Module I, Lecture 11: Product Operator Formalism

We saw in the previous lectures that the density matrix can be eliminated from the equations of motion and the time dynamics problem reformulated in terms of observables:

$$\frac{\partial}{\partial t}\langle A \rangle = \mathrm{Tr}\left(\hat{A}^{\dagger} \frac{\partial}{\partial t} \hat{\rho} \right) = \mathrm{Tr}\left(-i\hat{A}^{\dagger}\left[\hat{H}, \hat{\rho} \right] \right) = -i\mathrm{Tr}\left(\hat{A}^{\dagger}\hat{H}\hat{\rho} - \hat{A}^{\dagger}\hat{\rho}\hat{H} \right) =$$

$$= -i\mathrm{Tr}\left(\hat{A}^{\dagger}\hat{H}\hat{\rho} - \hat{H}\hat{A}^{\dagger}\hat{\rho} \right) = i\mathrm{Tr}\left(\left[\hat{H}, \hat{A} \right]^{\dagger} \hat{\rho} \right) = i\left\langle \left[\hat{H}, \hat{A} \right] \right\rangle$$

(1)

where $\hat{A}$ is the operator of the observable we are interested in. It turns out that simple rules may be formulated (at least for simple Hamiltonians) based in Equation (1), and they are much easier to use than the density operator formalism in many practical cases.

Spin state classification

Following the derivations given in the previous lecture, we will classify the basis of the density matrix space according to the physical meaning of the corresponding observable operators. Note that for historical reasons $\hat{L}_{Z}\hat{S}_{Z}\hat{I}_{Z}$ means $\hat{L}_{Z} \otimes \hat{S}_{Z} \otimes \hat{I}_{Z}$ crossed with the identity operators on any other spins that are not explicitly mentioned. The common classification identifies:

1. <u>Identity (unit) operator</u>: usually denoted $\hat{E}$. When a unit operator is supplied for a particular spin in the direct product of operators, the result corresponds to an average, with equal weights, over all possible states of that spin. Unit operators are typically included implicitly – *e.g.* in a two spin system, the $\hat{L}_{Z} \otimes \hat{E}$ operator corresponding to the average Z-magnetization of the first spin would be abbreviated to just $\hat{L}_{Z}$.

2. <u>Longitudinal single-spin orders</u>: $\hat{L}_{Z}$, $\hat{S}_{Z}$, *etc.* These correspond to population differences between energy levels that are one spin flip away from each other, they are also known as *longitudinal magnetization*.

3. <u>Longitudinal multi-spin orders</u>: $\hat{L}_{Z}\hat{S}_{Z}$, $\hat{L}_{Z}\hat{S}_{Z}\hat{I}_{Z}$, *etc.* These also correspond to population differences across levels connected by single-spin flips, but the sign of the population difference depends on the state that other spins have in a particular pair of energy levels. The other name for these states is *longitudinal correlations*.

4. <u>Transverse single-spin orders</u>: $\hat{L}_{X}$, $\hat{S}_{Y}$, $\hat{L}_{+}$, *etc.* These correspond to observable transverse magnetization in the system and originate from the presence of linear combinations of Hamiltonian eigenfunctions in the wavefunction.

5. <u>Transverse multi-spin orders</u>: $\hat{L}_{X}\hat{S}_{Y}$, $\hat{L}_{+}\hat{S}_{-}$, *etc.* Although they nominally involve transverse spin operators, these states do not yield observable transverse magnetization. For spin ensembles they correspond to correlations between the linear combination coefficients in wavefunctions across the ensemble.

6. <u>Mixed spin orders</u>: $\hat{L}_{Z}\hat{S}_{+}$, etc. These do not have a systematic classification and correspond to complicated correlations between longitudinal magnetization and time dynamics. Some mixed spin orders are interpretable ($\hat{L}_{Z}\hat{S}_{+}$ is the transverse precession of the S spin with the precession phase dependent on the state of spin L), but this is rarely the case in general.

Several specific spin states and classes of spin states have historical names:

1. Coherences: a spin state $\hat{\rho}$ having the following property under the commutation action by the total spin projection operator:

$$[\hat{L}_Z, \hat{\rho}] = k\hat{\rho} \qquad \hat{L}_Z = \sum_n \hat{L}_Z^{(n)} \tag{2}$$

is often referred to as k-*quantum coherence*. If a state is written as a Kronecker product of raising and lowering operators, *e.g.* $\hat{L}_+\hat{S}_-\hat{I}_Z$, then the coherence order k is equal to the number of "+" operators minus the number of "−" operators in the direct product (Z operators do not contribute). Of particular note are *single-quantum coherences* ($\hat{L}_+$ and $\hat{L}_-$) because they correspond to the observable transverse magnetization. Non-Hermitian $\hat{L}_\pm$ operators make an appearance because they correspond to quadrature-detected magnetization:

$$\langle\hat{L}_X\rangle \pm i\langle\hat{L}_Y\rangle = \langle\hat{L}_X \pm i\hat{L}_Y\rangle = \langle\hat{L}_\pm\rangle \tag{3}$$

2. Correlations: a spin state having k non-unit operators in its direct product representation is called a k-spin correlation because it describes the collective behaviour of those spins. High-order correlations often relax faster than low-order correlations.

3. Singlet and triplet: the following spin states are eigenfunctions of the symmetry operator that permutes the labels on the two particles:

$$|S\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle - |\beta\alpha\rangle\right), \quad |S\rangle\langle S| = \frac{1}{4}\hat{E} - \left(\hat{L}_X\hat{S}_X + \hat{L}_Y\hat{S}_Y + \hat{L}_Z\hat{S}_Z\right)$$

$$|T_+\rangle = |\alpha\alpha\rangle, \quad |T_0\rangle = \frac{1}{\sqrt{2}}\left(|\alpha\beta\rangle + |\beta\alpha\rangle\right), \quad |T_-\rangle = |\beta\beta\rangle \tag{4}$$

Because many spin interactions are symmetric with respect to the permutation of particle labels, these functions also span subspaces that are invariant under their Hamiltonians. In particular, the invariance of the singlet state under the dipolar Hamiltonian can in some cases make it very long-lived.

Practical analysis of pulse sequences is often performed in terms of coherence orders and correlation orders that the system is steered through by the sequence. Different coherence orders in particular respond differently to pulses and pulsed field gradients.

Evolution under Zeeman Hamiltonians

Spin states interconvert and evolve under the Hamiltonian according to Equation (1). For single-spin orders under Zeeman Hamiltonian, the following rules emerge after the commutators are evaluated (it is common to drop the angular brackets on the observables):

$$L_X \xrightarrow{\omega\hat{L}_Z} L_X\cos(\omega\tau) + L_Y\sin(\omega\tau)$$

$$L_Y \xrightarrow{\omega\hat{L}_Z} L_Y\cos(\omega\tau) - L_X\sin(\omega\tau) \tag{5}$$

$$L_Z \xrightarrow{\omega\hat{L}_Z} L_Z$$

these are known as *free precession rules*. Similar equations can be obtained (exercise) for evolution under $\omega\hat{L}_X$ and $\omega\hat{L}_Y$ Hamiltonians (typically encountered during RF or microwave pulses). All rules can be summarized in the following subspace rotation diagrams:
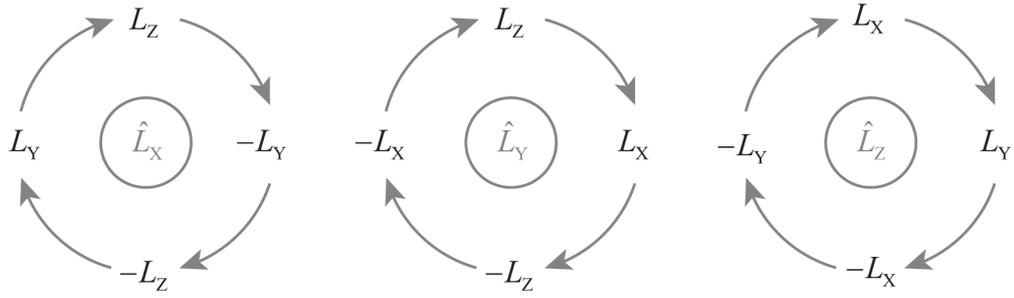
For example, under a pulse coming from the X direction:

$$L_Z \xrightarrow{\omega \hat{L}_X} L_Z \cos(\omega\tau) - L_Y \sin(\omega\tau) \xrightarrow{\omega\tau = \pi/2} -L_Y \qquad (6)$$

Pulses may also be specified by their effective flip angle – for example a $\pi/2$ pulse is a pulse of such duration and magnitude (practical choices depend on many hardware and sample considerations) as to have $\omega\tau = \pi/2$. A good practical example of using these evolution rules is the *spin echo* experiment on a system of two protons with different chemical shifts:
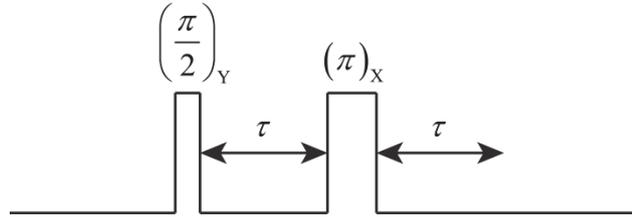
If the initial state of a two-spin system is $L_Z + S_Z$ (often the case for the thermal equilibrium at room temperature), then at the end of the pulse we have:

$$L_Z \xrightarrow{(\pi/2)_Y} L_Z \cos\left(\frac{\pi}{2}\right) + L_X \sin\left(\frac{\pi}{2}\right) = L_X$$

$$S_Z \xrightarrow{(\pi/2)_Y} S_Z \cos\left(\frac{\pi}{2}\right) + S_X \sin\left(\frac{\pi}{2}\right) = S_X \qquad (7)$$

This corresponds to the standard $\pi/2$ excitation pulse that places the magnetization in the transverse plane. After the first evolution period τ, we then have:

$$L_X \xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} L_X \cos(\omega_L\tau) + L_Y \sin(\omega_L\tau)$$

$$S_X \xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} S_X \cos(\omega_S\tau) + S_Y \sin(\omega_S\tau) \qquad (8)$$

Because the precession frequencies of the two spins are different, they are now out of phase with respect to one another in the transverse plane. Applying a π_X pulse on both spins flips some signs:

$$L_X \cos(\omega_L\tau) + L_Y \sin(\omega_L\tau) \xrightarrow{\pi_X} L_X \cos(\omega_L\tau) - L_Y \sin(\omega_L\tau)$$

$$S_X \cos(\omega_S\tau) + S_Y \sin(\omega_S\tau) \xrightarrow{\pi_X} S_X \cos(\omega_S\tau) - S_Y \sin(\omega_S\tau) \qquad (9)$$

Then, at the end of the second evolution period:

$$L_X \cos(\omega_L\tau) - L_Y \sin(\omega_L\tau) \xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} \begin{aligned} &\left(L_X \cos(\omega_L\tau) + L_Y \sin(\omega_L\tau)\right)\cos(\omega_L\tau) - \\ &-\left(L_Y \cos(\omega_L\tau) - L_X \sin(\omega_L\tau)\right)\sin(\omega_L\tau) = \\ &= L_X\left(\cos^2(\omega_L\tau) + \sin^2(\omega_L\tau)\right) = L_X \end{aligned} \qquad (10)$$

$$S_{\mathrm{X}}\cos\left(\omega_{\mathrm{S}}\tau\right)-S_{\mathrm{Y}}\sin\left(\omega_{\mathrm{S}}\tau\right)\xrightarrow{\;\omega_{\mathrm{L}}\hat{L}_{\mathrm{Z}}+\omega_{\mathrm{S}}\hat{S}_{\mathrm{Z}}\;}\begin{array}{l}\left(S_{\mathrm{X}}\cos\left(\omega_{\mathrm{S}}\tau\right)+S_{\mathrm{Y}}\sin\left(\omega_{\mathrm{S}}\tau\right)\right)\cos\left(\omega_{\mathrm{S}}\tau\right)-\\[4pt]-\left(S_{\mathrm{Y}}\cos\left(\omega_{\mathrm{S}}\tau\right)-S_{\mathrm{X}}\sin\left(\omega_{\mathrm{S}}\tau\right)\right)\sin\left(\omega_{\mathrm{S}}\tau\right)=\\[4pt]=S_{\mathrm{X}}\left(\cos^{2}\left(\omega_{\mathrm{S}}\tau\right)+\sin^{2}\left(\omega_{\mathrm{S}}\tau\right)\right)=S_{\mathrm{X}}\end{array}\quad(11)$$

so the evolution under Zeeman Hamiltonian has been reversed (the word "refocused" is often used in the literature) and we are back to $L_{\mathrm{X}}+S_{\mathrm{X}}$.

Evolution under weak scalar coupling

It may similarly be shown that the evolution under a weak scalar coupling $\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}$ (what exactly is meant by *weak* will be explained in Term 3) obeys the following set of rules:
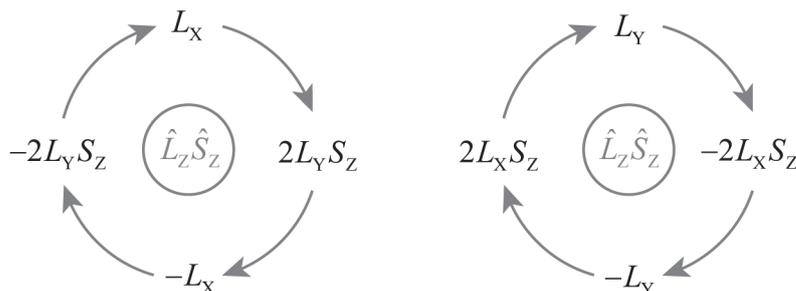

For example, for the L_{X} coherence in a weakly coupled two-spin system evolves into a two-spin order:

$$L_{\mathrm{X}}\xrightarrow{\;a\hat{L}_{\mathrm{Z}}\hat{S}_{\mathrm{Z}}\;}L_{\mathrm{X}}\cos\left(a\tau\right)+2L_{\mathrm{Y}}S_{\mathrm{Z}}\sin\left(a\tau\right)\qquad(12)$$

This particular process can be put to good use in a *coherence transfer* experiment. For a two-spin system containing ^{1}H and ^{15}N nuclei in resonance with their respective pulse and detection circuitry:

$$
\begin{aligned}
H_{\mathrm{Z}}&\xrightarrow{\;(\pi/2)_{\mathrm{Y}}\;}H_{\mathrm{X}}\\[2pt]
H_{\mathrm{X}}&\xrightarrow{\;a\hat{H}_{\mathrm{Z}}\hat{N}_{\mathrm{Z}}\;}H_{\mathrm{X}}\cos\left(a\tau\right)+2H_{\mathrm{Y}}N_{\mathrm{Z}}\sin\left(a\tau\right)\xrightarrow{\;a\tau=\pi/2\;}2H_{\mathrm{Y}}N_{\mathrm{Z}}\\[2pt]
2H_{\mathrm{Y}}N_{\mathrm{Z}}&\xrightarrow{\;(\pi/2)_{\mathrm{X}}\text{ on }H\;}2H_{\mathrm{Z}}N_{\mathrm{Z}}\xrightarrow{\;(\pi/2)_{\mathrm{Y}}\text{ on }N\;}2H_{\mathrm{Z}}N_{\mathrm{X}}\\[2pt]
2H_{\mathrm{Z}}N_{\mathrm{X}}&\xrightarrow{\;a\hat{H}_{\mathrm{Z}}\hat{N}_{\mathrm{Z}}\;}2H_{\mathrm{Z}}N_{\mathrm{X}}\cos\left(a\tau\right)+N_{\mathrm{Y}}\sin\left(a\tau\right)\xrightarrow{\;a\tau=\pi/2\;}N_{\mathrm{Y}}\\[2pt]
N_{\mathrm{Y}}&\xrightarrow{\;(\pi/2)_{\mathrm{X}}\text{ on }N\;}N_{\mathrm{Z}}
\end{aligned}\qquad(13)
$$

This pulse sequence moves the magnetization from the proton to the nitrogen, it is commonly used for ^{15}N sensitivity enhancement. This sequence has the following schematic representation:
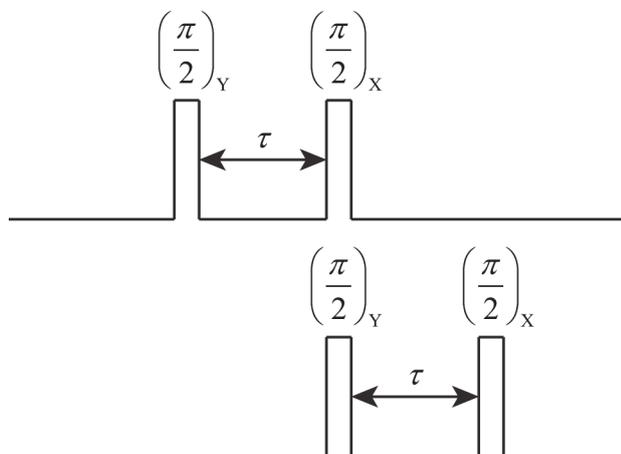
If the two nuclei are not precisely on resonance with their amplifiers, we would have to refocus the offsets using spin echoes. Weak scalar coupling is unaffected by simultaneous π-pulses on both nuclei, but is refocused if only one of the two nuclei is pulsed:

$$2H_Y N_Z \xrightarrow{\pi_X \text{ on } H} -2H_Y N_Z \xrightarrow{\pi_X \text{ on } N} 2H_Y N_Z \tag{14}$$

This leads to the following sequence (which is often encountered in modern NMR experiments):
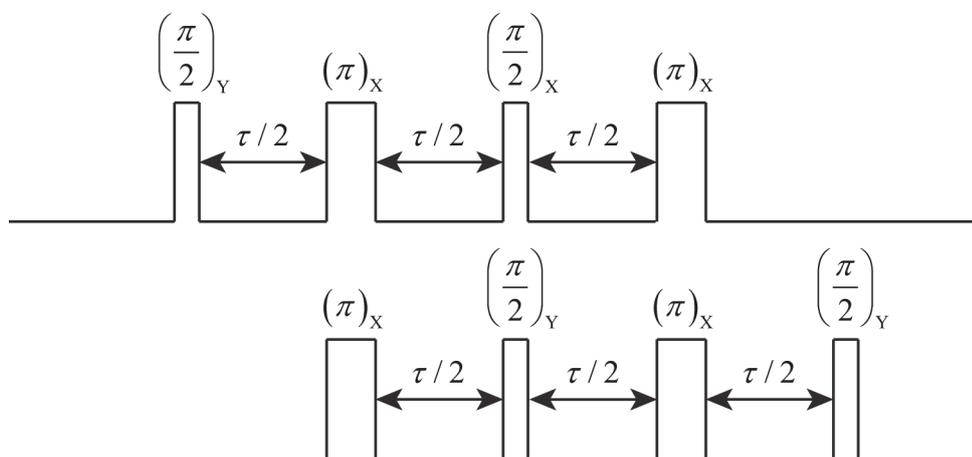
A similar analysis to the one presented in Equation (13) shows that this sequence accomplishes the same polarization transfer and is, at the same time, resilient to the resonance frequency mismatch. It should be noted that it only works well in weakly coupled systems.