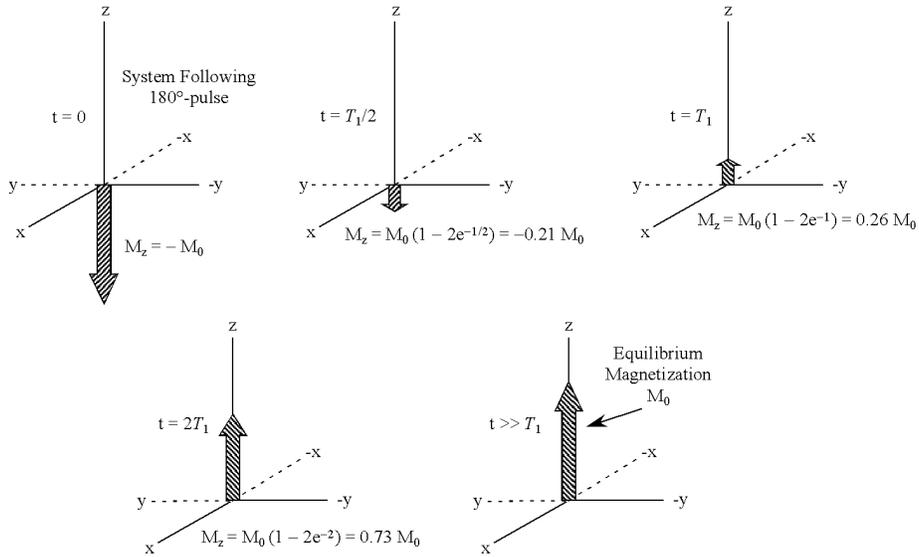
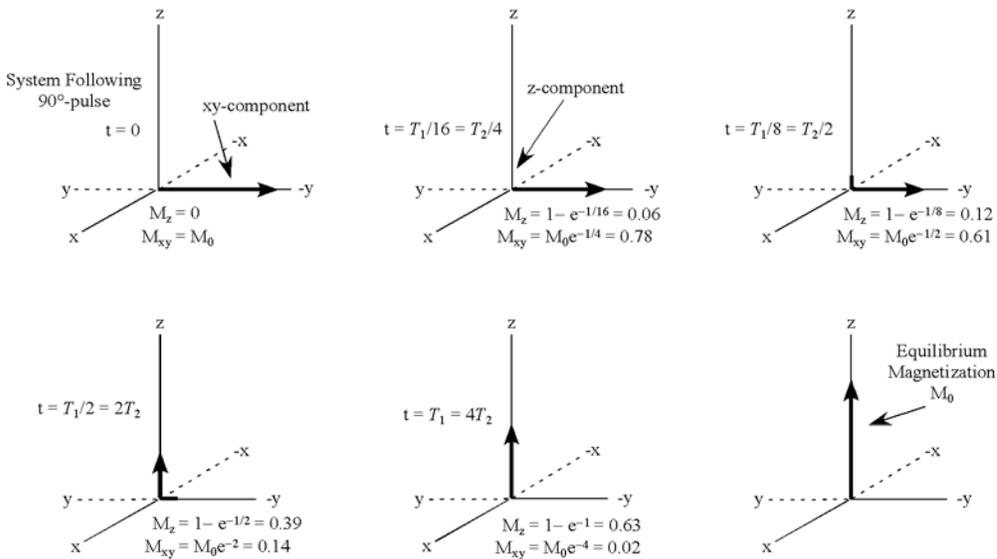


More NMR Relaxation

Longitudinal Relaxation



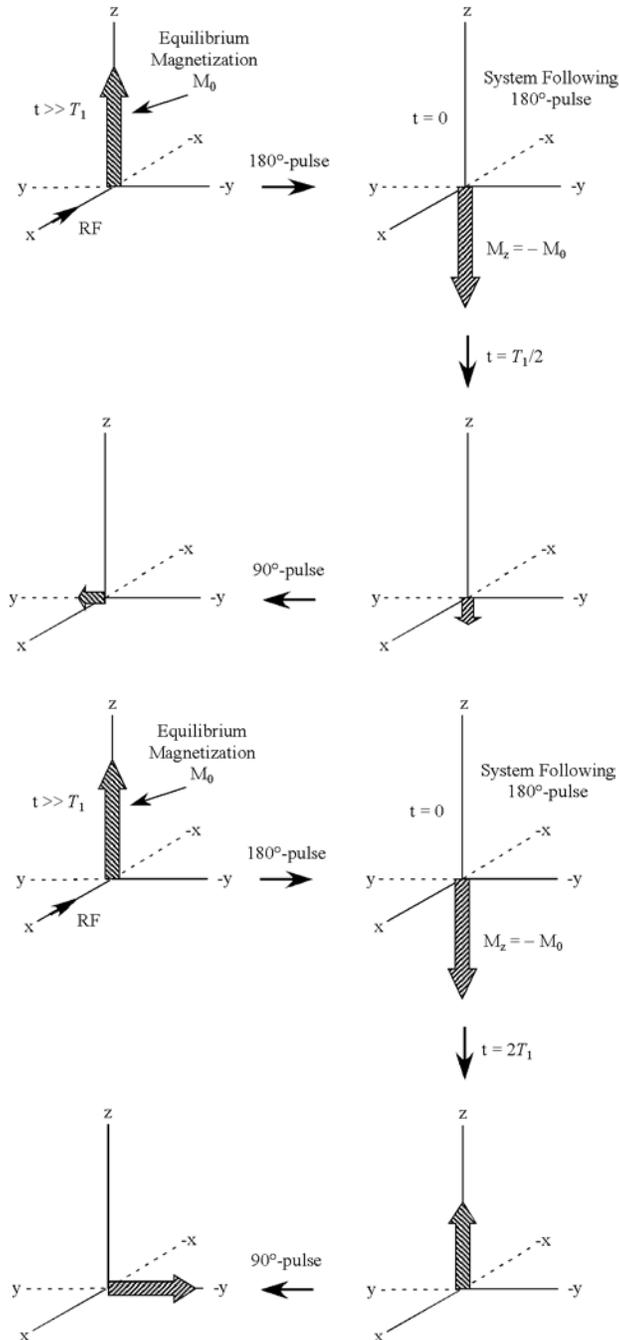
Transverse Relaxation



Experimental Determination of T_1

Gated Inversion Recovery Experiment

The gated inversion recovery pulse sequence makes use of a $180^\circ(x)$ -pulse followed by a delay during which time T_1 relaxation occurs, and is followed by a $90^\circ(x)$ -pulse which allows the recovered magnetization to be measured:



The experiment is repeated with an array of delays between the 180° -pulse and 90° -pulse that cover the range from complete inversion through complete recovery.

It is inconvenient to write vector diagrams and a shorthand notation has been adopted to describe pulse sequences:

$$180_x^\circ - \tau - 90_x^\circ - \text{detect}$$

In the inversion recovery experiment, typically, 10-20 delays are employed to support robust fitting of the intensity versus time data.

Detailed analysis shows that a few representative recovery points together with at least one long recovery point lead to acceptably accurate results.

In addition to the variable delay between the 180° -pulse and 90° -pulse we must also use an additional delay between experiments to insure that the spin system is at equilibrium at the beginning of each experiment.

The delay used between experiments is $> 5 T_1$ intervals:

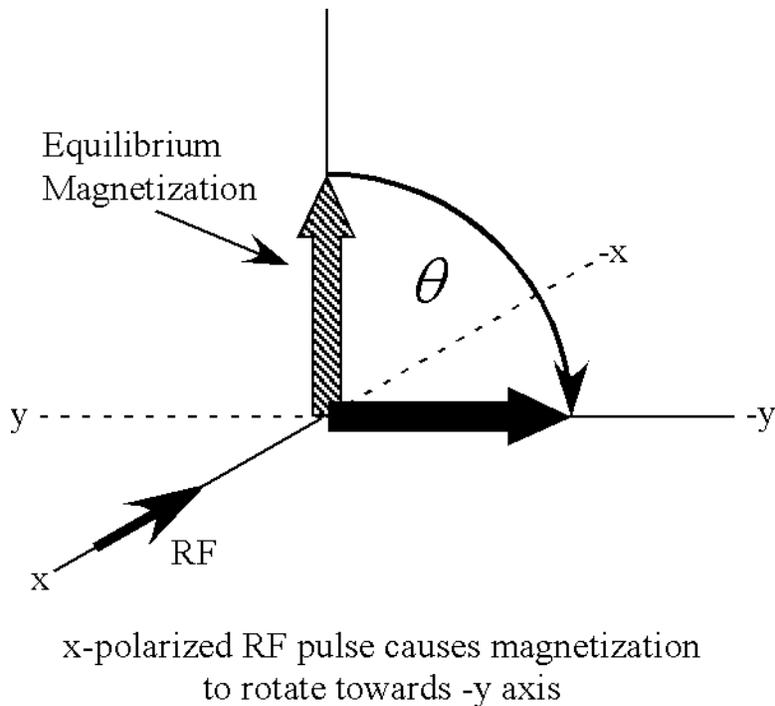
$$M(t) = M_0(1 - 2e^{-t/T_1}) = M_0(1 - 2e^{-5}) = 0.99M_0$$

Experimental Determination of T_2

A latent complication with the measurement of T_2 arises due to Larmor precession and the limited spatial homogeneity of the sample chamber.

If we consider a sample composed of spins in a single chemical environment, i.e., a single chemical shift, then we could set our carrier frequency to that exact resonance.

In such a situation, if we applied an exact $90^\circ(x)$ -pulse then the spins would be rotated exactly onto the $-y$ -axis as we have previously seen:

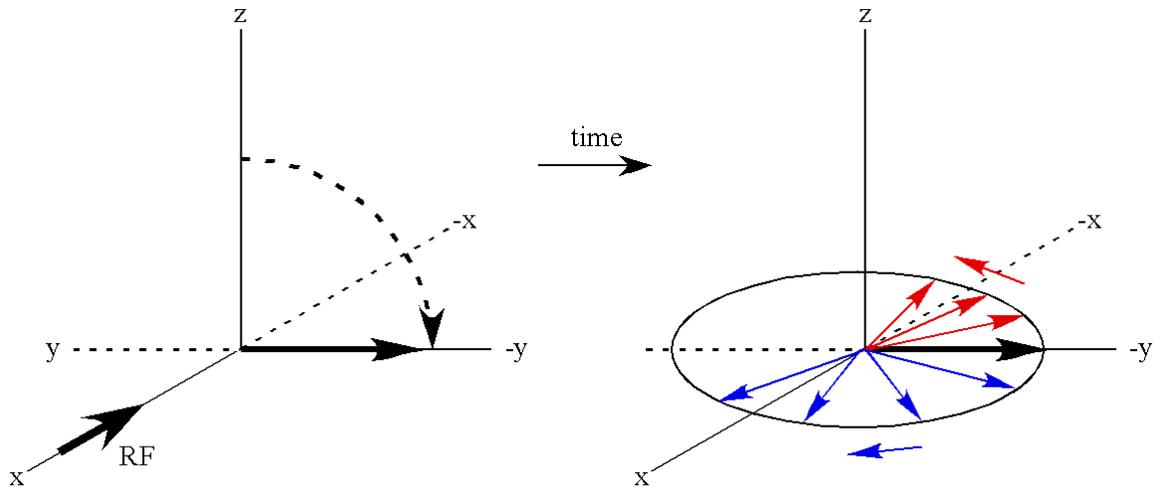


In our perfect-world experiment, the magnitude of the magnetization along the y -direction would decrease without complication due to T_2 relaxation as we have already noted.

In a real-world experiment however, the magnetic field in different parts of the sample vary, i.e., the chemical shift varies.

Spins affected by such spatial inhomogeneities actually precess about the applied static magnetic field.

Spins with resonance frequencies that are higher than the carrier frequency rotate in one sense, while spins with resonance frequencies lower than the carrier frequency rotate in the opposite sense:



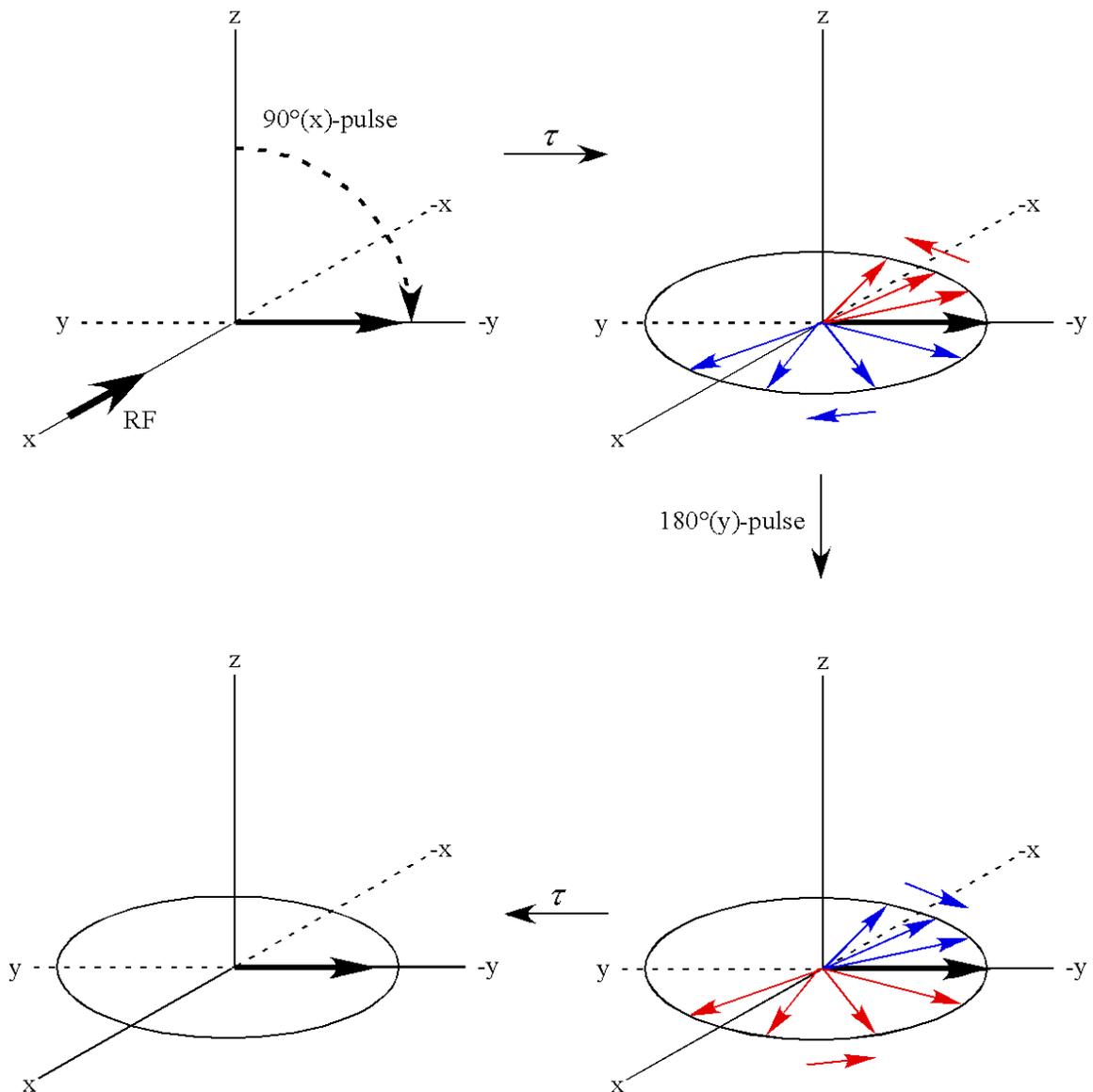
In a simple experiment the decrease in measured magnitude (intensity) will be indistinguishable from the actual T_2 relaxation and an experiment designed to compensate for the effect must be used.

The experiment is named the *Carr-Purcell-Meiboom-Gill* experiment, CPMG more commonly, and the approach is based on the original spin-echo technique invented by Hahn.

Imagine a system that contains multiple spins with different chemical shifts. In this situation, perhaps none of the spins may resonate at the carrier frequency. These spins will precess about the z-axis in the same ways as we have just discussed.

Hahn discovered that the direction of the precession could be reversed by applying a 180° -pulse – this experiment has become known as the Hahn spin-echo experiment because the intensity of monitored magnetization appears to first decrease and then increase again.

The Spin-Echo Experiment



In this experiment, the amplitude of magnetization recovered at the end of the sequence is not the original amount but is less due to T2 relaxation:

$$M_{xy}(t) = M_0 e^{-2\tau/T_2}$$

wherein τ is the interval during which time the spins are allowed to precess in the xy-plane – note that the overall evolution is 2τ .

In our shorthand notation we would write this sequence as:

$$90_x^\circ - \tau - 180_y^\circ - \tau - \text{detect}$$

In the CPMG variant of the spin-echo experiment, the $(\tau - 180_y^\circ - \tau)$ components of the Hahn echo experiment are repeated, thus allowing an array of time intervals to be produced.

The CPMG sequence may thus be written as:

$$90_x^\circ - (\tau - 180_y^\circ - \tau)_n - \text{detect}$$

Relaxation Mechanisms

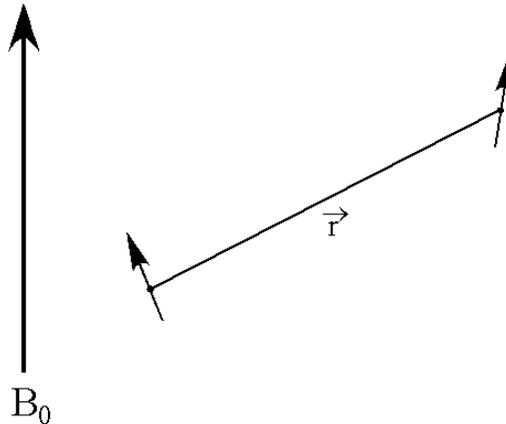
Now that we have a grasp of the experimental techniques, we turn to a consideration of the origins of the internal fluctuating EM fields.

The most common origin of internal EM fields arises from the modulation of the dipolar interaction.

The classical interaction energy for a pair of magnetic dipoles is given by the following expression:

$$E = \frac{\vec{\mu}_I \cdot \vec{\mu}_S}{r_{IS}^3} - 3 \frac{(\vec{\mu}_I \cdot \vec{r}_{IS})(\vec{\mu}_S \cdot \vec{r}_{IS})}{r_{IS}^5}$$

wherein \vec{r}_{IS} is the vector joining $\vec{\mu}_I$ and $\vec{\mu}_S$.



The QM version of this expression is obtained by making the following substitution:

$$\vec{\mu}_I = \hbar\gamma_I\vec{I}; \quad \vec{\mu}_S = \hbar\gamma_S\vec{S}$$

The energy of the interaction in the QM formalism is expressed as a Hamiltonian:

$$H_{dd} = \frac{1}{2} \frac{\gamma_I\gamma_S}{r_{IS}^3} (1 - 3\cos^2\theta) (3I_zS_z - \vec{I} \cdot \vec{S})$$

wherein θ is the angle between r and the applied magnetic field (assume z-direction).

The time-dependent version of the Schrödinger Equation indicates that the time-evolution of the spin systems is prescribed by the details of the Hamiltonian operator:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H |\psi(t)\rangle$$

Note that the interaction energy depends upon the cube of the internuclear distance and the orientation between the two spins and the applied magnetic field.

As the molecule tumbles in solution, the magnitude of the vector that between the two dipoles remains constant, but the orientation will clearly change, leading to a modulation of the energy.

The manner in which the orientation changes in time may be analyzed by considering the projection of a vector in the molecular frame over time. The expression that accounts for this behavior is called an *autocorrelation function* (or simply the correlation function), and is usually written as $G(\tau)$.

The exact form of the correlation depends upon the nature of the motion. For Brownian motion $G(\tau)$ may be suitably modeled as an exponential decay. The correlation function may thus be written as:

$$G(\tau) = e^{-t/\tau}$$

The rate of tumbling for a spherical molecule is characterized by a *correlation time*, τ that may be approximated using the following expression:

$$\tau = \frac{\eta V_{eff}}{k_b T}$$

wherein η is the solution viscosity, V_{eff} is the effective molecular volume, k_b is Boltzmann's constant and T is the temperature in K.