QUANTUM MECHANICAL DESCRIPTION OF A ONE PULSE EXPERIMENT

$$\Psi_o \xrightarrow{\mathcal{H}} \Psi(t) \xrightarrow{R} \Psi' \xrightarrow{\mathcal{H}} \Psi'(t) \quad S(t) = <\Psi'(t)|S_x|\Psi'(t)>$$
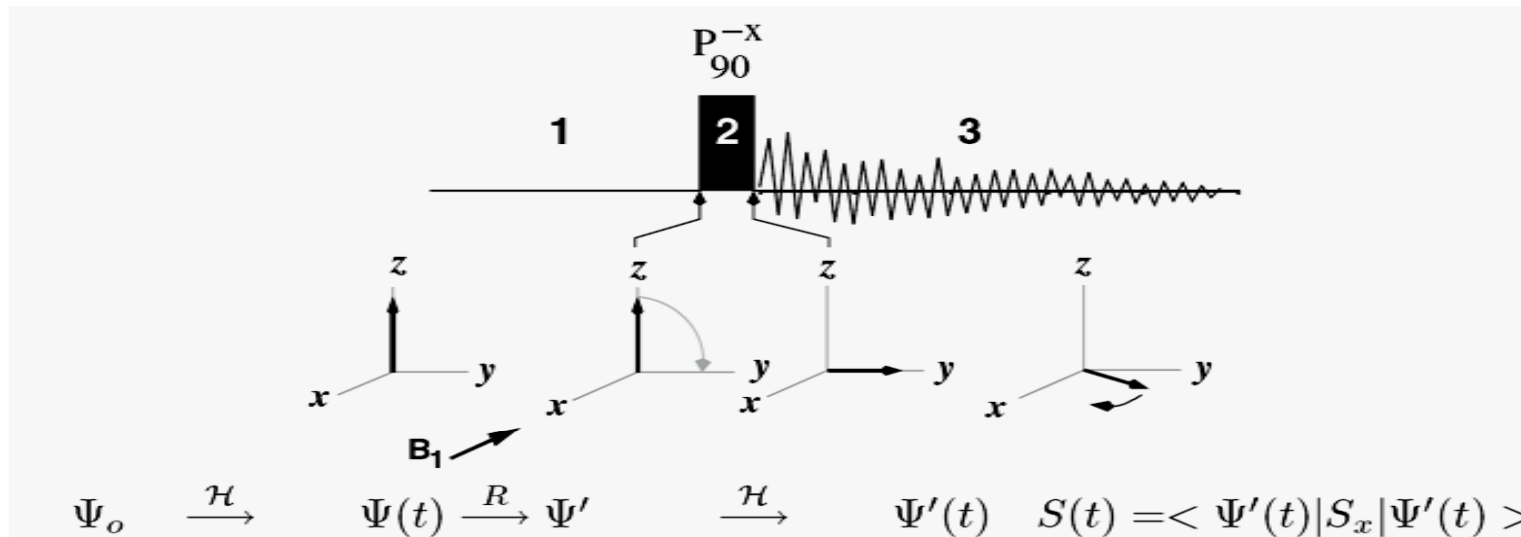
Figure 5.1. Quantum and classical description of a one–pulse experiment. The pulse sequence and resultant FID are shown in the top section of the figure. The experiment is divided into three sections: (1) **Preparation period**, prior to the pulse; (2) **Excitation** by a 90° RF-pulse along the minus x-axis. **(3)The detection period.**

Quantum mechanically the magnetization is represented by a wavefunction, pulses become rotation operators, and the detected signal is the expectation value of the x- and y- components of the spin angular momentum.

The operator for the spin angular momentum along *u is*

$$S_u = S_x \sin(\theta)\cos(\phi) + S_y \sin(\theta)\sin(\phi) + S_z \cos(\theta) \;=\; \frac{\hbar}{2}\begin{bmatrix} \cos(\theta) & \sin(\theta)e^{i\phi} \\ \sin(\theta)e^{-i\phi} & -\cos(\theta) \end{bmatrix}$$

(Remembering: $\quad S_x = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad S_y = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad S_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$)
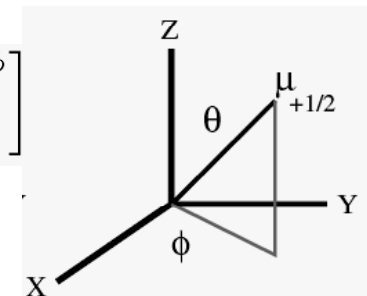
This operator has eigenvectors (written in terms of the eigenvectors of the Hamiltonian, $u_{+1/2}$, $u_{-1/2}$):

$$|+>_u = \cos(\frac{\theta}{2})e^{-i\phi/2}|u_{+1/2}> + \sin(\frac{\theta}{2})e^{i\phi/2}|u_{-1/2}> \qquad (5.3)$$

$$|->_u = -\sin(\frac{\theta}{2})e^{-i\phi/2}|u_{+1/2}> + \cos(\frac{\theta}{2})e^{i\phi/2}|u_{-1/2}> \qquad (5.4)$$

The wavefunctions $|+>_u$ and $|->_u$ describe the basis vectors of a spin oriented along the u axis.

5.1 Preparation: Evolution of the System Under B_o: $\quad i\hbar\dfrac{d\psi}{dt} = \mathcal{H}\psi = E\Psi$

If Ψ is an eigenfunction of the Hamiltonian ($H\Psi = E_u\Psi$). then the above equation can be integrated directly to give the following; $\quad \psi(t) = \psi(0)e^{\frac{-iEt}{\hbar}}$

For the eigenfunctions of a spin one-half particle, the time dependence of the eigenfunctions are explicitly: $\quad u_{+1/2}(t) = u_{+1/2}(0)e^{\frac{+i\omega_S t}{2}} \qquad u_{-1/2}(t) = u_{-1/2}(0)e^{\frac{-i\omega_S t}{2}}$

The time dependence of $|+>$ state is:

$$
\begin{aligned}
|+(t)> \; &= \; \cos(\frac{\theta}{2})e^{-i\phi/2}e^{+i\frac{\omega_S t}{2}}|u_{+1/2}> + \sin(\frac{\theta}{2})e^{i\phi/2}e^{-i\frac{\omega_S t}{2}}|u_{-1/2}> \\
&= \; \cos(\frac{\theta}{2})e^{-i(\phi-\omega_S t)/2}|u_{+1/2}> + \sin(\frac{\theta}{2})e^{i(\phi-\omega_S t)/2}|u_{-1/2}> \qquad (5.8)
\end{aligned}
$$

Comparing Eq. 5.3 to Eq. 5.8 shows that: $\qquad \theta(t) = \theta_0 ; \qquad \phi(t) = \phi_0 - \omega_s t$

Thus, the angle of u with respect to the field, θ, does not change in time, but u precesses around ^k with an angular velocity ω_s, the absorption frequency of the transition.
Note that this precession is identical to the classical precession of the magnetic moment about the Bo field.

The expectation values of the z- and x-components of the angular momentum of the system are easily calculated for the basis functions (See 5.8): $u_{+1/2} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$; $u_{-1/2} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

$$|+(t)> = \begin{bmatrix} \cos(\frac{\theta}{2})e^{-i(\phi_o - \omega_S t)/2} \\ \sin(\frac{\theta}{2})e^{i(\phi_o - \omega_S t)/2} \end{bmatrix} = \begin{bmatrix} \cos(\frac{\theta}{2})e^{-i\phi(t)/2} \\ \sin(\frac{\theta}{2})e^{i\phi(t)/2} \end{bmatrix}$$

$$<S_z> = <+(t)|S_z|+(t)> = \begin{bmatrix} \cos(\frac{\theta}{2})e^{+i\phi(t)/2} & \sin(\frac{\theta}{2})e^{-i\phi(t)/2} \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \cos(\frac{\theta}{2})e^{-i\phi(t)/2} \\ \sin(\frac{\theta}{2})e^{i\phi(t)/2} \end{bmatrix}$$

$$= \frac{\hbar}{2}\left[\cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2}\right] = \frac{\hbar}{2}\cos\theta$$

$$<S_x> = \begin{bmatrix} \cos(\frac{\theta}{2})e^{+i\phi(t)/2} & \sin(\frac{\theta}{2})e^{-i\phi(t)/2} \end{bmatrix} \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} \cos(\frac{\theta}{2})e^{-i\phi(t)/2} \\ \sin(\frac{\theta}{2})e^{i\phi(t)/2} \end{bmatrix} = \frac{\hbar}{2}\sin\theta\cos(\phi_o - \omega_S t)$$

Note that the z-component of the angular momentum is not time dependent. Since the energy of the system is directly proportional to S_z, the energy of the system is also time invariant, as one would expect for a spin in a static magnetic field. In contrast, the x-component is time dependent, oscillating with a frequency equal to ω_s. The spin is precessing about the static magnetic field at its Larmor frequency, as expected from the classical model.

5.2 Excitation: Effect of Application of B1:

The Hamiltonian operator in the presence of the B_1 field on the x-y lane is given by:

$$\mathcal{H} = -\gamma\vec{S}\cdot[\vec{B}_o + \vec{B_1}(t)] = \omega_s S_z + \omega_1[\cos(\omega t)S_x + \sin(\omega t)S_y]$$

Using the definitions of the Sx, Sy, and Sz operators it is possible to express the Hamiltonian in matrix form as the following:

$$\mathcal{H} = \frac{\hbar}{2}\begin{bmatrix} \omega_s & \omega_1 e^{-i\omega t} \\ \omega_1 e^{+i\omega t} & -\omega_s \end{bmatrix} \quad (5.13)$$

Choose an arbitrary wavefunction : $\quad \psi = a_+ u_{+1/2} + a_- u_{-1/2} = \begin{bmatrix} a_+ \\ a_- \end{bmatrix} \quad (5.15)$

Then the evolution of ψ is given by:

$$i\hbar \frac{d\psi}{dt} = H\psi$$

Substitute H and ψ we got:

$$i\frac{da_+}{dt} = \frac{\omega_s}{2}a_+ + \frac{\omega_1}{2}e^{-i\omega t}a_- \qquad i\frac{da_-(t)}{dt} = \frac{\omega_1}{2}e^{i\omega t}a_+ - \frac{\omega_s}{2}a_- \qquad (5.17)$$

   Equations 5.16 and 5.17 indicate that the wave function now becomes time dependent, i.e. the probability that the system will be found in one of the two eigenfunctions of the Hamiltonian changes with time. These time dependent equations are difficult to solve in their current form. It will be more convenient to analyze in the rotating frame. The operator for rotation about the z-axis at a rate of $w_r t$ is (Eq. 4.101 on p. 133):

$$R_z(-\omega_r t) = \cos\frac{-\omega_r t}{2}\tilde{1} - i\sigma_z \sin\frac{-\omega_r t}{2}$$

$$= \begin{bmatrix} \cos\frac{-\omega_r t}{2} - i\sin\frac{-\omega_r t}{2} & 0 \\ 0 & \cos\frac{-\omega_r t}{2} + i\sin\frac{-\omega_r t}{2} \end{bmatrix} = \begin{bmatrix} e^{+i\frac{\omega_r}{2}t} & 0 \\ 0 & e^{-i\frac{\omega_r}{2}t} \end{bmatrix} \qquad (5.20)$$

Where σ is the Pauli matrix

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (4.97)$$

The angular momentum $S_u = (\hbar/2)\sigma_u$ and $\sigma^2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

The effect of this rotation on the wave function is:

$$\psi' = R_z(-\omega_r t)\psi = \begin{bmatrix} e^{+i\frac{\omega_r}{2}t} & 0 \\ 0 & e^{-i\frac{\omega_r}{2}t} \end{bmatrix}\begin{bmatrix} a_+ \\ a_- \end{bmatrix} = \begin{bmatrix} a_+ e^{+i\frac{\omega_r}{2}t} \\ a_- e^{-i\frac{\omega_r}{2}t} \end{bmatrix} \qquad (5.23)$$

The coefficients in the rotating frame are: $\quad a_+^r = e^{i\omega_r t/2}a_+ \qquad a_-^r = e^{-i\omega_r t/2}a_-$

Substituting these into eq. 5.16 and 5.17 and after some math we got:

$$i\frac{da_+^r}{dt} = \frac{(\omega_S - \omega_r)}{2}a_+^r + \frac{\omega_1}{2}e^{-i(\omega-\omega_r)t}a_-^r \quad \text{and} \quad i\frac{da_-^r}{dt} = \frac{\omega_1}{2}e^{+i(\omega-\omega_r)t}a_+^r(t) + -\frac{(\omega_S - \omega_r)}{2}a_-^r$$

The coefficients of the a^r_+ and a^r_- terms can be used to define the effective Hamiltonian in the rotating frame. After some math and assume that the rotation rate of the coordinate system is equal to the frequency of the B1 pulse, i.e. $\omega = \omega_r$, and we define $\Delta\omega = \omega_s - \omega_r$ for th eon resonance condition:

$$\mathcal{H}_{eff} = \frac{\hbar}{2}\begin{bmatrix} \Delta\omega & \omega_1 \\ \omega_1 & -\Delta\omega \end{bmatrix} = \frac{\hbar}{2}\begin{bmatrix} 0 & \omega_1 \\ \omega_1 & 0 \end{bmatrix} = \omega_1 S_x$$

The time evolution of the system in the rotating frame during the RF-pulse can be calculated from the Schrodinger equation to give:

$$\Psi(t) = e^{(-i/\hbar)S_x\omega_1 t}\Psi(0) = R_x(\omega_1\tau)\Psi(0) \qquad (5.27)$$

The above expressions shows that the time evolution of the system during a pulse is equivalent to a rotation. The direction of the rotation axis is defined by the direction of the pulse and the rotation angle is given by $\omega_1\tau$, where τ is the duration of the pulse.

5.2.1 The Resonance Condition

Since the evolution of the system during the pulse is simply described by a rotation operator, it is easy to calculate the state of the system after the pulse, given the state of the system before the pulse. Taking the specific case of a system beginning in the $u_{+1/2}$ state ($a_+ = 1$), the effects of a 90°, 180°, or 360° pulse on this state are as follows (See Eqs. 4.121, 4.126, and 4.127, in Chapter 4):

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix} \xrightarrow{R_x(\pi/2)} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \qquad \begin{bmatrix} 1 \\ 0 \end{bmatrix} \xrightarrow{R_x(\pi)} \begin{bmatrix} 0 \\ -i \end{bmatrix} \qquad \begin{bmatrix} 1 \\ 0 \end{bmatrix} \xrightarrow{R_x(2\pi)} \begin{bmatrix} -1 \\ 0 \end{bmatrix}$$

The probability of finding the system in the $u_{-1/2}$ after the pulse, $P_{-1/2}$, is just $a^*_- a_-$, giving:

$$P_{-1/2} : 0 \xrightarrow{R_x(\pi/2)} 1/2 \qquad 0 \xrightarrow{R_x(\pi)} 1 \qquad 0 \xrightarrow{R_x(2\pi)} 0$$

The probability of finding the system in the $u_{-1/2}$ state, $P_- = a^*_- a_-$, can be calculated using the effective Hamiltonian in the rotating frame. The dependence of P_- on the frequency offset ($\Delta w = w_s - w$) and pulse length, τ, is given by Eq. 5.32 (see Cohen-Tannoudji *et al.* [42] for more details). This transition probability is shown in Fig. 5.2 for an on-resonance pulse and a pulse that is 6000 Hz off resonance. The field strength of the pulse, w_1 was 2500 Hz, giving a 90° pulse of 100 μsec. Note that the transition probability oscillates with time. In the case of the on-resonance pulse, there is complete conversion of the system from the $u_{+1/2}$ state to the $u_{-1/2}$ state in 200 μsec. This corresponds to a 180° pulse, or complete inversion of the magnetization. At four times the 90° pulse length, or 400 μsec, the system is returned to the original state, corresponding to a 360° pulse. The transition probabilities for the on-resonance pulses in Fig. 5.2 (solid curve) are identical to those presented in Eqs. 5.31, as expected.

$$P_-(t) = \frac{\omega_1^2}{\omega_1^2 + (\Delta\omega)^2} \sin^2\left[\sqrt{\omega_1^2 + (\Delta\omega)^2}\,\frac{\tau}{2}\right] \qquad (5.32)$$

Figure 5.2. Effect of frequency offset on transition probabilities. The probability of finding the system in the $u_{-1/2}$ state, after starting entirely in the $u_{+1/2}$ state at t=0 is shown for an on-resonance pulse (solid line) and a pulse that is 6000 Hz off-resonance (dashed line).
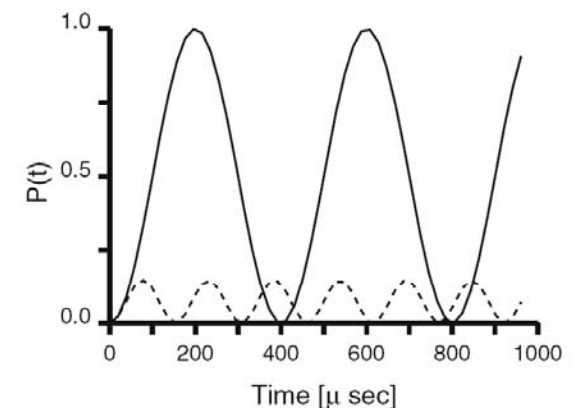
In the case of an off-resonance pulse, the extent of conversion between states is significantly smaller, showing that an off-resonance pulse is less efficient at causing transitions. Also note that the frequency of the oscillations of P(t) has increased for the off-resonance pulse. This is due to the fact that the effective magnetic field is larger than for the on-resonance spins, causing a faster transition rate, or a faster precessional rate in the classical model.

5.3 Detection: Evolution of the System Under B_o

After the pulse, the magnetization will precess about B_o, as it did during the preparation period. The difference between the state of the system prior to the pulse and after the pulse is that the system will have been rotated to a new direction, u by the application of the RF-pulse. As before, the z-component of the spin angular momentum of the system will be time invariant. In contrast, the expectation value of S_x will evolve as $\cos(w_s t)$, while the expectation value of Sy will evolve as $\sin(w_s t)$, generating the cosine and sine modulated signals in the detection coil.

Chapter 6   THE DENSITY MATRIX & PRODUCT OPERATORS

The system at the beginning of the experiment:
$$\Psi(0) = \sum c_i(o)u_i$$

At the end of the NMR experiment:
$$\Psi(t) = \sum c_i(t)u_i$$

Regardless of the change in the coefficients, it is possible to calculate the expectation value of any observable. For example, the signal detected in the real channel of the receiver, S_x, is given by:

$$< S_x > \quad = \quad < \Psi|S_x|\Psi > \quad = \quad \sum_{ij} c_i^*(t)c_j(t) < u_i|S_x|u_j >$$

However, in most NMR experiments, the detected signal arises from an ensemble of N spins, therefore, the average expectation value of S_x is the actual observable:

$$\overline{< S_x >} = \sum_N \sum_{ij} c_i^*(t)c_j(t) < u_i|S_x|u_j >$$

This ensemble average can be obtained in one of two ways. The first method involves calculating the evolution of all N wavefunctions through the experiment and then averaging over all N spins. This procedure is very tedious. The second method use density matrix approach, which is more concise and manipulatable.

The density matrix is a matrix whose elements contain information on the average probability of all possible states of the ensemble. Instead of following the evolution of the different wavefunctions through the experiment, the evolution of the density matrix is followed. At the end of the experiment, the average expectation values are obtained from the final density matrix. The close correspondence between the wavefunction and the density matrix is illustrated below:

$$\Psi_o \xrightarrow{\mathcal{H}} \Psi(t) \xrightarrow{R} \Psi' \xrightarrow{\mathcal{H}} \Psi'(t) \qquad S(t) = < \Psi'(t)^*|S_x|\Psi'(t) >$$
$$\rho_o \xrightarrow{\mathcal{H}} \rho(t) \xrightarrow{R} \rho' \xrightarrow{\mathcal{H}} \rho'(t) \qquad S(t) = Trace[\rho S_x]$$

6.1 Introduction to the Density Matrix

The information on the ensemble average of a system is contained in the ensemble average of the pairwise products of the coefficient that are associated with the basis vectors, for example:

$$< S_x > = \sum_N \sum_{ij} c_i^*(t)c_j(t) < u_i|S_x|u_j > = \sum_{ij} \overline{c_i^*(t)c_j(t)} < u_i|S_x|u_j >$$

Therefore, if we specified the value of: $\overline{c_i^*(t)c_j(t)}$ for all possible values of i and j, then the properties of the system are completely determined. The density matrix, ρ, consists of all such products.

The mth, nth element of the density matrix (ρmn) for an arbitrary, time-dependent, wavefunction is obtained as follows:

$$\rho_{mn}(t) = < u_m|\psi(t) >< \psi(t)|u_n > = < u_m|\psi(t) > c_n^*(t) = c_m(t)c_n^*(t)$$

For a system with two basis vectors the density matrix is:

$$\rho = \begin{bmatrix} c_1 c_1^* & c_1 c_2^* \\ c_2 c_1^* & c_2 c_2^* \end{bmatrix} \qquad (6.7)$$

The matrix elements of the density matrix, as defined by Eq. 6.6 are of the same form as the matrix elements of an operator. Hence the density matrix is an operator, and will be transformed by rotations with the same rules as any other operator:

$$\rho' = R\rho R^\dagger$$

6.1.1 Calculation of Expectation Values From ρ

The expectation value for an observable:

$$A = < \psi|A|\psi > = \sum_{k,p} < c_k^* u_k|A|c_p u_p > = \sum_{k,p} c_p c_k^* < u_k|A|u_p >$$

$$= \sum_{k,p} \rho_{pk} < u_k|A|u_p > = \sum_{k,p} < u_p|\rho|u_k >< u_k|A|u_p > = \sum_p \rho_{pp} A_{pp}$$

$$= \mathrm{Trace}[\rho A] \quad \text{(The trace of a matrix is simply the sum of its diagonal elements)}$$

➔ IF we know the density matrix of the system at anytime we can easily calculate the expectation values of an operator from that density matrix. E.g. The signal detected for the real dat channel would be:

$$M_x = \mathrm{Trace}(\rho S_x)$$

6.1.2 Density Matrix for a Statistical Mixture

For the case of a single isolated spin, representation of the system by either its wavefunction or density matrix are essentially equivalent and equally tedious. However, if there is a statistical mixture of states, such as the large number of molecules in a typical NMR sample, the density matrix is much more convenient. For an ensemble of spins, the total state of the system is given by:

$$\Psi = \sum_{k=0}^{N} p_k \psi_k$$

where p_k is the statistical probability of finding a spin in a particular state. p_k is the fraction of the kth mixed state or sub-system in the sample, and ψ_k corresponds to the wavefunction for that sub-system. Each ψ_k is a linear combination of the basis functions:

$$\psi_k = \sum_i c_i^k u_i$$

where c_j^k are the normal quantum mechanical probabilities associated with finding the wavefunction in the ith state. The expectation value of any operator, A, for the kth sub-system is:

$$A_k = < \psi_k | A | \psi_k >$$

The average value of this observable for the entire system is the expectation value associated with a particular state, multiplied by the statistical probability of that particular state.

$$\overline{A} = \sum_k p_k A_k$$

The expectation value of the system in the kth sub-state is:

$$A_k = \text{Trace}\,(\rho^k A) = \sum_j \rho_{jj}^k A_{jj}$$

Therefore, the average expectation value over the entire ensemble of sub-states is:

$$\overline{A} = \sum_k p_k \text{Trace}(\rho^k A) = \sum_k p_k \sum_j \rho_{jj}^k A_{jj} = \sum_j \sum_k p_k \rho_{jj}^k A_{jj}$$

$$= \sum_j \bar{\rho}_{jj} A_{jj} = \text{Trace}[\bar{\rho} A]$$

The important result is that the average expectation value can be obtained from the average density matrix in exactly the same fashion as the expectation value of a single spin was obtained from its density matrix (see Eq. 6.9).

As an example consider the wavefunction for a spin that is oriented at an angle θ and φ in polar coordinates:

$$\Psi = \cos(\frac{\theta}{2})e^{-i\phi/2}|u_{+1/2}> + \sin(\frac{\theta}{2})e^{i\phi/2}|u_{-1/2}>$$

The density matrix for this state is:

$$\rho = \begin{bmatrix} \cos^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{-i\phi} \\ \cos(\theta/2)\sin(\theta/2)e^{+i\phi} & \sin^2(\theta/2) \end{bmatrix}$$

The expectation value for S$_x$ is: $< S_x >= \text{Trace}(\rho S_x)$

$$\begin{aligned} \rho S_x &= \begin{bmatrix} \cos^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{-i\phi} \\ \cos(\theta/2)\sin(\theta/2)e^{+i\phi} & \sin^2(\theta/2) \end{bmatrix} \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ &= \frac{\hbar}{2}\begin{bmatrix} \cos(\theta/2)\sin(\theta/2)e^{-i\phi} & \cos^2(\theta/2) \\ \sin^2(\theta/2) & \cos(\theta/2)\sin(\theta/2)e^{+i\phi} \end{bmatrix} \end{aligned}$$

$$\begin{aligned} < S_x > &= \text{Trace}(\rho S_x) = \frac{\hbar}{2}\left[\cos\frac{\theta}{2}\sin\frac{\theta}{2}e^{-i\phi} + \cos\frac{\theta}{2}\sin\frac{\theta}{2}e^{+i\phi}\right] \\ &= \frac{\hbar}{2}2\cos\frac{\theta}{2}\sin\frac{\theta}{2}\left[\frac{e^{i\phi}+e^{-i\phi}}{2}\right] = \frac{\hbar}{2}2\cos\frac{\theta}{2}\sin\frac{\theta}{2}\cos\phi \end{aligned}$$

If the spin is oriented such that its magnetic moment is along the x-axis, then θ = 90, and φ = 0. The expectation value of S$_x$ is then, $< S_x >= \frac{\hbar}{2}2\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2}} = \frac{\hbar}{2}$ as expected:

Calculation of the expectation value of S$_y$ for this example yields <Sy >= 0.

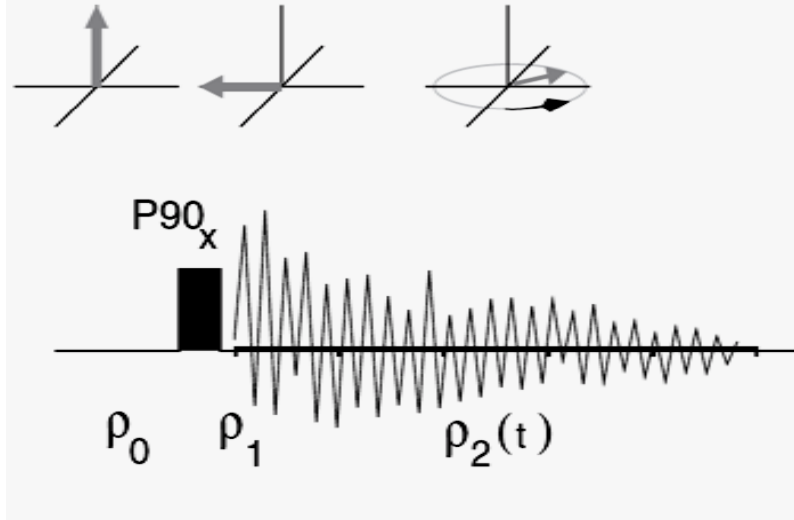## 6.2 One-pulse Experiment: Density Matrix Description

Figure 6.2 Density matrix description of the one-pulse experiment. The top part of the figure shows the classical description of a one-pulse NMR experiment. The density matrix ρ_o defines the system prior to the pulse, ρ_1 is the system immediately after the pulse, and $\rho_2(t)$ defines the time evolution of the system during detection of the free induction decay.

The density matrix that describes an ensemble of spins at thermal equilibrium, or ρ_o, is required. This density matrix should reflect the fact that the average value of $< S_x >$ and $< S_y >$ are zero, and it should also reflect the population difference between the ground and the excited state at thermal equilibrium.

The population difference at thermal equilibrium is given by the Boltzmann distribution:

$$\frac{e^{-E/kT}}{Z}$$

Using the Boltzmann distribution as an operator gives the desired form of the density matrix. A single element of the density matrix is:

$$\rho_{pn} = < u_p | \frac{e^{-\mathcal{H}/kT}}{Z} | u_n >$$

And the entire density matrix is:

$$\rho = \frac{1}{Z} \begin{bmatrix} < u_1 | e^{-\mathcal{H}/kT} | u_1 > & < u_1 | e^{-\mathcal{H}/kT} | u_2 > \\ < u_2 | e^{-\mathcal{H}/kT} | u_1 > & < u_2 | e^{-\mathcal{H}/kT} | u_2 > \end{bmatrix} = \frac{1}{Z} \begin{bmatrix} e^{-E_1/kT} < u_1 | u_1 > & e^{-E_2/kT} < u_1 | u_2 > \\ e^{-E_1/kT} < u_2 | u_1 > & e^{-E_2/kT} < u_2 | u_2 > \end{bmatrix}$$

$$= \frac{1}{Z} \begin{bmatrix} e^{-E_1/kT} & 0 \\ 0 & e^{-E_2/kT} \end{bmatrix} = \frac{1}{Z} \begin{bmatrix} e^{+\hbar\omega_o/2kT} & 0 \\ 0 & e^{-\hbar\omega_o/2kT} \end{bmatrix}$$

Expanding the exponential as a series and taking only the first term ($e^a \approx 1 + a$) we find:

$$\rho = \frac{1}{Z}\begin{bmatrix} 1+\gamma & 0 \\ 0 & 1-\gamma \end{bmatrix} = \frac{1}{Z}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{Z}\frac{\omega_o}{kT}\frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (6.28)$$

Where $\gamma = \hbar\omega_o/2kT$.

One can see that this matrix is composed of the unit matrix plus S_z. Since the unit matrix has no effect on any of the common observables we can ignore it 1. Furthermore, since we are only interested in the changes in the amplitudes and the time evolution of the individual elements of the density matrix, we can also ignore constants. Therefore, the density operator for a system under thermal equilibrium can be written:

$$\rho_0 = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = S_z$$

To simplify the calculations even further, can be removed from the expression using the following representation of angular momentum operators: Thus, ρ_o is equal to the matrix I_z.

$$I_x = \frac{S_x}{\hbar} = \frac{1}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad I_y = \frac{S_y}{\hbar} = \frac{1}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \qquad I_z = \frac{S_z}{\hbar} = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad (6.30)$$

6.2.1 Effect of Pulses on the Density matrix

$$\rho' = R\rho R^\dagger = e^{-iP}\rho e^{iP}$$

$$R_\phi(\alpha) = e^{-iP} = \begin{bmatrix} \cos(\frac{\alpha}{2}) & -i\sin(\frac{\alpha}{2})e^{-i\phi} \\ -i\sin(\frac{\alpha}{2})e^{i\phi} & \cos(\frac{\alpha}{2}) \end{bmatrix} \qquad R_x(\pi/2) = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}$$

The density matrix after this pulse is given by:

$$\rho_1 = R_x I_z R_x^\dagger = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & -i \\ -i & 1 \end{bmatrix}\frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\frac{1}{\sqrt{2}}\begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} = \frac{1}{2}\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix} = -I_y$$

If we calculate the expectation value of S_x, S_y, and S_z for this density matrix, we find:

$$\langle Sx \rangle = 0; \quad \langle S_y \rangle = -1; \quad \langle S_z \rangle = 0 \qquad (6.34)$$

Note that the off-diagonal elements of the density matrix after the pulse are clearly non-zero. This implies that the ensemble average of this element of the density matrix is non-zero. Therefore, after the pulse, the distribution of the spins about the z-axis is no longer random - a preferred direction of the spins has been induced by the pulse. Specifically, the ensemble of spins has become coherent, with each spin having the same value of φ (compare to Eq. 6.24).

6.2.1.1 Free Precession: Time evolution of the Density Matrix