plot, however the complete flipping can occur only at resonant condition $\omega = \omega_0$, as seen below.

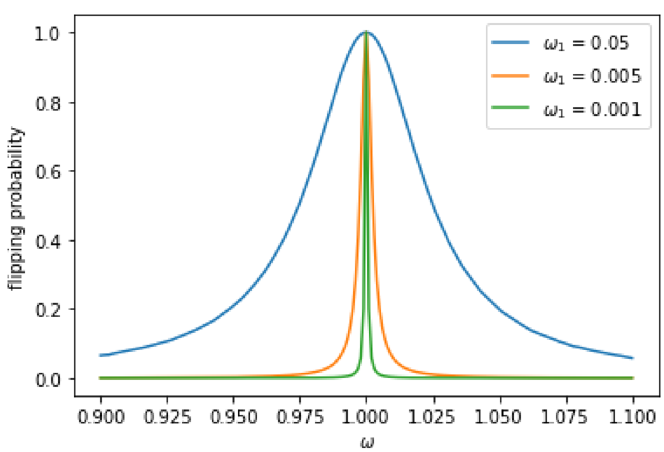

Figure 2.4: Flipping probability vs ω at different values of ω_1

The flipping probability touches 1 at resonant condition $\omega = \omega_0$=1. When $\omega \neq \omega_0$, the flipping probability lies between 0 and 1. We see that flipping probability curve changes with ω_1 of the R.F field. As ω_1 decrease, the curve gets narrower and hence increasing the precision of resonance.

Interestingly, we also observe some wiggles in the probability graph. So to analyse the curves, we need to study them in frequency domain. For that we apply fast Fourier transform and plot the power spectrum. Here for non resonant condition,

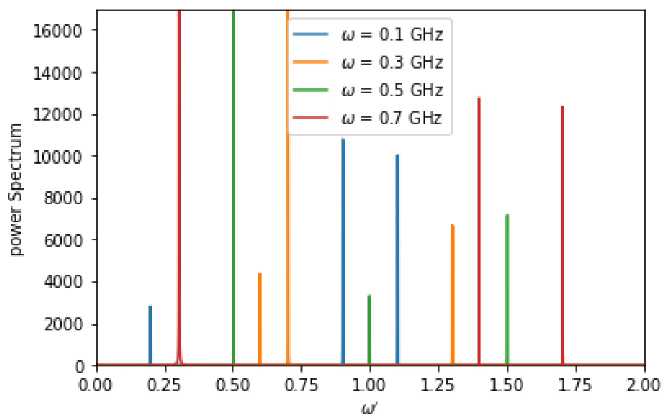

Figure 2.5: Power spectrum at different values of ω. The conditions: $\omega_0 = 1$ and $\omega_1 = 0.1$

In the power spectrum, three peaks are observed for each value of ω. They are positioned at $\omega' = 2\omega$, and other two at $\omega' = \omega_0 \pm \omega$. So the positions do not depend on the value of ω_1.

Now, to study them more closer, we plot the curves in semi-log scale for $\omega \to \omega_0$.

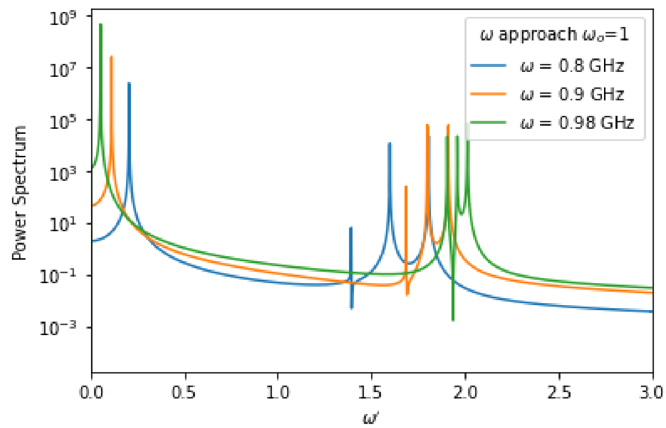

Figure 2.6: Power spectrum at different values of ω in semilog scale for $\omega \to \omega_0$. The conditions: $\omega_0 = 1$ and $\omega_1 = 0.1$

The intensity of the power spectrum increases as the ω approaches the resonant condition $\omega = \omega_1$. At the resonant condition, the positions are dependent on ω_1.

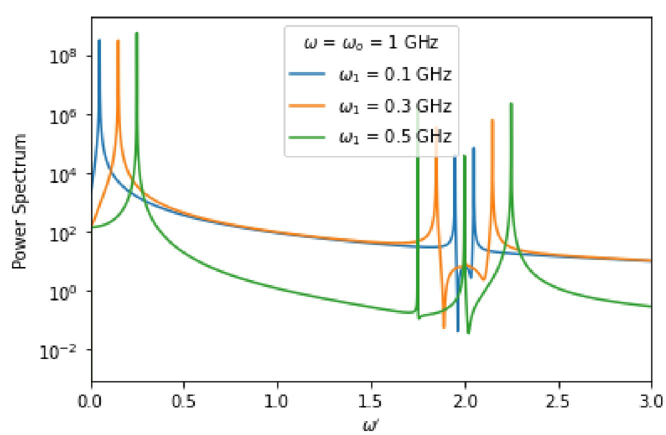

Figure 2.7: Power spectrum at different values of ω_1 for resonant condition. The conditions: $\omega = \omega_0 = 1$

We again see three peaks, at positions $\omega' = \omega_1/2$ and $\omega' = 2\omega_0 \pm \omega_1/2$. We have seen small wiggles earlier in the probability curve which was in the time domain. After Fourier transform, we were able to separate out low amplitude oscillations, which are the low intensity peaks in power spectrum. As we see in the above plot, the peak at $\omega' = \omega_1/2$ has the highest peak which denotes the probability curve. The other peaks have relatively low intensities thus represents the small wiggles in the probability curve. We can also see from the plot that the height of the peaks decreases with decreasing ω_1. Thus the wiggles decreases in intensity as the value of $\omega_1 \rightarrow 0$.

Classical picture-

Bloch equations

3.1 Theory

We will be talking about classical theory, so we consider macroscopic magnetization of the sample which is a vector that relaxes towards its thermal equilibrium value based on the interaction between spins and of the spin system with the lattice. Apart from the relaxation, this descriptions also describes the quantum mechanical picture i.e the magnetic moment operator. Here we will solve the Bloch equations and study the behaviour of magnetisation.

Say a static, homogeneous field B_0 is applied on z direction and a rotating field, B_1 is present on x,y plane.

The magnetization M have components $M_x,\ M_y,\ M_z$, and the interaction between magnetisation and the fields is governed by,

$$\left(\frac{dM}{dt}\right)_{fields} = \gamma M \times (B_0 + B_1) \tag{3.1}$$

where, γ is the gyromagnetic ratio.

The z component of M will return to its thermal equilibrium value, M_0 following first order kinetic law.

$$\left(\frac{dM_z}{dt}\right)_{relax} = -\frac{M_0 - M_z}{T_1} \tag{3.2}$$

M_0 is given by the Curie-Langevin Law[6]. T_1 is spin-lattice relaxation time or the time constant.

The x and y components of M also tends to their equilibrium value by redistribution the spins on x, y plane, given by,

$$\left(\frac{dM_{x,y}}{dt}\right)_{relax} = -\frac{M_{x,y}}{T_2} \tag{3.3}$$

T_2 is spin-spin relaxation time.

Adding up the equations (as vector sum) will give the resultant behaviour of magnetisation with time,

$$\frac{dM}{dt} = \gamma M \times (B_0 + B_1) + \frac{k(M_0 - M_z)}{T_1} - \frac{iM_z}{T_2} - \frac{jM_y}{T_2} \tag{3.4}$$

where i,j and k are the unit vectors along x,y and z axis.

So we got the Bloch equations, but it is difficult to solve considering all the directional components. Hence, we use rotational coordinate system. We define a rotating frame where z' axis of rotating frame coincides with z axis of the original fixed frame and x' and y' rotates around z or z' at angular frequency $\Omega = \Omega k$. Therefore we can write,

$$\left(\frac{d}{dt}\right)_{fixed} = \left(\frac{d}{dt}\right)_{rotating} + \Omega \times \tag{3.5}$$

k stays the same, i $\rightarrow$ i' and j $\rightarrow$ j'. The Bloch equation on rotating frame becomes,

$$\frac{dM}{dt} = \gamma M \times (B_a + B_1) + \frac{k(\omega_0 - \omega)}{T_1} - \frac{i'u}{T_2} - \frac{j'v}{T_2} \tag{3.6}$$

where $B_a = B_0 + (\Omega/\gamma)k$ is the apparent field. u,v and w are the components of M in the rotating frame.

We assume γ to be positive. When there is no B_1 and the relaxation time is zero, the magnetisation M seems constant in rotating frame given $\Omega = \gamma B_0 = \omega_0$, hence in the static frame the M is rotating with larmor frequency Ω. This is called free precession. Now time dependent B_1 field is introduced, at resonant condition ($\omega = \omega_0$). In rotating frame at $\Omega = \omega_0$, the B_1 is fixed as the frequency matches with rotation of B_1. The M preceses around B_1(along x' axis) at angular frequency $\omega_1 = -\gamma B_1$. This motion of M where the magnetization initially at equilibrium, gets a transverse component due to r.f. field is called nutation. When the resonant condition is not met, let B_1 rotate around with frequency ω and the rotating frame is also rotating at $\Omega = \omega$. The effective field will be,

$$B_e = (B_0 + \frac{\Omega}{\gamma})k + B_1 i'$$

The nutation motion will occur around the effective field with angular frequency $\omega_e = \gamma|B_e|$

We define $\Delta = \omega = \omega_0$ and $\omega_1 = \gamma B_1$. The Bloch equations in rotating field are given by,

$$\frac{du}{dt} = -\frac{u}{T_2} + \Delta v \tag{3.7}$$

$$\frac{dv}{dt} = -\Delta u - \frac{v}{T_2} - \frac{\omega_1}{w} \tag{3.8}$$

$$\frac{dw}{dt} = \omega_1 v - \frac{w}{T_1} + \frac{\omega_0}{T_1} \tag{3.9}$$

We are going to solve this ODEs in Python and study further changing its various parameters[2].

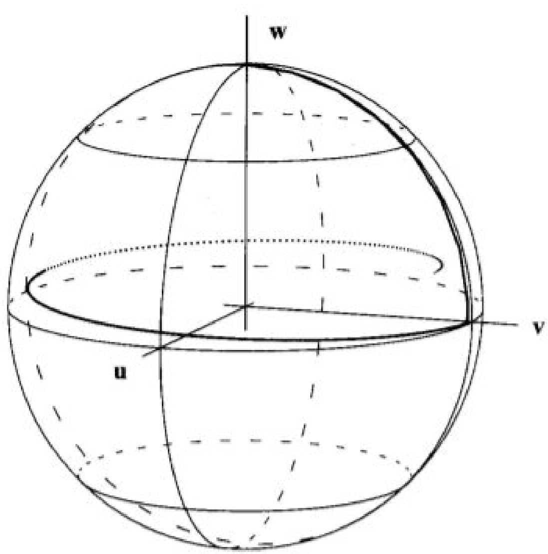

Figure 3.1: The rotating frame components of magnetisation

3.2 Simulation

3.2.1 Free precession

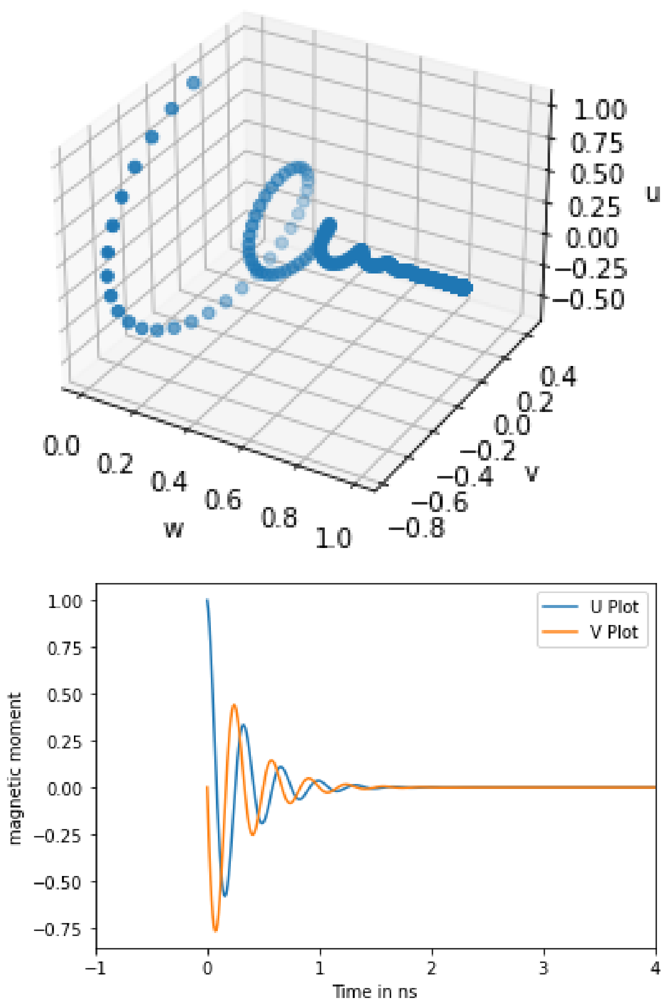

Figure 3.2: (a) Behaviour of magnetisation (u,v,w components) in free precession (b) u and v with respect to time t, (Conditions: T1=1s T2=0.3s, $\Delta/2\pi = 3$ Hz)

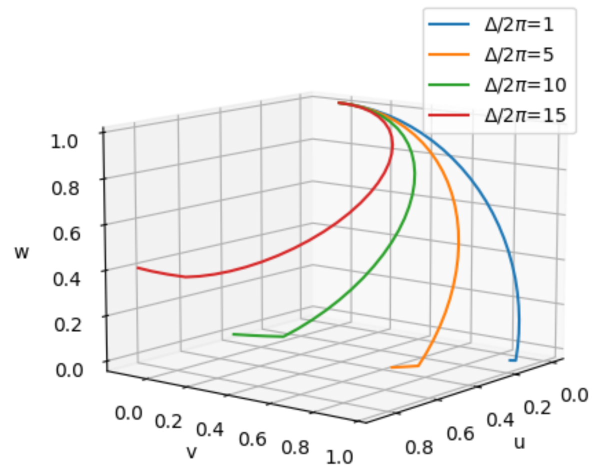

Figure 3.3: Magnetisation for a short period, for different values of Δ (conditions: T1=1s, T2=0.3s, $\omega_1/2\pi$=10Hz, $\Delta/2\pi = 1, 5, 10, 15$ Hz)

The initial conditions are taken to be $(u, v, w) = (1, 0, 0)$, which means M starts from u axis (Figure 3.1). The 3-D and 2-D plots are shown. The u and v relaxes to 0 and $\omega \to 1$. Figure 3.2 shows magnetisation for short period for various values of Δ. We observe free precession, which starts with $(u, v, w) = (0, 0, 1)$, that is from w axis.

3.2.2 90 degree pulse

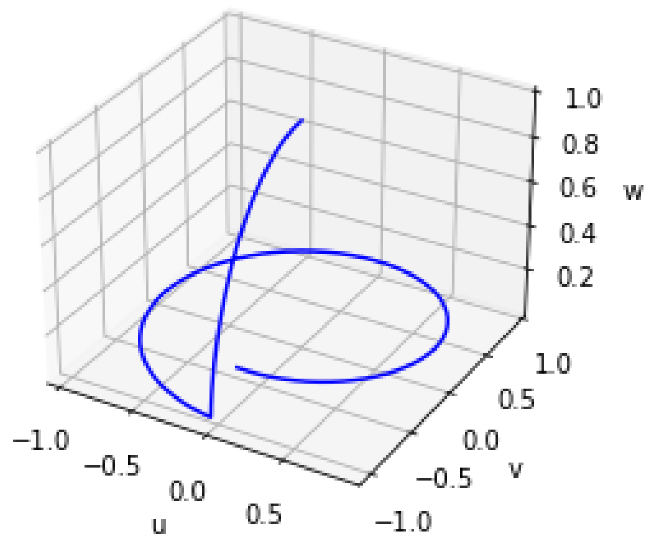

Figure 3.4: The path followed by the magnetisation vector after a 90 degree pulse (Conditions: T1=T2=10s, $\gamma B_1/2\pi = 10$ Hz, $\Delta/2\pi = 0.5$ Hz, $\tau = 0.025$)

The initial position is at $(u, v, w) = (0, 0, 1)$. The r.f field is applied for a certain amount of time τ. The flip angle is defined as,

$$\theta = \omega_e \tau = \omega_1 \tau$$

For $\theta = 90^o$, the r.f applied is called 90 degree pulse. The behaviour of the magnetisation vector for 90 degree pulse is given above. For $\theta = 180^o$, the r.f applied is called 180 degree pulse. The plot is given below.

3.2.3 180 degree pulse

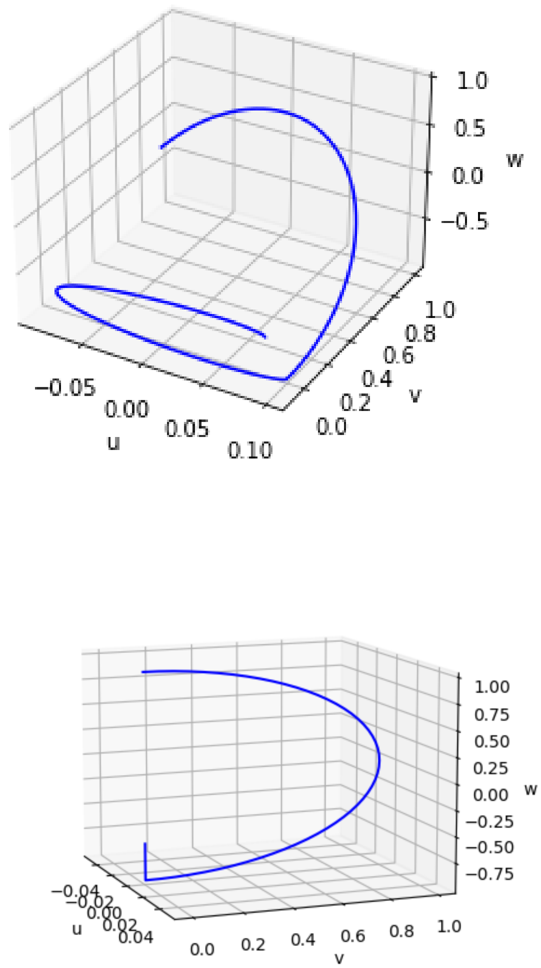

Figure 3.5: (a) Behaviour of magnetisation (u,v,w components) after 180 degree pulse, at non-resonant condition (b) At resonant condition, (Conditions: T1=T2=10s, $\gamma B_1/2\pi = 10$ Hz, $\Delta/2\pi = 0.5$ and 0 Hz, $\tau = 0.05$)

Conclusion

The simulation was successfully done in Python. The reference codes and Jupyter notebooks given in the paper are uploaded on github[2]. Various scenarios was studied in both quantum and classical picture. The differential equations were solved by odeint for both cases as it is easy to use and very accurate. Various conditions were seen. The wiggles in the probability curve was explained by the power spectrum in frequency domain, where we saw multiple low intensity peaks (2 peaks) describing low amplitude oscillations. It is also shown that the precision of resonant peaks increases with decrease in ω_1.

We also studied the involvement of relaxation time using Bloch equation. It arises from the need to reach the equilibrium state for the spin.

Acknowledgement

First of all, I would like to thank our professor, Dr.Pratap Kumar Sahoo and scientific officer, Dr. Santosh Babu Gunda for guiding us.

I also would like to thank my friends, who were there in the same experiment, for explaining certain concepts that I found hard to grasp.
I would like to thank SPS for giving this great opportunity. It was fun and kind of new experience for all of us.

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