

Block equations to the vector paradigm

Assume that there are $N = N_\alpha + N_\beta$ identical, isolated spins aligned along an external magnetic field in the Z direction with the population ratio of N_α and N_β given by a Boltzmann distribution (Eqn 1).

$$\frac{N_\alpha}{N_\beta} = e^{g_N \beta_N \Delta E / kT} \quad (1)$$

Where g_N is the magnetogyric ratio of nucleus N, β_N is the nuclear magneton for nucleus N, ΔE is the energy difference between the α and β states, k is Boltzmann's constant, and T is the absolute temperature. At thermal equilibrium $N_\alpha > N_\beta$, and there will be a net (classical) macroscopic magnetization M_0 aligned along the Z axis with no magnetization components along the X and Y axes. Based on time-dependent perturbation theory, it can be shown that if the populations of N_α and N_β are perturbed away from their thermal equilibrium values, the system will decay exponentially back to the equilibrium values. Eqn. 2 where $M_Z = N_\alpha - N_\beta$

$$\frac{dM_Z}{dt} = -\frac{M_Z - M_0}{T_1} \quad (2)$$

The parameter T_1 is the longitudinal or spin-lattice relaxation time and is a characteristic of the spin system. The macroscopic magnetization can be rotated to lie in any direction through the application of an oscillating magnetic field. The components of the magnetization along the transverse axes decay to zero (Eqns. 3).

$$\frac{dM_X}{dt} = -\frac{M_X}{T_2} \quad (3)$$

$$\frac{dM_Y}{dt} = -\frac{M_Y}{T_2}$$

The parameter T_2 is the transverse or spin-spin relaxation time. In general, this relaxation time is different than T_1 .

To complete the description of the motion of the macroscopic magnetization, the spin angular momentum, a strictly quantum mechanical quantity, must be included. Although this is a quantum effect, it can be thought of as the effect of a gyroscopic motion of a bar magnet placed in an external magnetic field. The angular momentum due to the gyroscopic motion causes the magnetization to precess around the external magnetic field, just as a gyroscope precesses in a gravitational field. The equation of motion, temporarily in the absence of relaxation, is given as the cross product of the magnetization and the magnetic field (Eqn 4).

$$\frac{d\mathbf{M}}{dt} = \gamma_N (\mathbf{M} \times \mathbf{H}) \quad (4)$$

Here \mathbf{M} represents the macroscopic magnetization containing angular momentum due to the gyroscopic motion and \mathbf{H} is a uniform magnetic field; γ_N is the magnetogyric ratio of the nucleus.

The cross product of Eqn. 4 is given in determinant form in Eqn 5.

$$\gamma_N \begin{bmatrix} i & j & k \\ M_X & M_Y & M_Z \\ H_X & H_Y & H_Z \end{bmatrix} \quad (5)$$

For an external magnetic field along the Z axis, one obtains Eqn. 6.

$$\gamma_N \begin{bmatrix} i & j & k \\ M_X & M_Y & M_Z \\ 0 & 0 & H_Z \end{bmatrix} \quad (6)$$

The Larmor precession frequency of the rotation is given by $\gamma_N \mathbf{H}$; for protons ($\gamma_H = 42.55 \text{ MHz/T}$) in a 14.1 Tesla magnetic field this frequency is 600 MHz. The chemical shifts of common nuclei are typically in the range of the audio frequencies (0-200 kHz). The large difference between the Larmor precession frequency and the chemical shift frequencies suggests that the motion can be simplified by the introduction of a rotating coordinate system. Essentially, this is a trick to remove the large not-very-interesting Larmor frequency and leave only the important frequencies due to the chemical shifts. It can be thought of as applying a fictitious magnetic field opposing that of the 14.1 T external magnetic field. The frequency for a nucleus precessing exactly at the Larmor frequency (on-resonance) under these conditions becomes zero. For resonances that are not on-resonance, the frequency is non-zero and will precess in the rotating frame. Mathematically, the \mathbf{H} in Eqn. 4-6 is replaced with an effective field $\mathbf{H}^e = \mathbf{H} - \omega_L/\gamma$. This is equivalent to the axes rotating at an angular velocity of the Larmor frequency. Upon solving the determinant in Eqn. 6, Eqns. 7 are obtained.

$$\begin{aligned} \frac{dM_X}{dt} &= -\Omega M_Y \\ \frac{dM_Y}{dt} &= \Omega M_X \\ \frac{dM_Z}{dt} &= 0 \end{aligned} \quad (7)$$

Ω is the chemical shift frequency in the rotating frame, $-\gamma_N \mathbf{H}^e$. The particular algebraic sign for Ω arises from the convention that a positive chemical shift frequency is assumed to be greater than the rotating frame frequency. The direction of motion is given by a right handed coordinate system, $x \rightarrow y \rightarrow -x \rightarrow -y$. Equations 7 indicate that the magnetization vector will precess (rotate) around the Z axis indefinitely. Combining Eqns. 7 with the relaxation equations (Eqns 2 and 3) yields the Bloch equations for precession of the magnetization in a static magnetic field (Eqns. 8).

$$\begin{aligned}
\frac{dM_x}{dt} &= -\Omega M_y - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= \Omega M_x - \frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= -\frac{(M_z - M_0)}{T_1}
\end{aligned} \tag{8}$$

These equations describe the evolution of a magnetization vector of an isolated spin during a free precession period. When an RF field is applied the Bloch equations are transformed to those in Eqns 9. Where Ω is the chemical shift offset; ω_0 is the rotating frame frequency; B_1 , ω , and ϕ are the magnitude, frequency, and phase of the applied RF field, respectively.

$$\begin{aligned}
\frac{dM_x}{dt} &= -M_x * 1/T_2 - M_y * \Omega + M_z * \omega_y \\
\frac{dM_y}{dt} &= M_x * \Omega - M_y * 1/T_2 - M_z * \omega_x \\
\frac{dM_z}{dt} &= -M_x * \omega_y + M_y * \omega_x - (M_z - M_0) * 1/T_1
\end{aligned} \tag{9}$$

$$\begin{aligned}
\omega_x &= -\gamma B_1 \cos(\phi) \\
\omega_y &= -\gamma B_1 \sin(\phi) \\
\Omega &= \omega_0 - \omega_{RF}
\end{aligned}$$

In pulsed NMR spectroscopy, the applied radio frequency is usually much greater than the offset frequency due to chemical shifts and the duration of the RF pulse is much shorter than $1/T_1$ and $1/T_2$. Under these conditions the terms arising from the applied RF field dominate and the Bloch equations are given by Eqn 10.

$$\begin{aligned}
\frac{dM_x}{dt} &= M_z * \omega_y \\
\frac{dM_y}{dt} &= -M_z * \omega_x \\
\frac{dM_z}{dt} &= -M_x * \omega_y + M_y * \omega_x
\end{aligned} \tag{10}$$

From the solution of the set of differential equations in Eqns. 8, the lineshape for the NMR resonance can be determined.

There are two components of the lineshape: one is in-phase with the exciting RF field and one is 90° out-of-phase. The Lorentzian absorption lineshape (in-phase) is given and the dispersive (out-of-phase) lineshape are given in Eqn. 11.

A plot of these lineshapes are plotted in Figure 1. One useful parameter is the linewidth of the absorption at half-height ($\Delta\nu_{1/2}$). This is given as $1/\pi T_2$ Hz.

$$A = k * \frac{T_2}{1 + T_2^2 \Delta\omega^2} \quad (11)$$

$$D = k * \frac{\Delta\omega T_2}{1 + T_2^2 \Delta\omega^2}$$

Eqns. 9 can be also written in matrix form (Eqn. 12).

$$\frac{d}{dt} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} = \begin{bmatrix} 1/T_2 & -\Omega & \omega_y \\ \Omega & 1/T_2 & -\omega_x \\ -\omega_y & \omega_x & 1/T_1 \end{bmatrix} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ M_0 * 1/T_1 \end{bmatrix} \quad (12)$$

These equations form a set of inhomogeneous differential equations. This arises since the rates of the X and Y components depend only the magnitude of the Y and X magnetization, respectively, whereas the Z magnetization depends on the difference from the equilibrium state. The inhomogeneous character of these equations makes the calculation of the propagation of the magnetization in a pulse sequence difficult if the Hamiltonian is time dependent, as it is in all useful pulse sequences. Solutions to these equations provide a detailed method to follow spin dynamics in the presence of relaxation and RF fields. A method to convert the set of inhomogeneous equations to homogeneous is described below.

$$\frac{d}{dt} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} = \begin{bmatrix} 0 & -\Omega & \omega_y \\ \Omega & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{bmatrix} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} \quad (13)$$

There are two simplifications that are commonly applied to eliminate the inhomogeneous character:

Solution 1: If relaxation is ignored, a homogeneous set of differential equations is obtained (Eqn. 13). This simplification gives rise to the simple vector description of the evolution of the magnetization vector. The magnitude of the vector remains constant in this simplification. Solution 2: relaxation is introduced during free precession periods, but since the Hamiltonian during a pulse does not commute with the density operator, relaxation is ignored during all

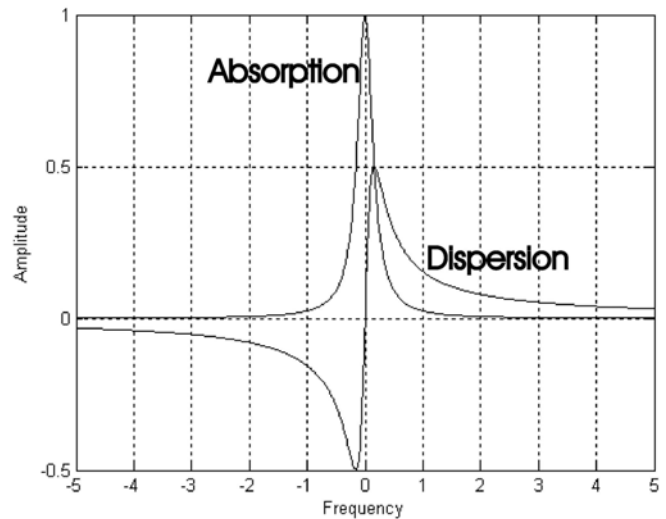


Figure 1. Lorentzian absorption and dispersion lineshapes. Note that the dispersion line has finite amplitude over a much wider range than the absorption line. This is important to remember in setting spectral widths.

pulses. This is not a bad approximation when the pulse time is much shorter than the relaxation rates. In this simplification the length of the vector does not remain constant. While the introduction of relaxation during the free precession periods makes a computation a bit more realistic, the simplest approach of totally ignoring relaxation leads to a very intuitive picture of the motion of the magnetization.

The formal solution to Eqn. 13 given in Eqn. 14.

$$\begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix}_t = e^{\begin{bmatrix} 0 & -\Omega & \omega_y \\ \Omega & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{bmatrix} * t} \begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix}_0 \quad (14)$$

Or, by simplifying, one obtains Eqn. 15 with R being the rate matrix arising from the gyroscopic motion of the nuclear spin. A compact version of this equation is given in Eqn. 15.

$$\mathbf{M}_t = e^{-R*t} \mathbf{M}_0 \quad (15)$$

The exponential matrix can be simplified by various methods (Appendix 1) to yield the simple matrix equation in Eqn 16, where **A** is a 3 X 3 rotation matrix in three dimensional space.

$$\mathbf{M}_t = \mathbf{A} \mathbf{M}_0 \quad (16)$$

In the special case where only chemical shift is present (free precession yielding rotation around the Z axis), matrix **A** becomes simply a Z-axis rotation matrix (Eqn. 17). The transverse components M_x and M_y evolve.

$$e^{\begin{bmatrix} 0 & -\Omega & 0 \\ \Omega & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} * t} = \begin{bmatrix} \cos(\Omega t) & -\sin(\Omega t) & 0 \\ \sin(\Omega t) & \cos(\Omega t) & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (17)$$

If the frequency due to the applied RF field B_1 (along the X axis) is much greater than the chemical shift Ω , the latter can be ignored and a simple X-axis rotation matrix is obtained for an X axis rotation (Eqn. 18).

$$e^{\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -\omega_x \\ 0 & \omega_x & 0 \end{bmatrix} * t} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\omega_x t) & -\sin(\omega_x t) \\ 0 & \sin(\omega_x t) & \cos(\omega_x t) \end{bmatrix} \quad (18)$$

Changing the phase of the applied RF field to generate a Y axis rotation yields Eqn. 19.

$$e^{\begin{bmatrix} 0 & 0 & \omega_y \\ 0 & 0 & 0 \\ -\omega_y & 0 & 0 \end{bmatrix} * t} = \begin{bmatrix} \cos(\omega_y t) & 0 & \sin(\omega_y t) \\ 0 & 1 & 0 \\ -\sin(\omega_y t) & 0 & \cos(\omega_y t) \end{bmatrix} \quad (19)$$

These rotation matrices are used to calculate the (approximate) trajectory of the magnetization in the absence of relaxation.

If there is more than one non-commuting (Appendix 2) operator in the exponential matrix, then the resulting rotation matrices are no longer along the X, Y, or Z axis. In other words if the RF field strength along the X axis is comparable to the chemical shift offset, then the rotation occurs simultaneously around the Z and Y axis. This does not lead to a simple rotation matrix around one of the X, Y, or Z axis, but a rotation about an axis that is tilted away from all of the axes.

As an example of two simultaneous, non-commuting rotations, consider a RF pulse causing a rotation about the X axis at a frequency ω_1 for a time t with a simultaneous Z rotation due to a chemical shift offset Ω . The exponential rate matrix and the corresponding rotation matrix is given in Eqn 20. Note that the frequency ω_e is the vector sum of ω_1 and Ω , a consequence of the introduction of a rotating coordinate system. This leads to a rotation axis that is tilted out of the XY plane having a magnitude greater than either ω_1 or Ω individually.

$$e^{\begin{bmatrix} 0 & -\Omega & 0 \\ \Omega & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{bmatrix} * t} = \begin{bmatrix} \left(\frac{\omega_1}{\omega_e}\right)^2 + \left(\frac{\Omega}{\omega_e}\right)^2 \cos(\omega_e t) & -\frac{\Omega}{\omega_e} \sin(\omega_e t) & -\frac{\omega_1 \Omega}{\omega_e^2} (1 - \cos(\omega_e t)) \\ \frac{\Omega}{\omega_e} \sin(\omega_e t) & \cos(\omega_e t) & -\frac{\omega_1}{\omega_e} \sin(\omega_e t) \\ -\frac{\omega_1 \Omega}{\omega_e^2} (1 - \cos(\omega_e t)) & \frac{\omega_1}{\omega_e} \sin(\omega_e t) & \left(\frac{\Omega}{\omega_e}\right)^2 + \left(\frac{\omega_1}{\omega_e}\right)^2 \cos(\omega_e t) \end{bmatrix} \quad (20)$$

$$\omega_e = \sqrt{\Omega^2 + \omega_1^2}$$

The unwieldy nature of these rotation matrices can be bypassed through the use of similarity transforms to move the system into a tilted frame of reference, perform a rotation, and then return the system back from the tilted frame. Eqn. 21 gives the appropriate similarity transform for this situation. Acting on a column vector at the right, the rightmost rotation $R_y(\tan^{-1} \Omega/\omega_1)$ rotates the tilted rotation axis to along the X axis. The next R_x rotation rotates the magnetization vector with consideration that the frequency of the rotation is greater than ω_1 .

$$R_y\left(\tan^{-1} \frac{\Omega}{\omega_1}\right) R_x\left(\frac{\sqrt{\Omega^2 + \omega_1^2}}{\omega_1} * \omega_1 t\right) R_y\left(-\tan^{-1} \frac{\Omega}{\omega_1}\right) \quad (21)$$

For situations in which the chemical shift frequency is similar to the RF, the motion of the magnetization is no longer a simple rotation about the X, Y or Z axes. In the analysis of pulse sequences, it is commonly assumed that the applied RF is infinitely greater than the chemical shift frequency leading to the simplification in Eqn. 10. In the presence of relaxation, the use of similarity transforms is not possible (see below).

The rotation matrices obtained from the exponentiation of the rate matrix of nuclear precession lead to the well known evolution of the product operators for a single spin. The magnetization for a single isolated spin can be represented by the column matrix in Eqn 23.

$$\begin{bmatrix} M_x \\ M_y \\ M_z \end{bmatrix} \equiv \begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix} \quad (23)$$

At equilibrium, the magnetization vector lies along the Z axis and is represented by Eqn. 24.

$$\begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = I_z \quad (24)$$

Applying a θ rotation of the magnetization vector around the X axis yields Eqn. 25.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos(\theta) & -\sin(\theta) \\ 0 & \sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ -\sin(\theta) \\ \cos(\theta) \end{bmatrix} \quad (25)$$

Or in standard product operator terms one obtains Eqn 26.

$$I_z \xrightarrow{\theta \hat{I}_x} I_z \cos(\theta) - I_y \sin(\theta) \quad (26)$$

The extension to more than one isolated spin involves the Bloch equations for each spin individually. For two spins in the absence of relaxation, this leads to the 6X6 matrix in Eqn. 27. Note that since the spins are isolated no matrix elements connect the **I** and **S** spins.

$$\frac{d}{dt} \begin{bmatrix} I_x \\ I_y \\ I_z \\ S_x \\ S_y \\ S_z \end{bmatrix} = \begin{bmatrix} 0 & -\Omega_I & \omega_y^I & 0 & 0 & 0 \\ \Omega_I & 0 & -\omega_x^I & 0 & 0 & 0 \\ -\omega_y^I & \omega_x^I & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\Omega_S & \omega_y^S \\ 0 & 0 & 0 & \Omega_S & 0 & -\omega_x^S \\ 0 & 0 & 0 & -\omega_y^S & \omega_x^S & 0 \end{bmatrix} \begin{bmatrix} I_x \\ I_y \\ I_z \\ S_x \\ S_y \\ S_z \end{bmatrix} \quad (27)$$

The solution is the same as above. The same simplifications for chemical shift and RF rotations apply as for the single spin case. That is, since different spins always commute simultaneous I and S rotations *e.g.* $I_x + S_y$ yield simple spin specific rotation matrices around X, Y, or Z, but simultaneous non-commuting rotations such as $I_z + I_x$ or $S_z + S_y$ do not

give simple rotation matrices. Simultaneous non-commuting rotations can be dealt with by similarity transforms (tilted frames) or by solving the exponential matrix numerically.

Relaxation can be reintroduced to this description by several methods. A very clever method is to transform the inhomogeneous equation into a homogeneous one by adding a row and column to the matrix to introduce the difference from equilibrium (Jeener, Levitt, Allard, Ernst##). An example of this is shown in Eqn. 28.

$$\frac{d}{dt} \begin{bmatrix} E/2 \\ M_x \\ M_y \\ M_z \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1/T_2 & -\Omega & \omega_y \\ 0 & \Omega & 1/T_2 & -\omega_x \\ -2(1/T_1 * M_0) & -\omega_y & \omega_x & 1/T_1 \end{bmatrix} \begin{bmatrix} E/2 \\ M_x \\ M_y \\ M_z \end{bmatrix} \quad (28)$$

The element (1,4) of the matrix introduces the equilibrium magnetization. This leads to Eqn. 29 for the time dependence of M_z in the presence of a RF field, which is identical to that given in Eqn 14.

$$\begin{aligned} \frac{d}{dt} M_z &= -(-1/T_1 * M_0 - \omega_y M_x + \omega_x M_y + 1/T_1 M_z) \\ \frac{d}{dt} M_z &= -(-\omega_y M_x + \omega_x M_y - 1/T_1 (M_0 - M_z)) \end{aligned} \quad (29)$$

Equation 28 can be solved using the matrix exponential. The resulting matrix is not a simple rotation matrix since the relaxation terms do not preserve the length of the vector. However when relaxation occurs during pulses, this method yields a complete description.

For a heteronuclear 2 spin system a set of differential equations can be set up similar to the following (no relaxation).

$$\frac{dI_x}{dt} = -\Omega I_y + \omega_y I_z - \pi J 2I_y S_z$$

From these differential equations, the rate matrix is obtained

$$\frac{d}{dt} \begin{bmatrix} I_x \\ I_y \\ I_z \\ S_x \\ S_y \\ S_z \\ 2I_x S_z \\ 2I_y S_z \\ 2I_z S_x \\ 2I_z S_y \\ 2I_x S_x \\ 2I_x S_y \\ 2I_y S_x \\ 2I_y S_y \\ 2I_z S_z \end{bmatrix} = - \begin{bmatrix} 0 & \Omega_I & -\omega_{Iy} & 0 & 0 & 0 & 0 & \pi J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\Omega_I & 0 & \omega_{Ix} & 0 & 0 & 0 & -\pi J & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \omega_{Iy} & -\omega_{Ix} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \Omega_S & -\omega_{Sy} & 0 & 0 & 0 & \pi J & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\Omega_S & 0 & \omega_{Sx} & 0 & 0 & -\pi J & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \omega_{Sy} & -\omega_{Sx} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \pi J & 0 & 0 & 0 & 0 & 0 & \Omega_I & 0 & 0 & \omega_{Sy} & -\omega_{Sx} & 0 & 0 & -\omega_{Iy} & 0 \\ -\pi J & 0 & 0 & 0 & 0 & 0 & -\Omega_I & 0 & 0 & 0 & 0 & 0 & \omega_{Sy} & -\omega_{Sx} & \omega_{Ix} & 0 \\ 0 & 0 & 0 & 0 & \pi J & 0 & 0 & 0 & 0 & \Omega_S & \omega_{Iy} & 0 & -\omega_{Ix} & 0 & -\omega_{Sy} & 0 \\ 0 & 0 & 0 & -\pi J & 0 & 0 & 0 & 0 & -\Omega_S & 0 & 0 & \omega_{Iy} & 0 & -\omega_{Ix} & \omega_{Sx} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\omega_{Sy} & 0 & -\omega_{Iy} & 0 & 0 & \Omega_S & \Omega_I & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \omega_{Sx} & 0 & 0 & -\omega_{Iy} & -\Omega_S & 0 & 0 & \Omega_I & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\omega_{Sy} & \omega_{Ix} & 0 & -\Omega_I & 0 & 0 & \Omega_S & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \omega_{Sx} & 0 & \omega_{Ix} & 0 & -\Omega_I & -\Omega_S & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \omega_{Ix} & -\omega_{Ix} & \omega_{Sy} & -\omega_{Sx} & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} I_x \\ I_y \\ I_z \\ S_x \\ S_y \\ S_z \\ 2I_x S_z \\ 2I_y S_z \\ 2I_z S_x \\ 2I_z S_y \\ 2I_x S_x \\ 2I_x S_y \\ 2I_y S_x \\ 2I_y S_y \\ 2I_z S_z \end{bmatrix}$$

This is the matrix representation for the evolution of the density operator in the Cartesian product operator basis in the absence of relaxation. It has a solution of the form

$$\mathbf{M}_t = e^{-R^* t} \mathbf{M}_0$$

Again if only one non-commuting rotation is used then the resulting matrix is a simple rotation matrix, here as 3 dimensional subspaces of 15 dimensional space.

In maybe, more familiar nomenclature

$$\frac{d}{dt} \sigma = -i \overline{H} \sigma = i [H, \sigma]$$

The solution to this equation in regular operators is

$$\sigma(t) = e^{-iHt} * \sigma(0) * e^{iHt}$$

Appendix 1

Connection of exponential rate matrices with rotation operators. (2dimensional case)

Rate matrix R, rate a, time t

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

$$e^{-Rat} = \left(1 + Rat + \frac{1}{2!}(Rat)^2 + \frac{1}{3!}(Rat)^3 + \dots \right)$$

$$= \left(1 + \frac{1}{2!}(Rat)^2 + \frac{1}{4!}(Rat)^4 + \dots \right) + \left(Rat + \frac{1}{3!}(Rat)^3 + \frac{1}{5!}(Rat)^5 + \dots \right)$$

$$= \left(1 + \frac{1}{2!} \left(\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} at \right)^2 + \frac{1}{4!} \left(\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} at \right)^4 + \dots \right) + \left(\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} at + \frac{1}{3!} \left(\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} at \right)^3 + \frac{1}{5!} \left(\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} at \right)^5 + \dots \right)$$

$$= \left(1 + \frac{1}{2!} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} (at)^2 + \frac{1}{4!} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} (at)^4 + \dots \right) + \left(\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} at + \frac{1}{3!} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} (at)^3 + \frac{1}{5!} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} (at)^5 + \dots \right)$$

$$= \cos(at) * I_E + \sin(at) * R$$

$$= \begin{bmatrix} \cos(at) & -\sin(at) \\ \sin(at) & \cos(at) \end{bmatrix}$$

2D rotation matrix

$$e^{-Rat} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \cos(at) & -\sin(at) \\ \sin(at) & \cos(at) \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \cos(at) \\ \sin(at) \end{bmatrix}$$

Commuting operators

$$A * B = B * A$$

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

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

Non-commuting operators

$$A * B \neq B * A$$

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

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

Appendix 3. Exponential commuting operators.

$$e^{A+B} = I + (A+B) + \frac{1}{2!}(A+B)^2 + \dots$$

$$e^A = I + A + \frac{1}{2!}A^2 + \dots$$

$$e^B = I + B + \frac{1}{2!}B^2 + \dots$$

$$e^A e^B = I + (A+B) + \frac{1}{2!}(A^2 + 2AB + B^2) + \dots$$

comparing the second order terms

$$\frac{1}{2!}(A+B)^2 = A^2 + AB + BA + B^2$$

and

$$\frac{1}{2!}(A^2 + 2AB + B^2)$$

$$e^{A+B} = e^A e^B \text{ only if } AB=BA$$