

4.10 Product operator formalism

The density matrix can be eliminated from the equations of motion and the time dynamics problem reformulated in terms of observables. For a specific observable $O(t)$:

$$\begin{aligned} \frac{\partial}{\partial t} \langle O \rangle &= \text{Tr} \left(\hat{O} \frac{\partial}{\partial t} \hat{\rho} \right) = \text{Tr} \left(-i \hat{O} [\hat{H}, \hat{\rho}] \right) = -i \text{Tr} \left(\hat{O} \hat{H} \hat{\rho} - \hat{O} \hat{\rho} \hat{H} \right) = \\ &= -i \text{Tr} \left(\hat{O} \hat{H} \hat{\rho} - \hat{H} \hat{O} \hat{\rho} \right) = i \text{Tr} \left([\hat{H}, \hat{O}] \hat{\rho} \right) = i \langle [\hat{H}, \hat{O}] \rangle \end{aligned} \quad (283)$$

where \hat{O} is the operator of the observable. For simple observables and simple Hamiltonians, the commutator $[\hat{H}, \hat{O}]$ only contains a small number of terms, and the dimension of the Lie closure (the subspace spanned by all commutators of \hat{H} and \hat{O}) is small. In such cases, evolution rules may be formulated as small geometric diagrams. These rules are useful for drafting magnetic resonance experiments.

4.10.1 Spin state classification

To map Liouville - von Neumann equation into geometric diagrams, the observable operators in Equation (283) must be given geometric and statistical meaning. Standard classification identifies:

1. **Unit operator:** \hat{E} . When a unit operator is supplied for a particular spin in the direct product, the result corresponds to an average, with equal weights, over all possible states of that spin. In the abbreviated notation used by the product operator formalism, unit operators are implicit – *e.g.* in a two spin system, the $\hat{L}_Z \otimes \hat{E}$ operator (the average Z projection of the first spin), is written \hat{L}_Z .
2. **Longitudinal magnetisation operators:** \hat{L}_Z, \hat{S}_Z , *etc.* These correspond to population differences between energy levels that are one spin flip away from each other.
3. **Longitudinal correlation operators:** $\hat{L}_Z \hat{S}_Z, \hat{L}_Z \hat{S}_Z \hat{I}_Z$, *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 the other spins have.
4. **Transverse magnetisation operators:** $\hat{L}_X, \hat{S}_Y, \hat{L}_+, \hat{S}_+$, *etc.* These correspond to non-zero projections of the corresponding spin on X and/or Y axis; they appear when the system is in a superposition of energy levels connected by one spin flip. Non-Hermitian \hat{L}_\pm operators correspond to quadrature-detected magnetization:

$$\langle \hat{L}_X \rangle \pm i \langle \hat{L}_Y \rangle = \langle \hat{L}_X \pm i \hat{L}_Y \rangle = \langle \hat{L}_\pm \rangle \quad (284)$$

This is possible because ensembles are not subject to uncertainty relation constraints.

5. **Transverse correlation operators:** $\hat{L}_X \hat{S}_Y, \hat{L}_+ \hat{S}_-$, *etc.* These correspond to superpositions of energy levels connected by multiple spin flips. They do not yield observable transverse magnetisation themselves, but may evolve into other states that do.
6. **Other product operators:** these correspond to complicated superposition states. Some of them may be interpretable – for example, $\hat{L}_Z \hat{S}_+$ is the transverse magnetisation of the S spin with the sign dependent on the Z projection of spin L .

Because the density matrix has a statistical meaning in ensembles, the word “operator” in this classification is sometimes replaced by “spin order”: $\hat{L}_Z \hat{S}_Z$ is called “longitudinal two-spin order”, etc.

Some operators have historical names:

1. **Coherences**: an operator $\hat{\rho}$ that is invariant under the commutation with the total \hat{L}_Z

$$[\hat{L}_Z, \hat{\rho}] = k \hat{\rho} \quad \hat{L}_Z = \sum_n \hat{L}_Z^{(n)} \quad (285)$$

is called k -quantum coherence. The following commutation relations

$$[\hat{L}_Z^{(n)}, \hat{L}_\pm^{(n)}] = \pm \hat{L}_\pm^{(n)} \quad (286)$$

then mean that the coherence order k is equal to the number of raising operators minus the number of lowering operators in the direct product.

2. **Correlations**: a product operator having k non-unit components in its direct product structure is called a k -spin correlation because it describes collective behaviour of those k spins.
3. **Singlet and triplet**: the following superposition states are eigenfunctions of the operator that permutes the labels on the two spins:

$$\begin{aligned} |S\rangle &= \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle) \\ |T_+\rangle &= |\alpha\alpha\rangle, \quad |T_0\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle), \quad |T_-\rangle = |\beta\beta\rangle \end{aligned} \quad (287)$$

The antisymmetric linear combination is called “singlet state” and the three symmetric combinations are called “triplet states”.

Design and analysis of magnetic resonance experiments are often performed with reference to coherence and correlation orders that the system is steered through.

4.10.2 Evolution under Zeeman Hamiltonians

In a magnetic field directed along the Z axis of the laboratory frame, the Zeeman interaction Hamiltonian for an isotropically shielded single spin is:

$$\hat{H} = \omega \hat{L}_Z, \quad \omega = -\gamma B_Z \quad (288)$$

Using Eq (283) with $\hat{O} = \{\hat{L}_X, \hat{L}_Y, \hat{L}_Z\}$ yields the following system of equations:

$$\begin{cases} \frac{\partial}{\partial t} \langle L_X \rangle = -\omega \langle L_Y \rangle \\ \frac{\partial}{\partial t} \langle L_Y \rangle = +\omega \langle L_X \rangle \\ \frac{\partial}{\partial t} \langle L_Z \rangle = 0 \end{cases} \quad (289)$$

where the angular brackets are usually dropped for convenience. When the initial condition is $\langle L_X \rangle = 1/2$ and $\langle L_Y \rangle = 0$, the solution is

$$\langle L_X(t) \rangle = \frac{1}{2} \cos(\omega t), \quad \langle L_Y(t) \rangle = \frac{1}{2} \sin(\omega t), \quad \langle L_Z(t) \rangle = 0 \quad (290)$$

Situations where the magnetic field is differently directed and the initial condition is different may be treated in a similar way. The solutions may be summarised in simple diagrams:

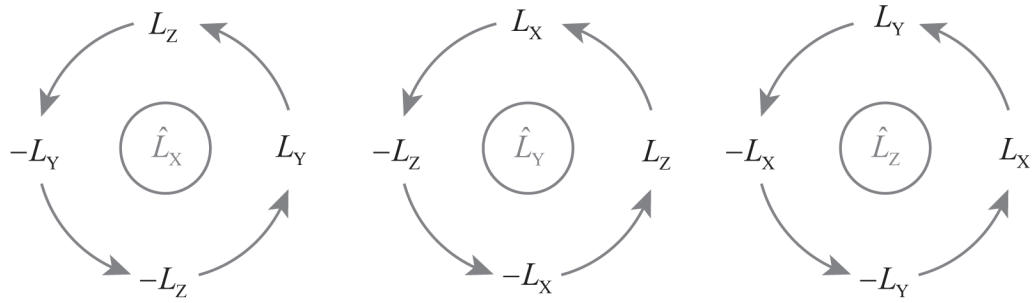


Figure 5. Spin state evolution diagrams under Zeeman interaction.

These diagrams are to be interpreted as rotations in the subspaces spanned by the two operators on the outside of the circle, generated by the operator that appears on the inside. Strictly speaking, the rightmost diagram encodes the following propagator group orbits:

$$\begin{aligned} e^{-i\omega\hat{L}_Z t} \hat{L}_X e^{+i\omega\hat{L}_Z t} &= \hat{L}_X \cos(\omega t) + \hat{L}_Y \sin(\omega t) \\ e^{-i\omega\hat{L}_Z t} \hat{L}_Y e^{+i\omega\hat{L}_Z t} &= \hat{L}_Y \cos(\omega t) - \hat{L}_X \sin(\omega t) \\ e^{-i\omega\hat{L}_Z t} \hat{L}_Z e^{+i\omega\hat{L}_Z t} &= \hat{L}_Z \end{aligned} \quad (291)$$

but they may also be viewed as rotations, which in some sense they are:

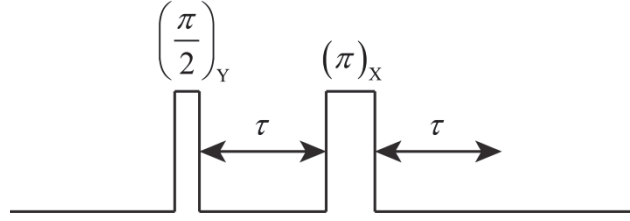
$$\begin{aligned} L_X &\xrightarrow{\omega\hat{L}_Z} L_X \cos(\omega t) + L_Y \sin(\omega t) \\ L_Y &\xrightarrow{\omega\hat{L}_Z} L_Y \cos(\omega t) - L_X \sin(\omega t) \\ L_Z &\xrightarrow{\omega\hat{L}_Z} L_Z \end{aligned} \quad (292)$$

The diagrams make it easy to analyse simple magnetic resonance experiments without resort to the density operator formalism. For example, for a 90-degree pulse with the B_1 field on the X axis of the rotating frame, the dynamics is:

$$L_Z \xrightarrow{\omega\hat{L}_X} L_Z \cos(\omega t) - L_Y \sin(\omega t) \xrightarrow{\omega t = \pi/2} -L_Y \quad (293)$$

The product of the amplitude term $\omega = -\gamma B_1$ and the pulse duration t is the flip angle. In pulse sequence diagrams, it is common to specify ωt product in radians, and to leave the choice of B_1 and t to the user.

A good practical example is the spin echo experiment on a system where two non-interacting spins have different Zeeman frequencies:



The thermal equilibrium state is $\alpha L_Z + \beta S_Z$ where α and β are some coefficients. At the end of the first pulse, we have:

$$\begin{aligned} L_Z &\xrightarrow{(\pi/2)_Y} L_Z \cos\left(\frac{\pi}{2}\right) + L_X \sin\left(\frac{\pi}{2}\right) = L_X \\ S_Z &\xrightarrow{(\pi/2)_Y} S_Z \cos\left(\frac{\pi}{2}\right) + S_X \sin\left(\frac{\pi}{2}\right) = S_X \end{aligned} \quad (294)$$

where $(\pi/2)_Y$ is a shorthand for the evolution under $\omega \hat{L}_Y$ or $\omega \hat{S}_Y$ for the duration of time t such that $\omega t = \pi/2$. We are now in the state $\alpha L_X + \beta S_X$ where the two spins have the same phase.

Because the Zeeman precession frequencies ω_L and ω_S of the two spins are different, they go out of phase relative to one another during the first evolution period τ :

$$\begin{aligned} L_X &\xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} L_X \cos(\omega_L \tau) + L_Y \sin(\omega_L \tau) \\ S_X &\xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} S_X \cos(\omega_S \tau) + S_Y \sin(\omega_S \tau) \end{aligned} \quad (295)$$

This is often undesirable, for example in MRI – when there is a broad distribution of precession frequencies in the sample, the total magnetisation across the sample quickly drops to zero as the spins go out of phase. However, this dephasing may be reversed by applying a π pulse. As per the left diagram in Figure 5, applying a π_X pulse on both spins flips the signs of L_Y and S_Y :

$$\begin{aligned} L_X \cos(\omega_L \tau) + L_Y \sin(\omega_L \tau) &\xrightarrow{\pi_X} L_X \cos(\omega_L \tau) - L_Y \sin(\omega_L \tau) \\ S_X \cos(\omega_S \tau) + S_Y \sin(\omega_S \tau) &\xrightarrow{\pi_X} S_X \cos(\omega_S \tau) - S_Y \sin(\omega_S \tau) \end{aligned} \quad (296)$$

Then, at the end of the second evolution period:

$$\begin{aligned} L_X \cos(\omega_L \tau) - L_Y \sin(\omega_L \tau) &\xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} (L_X \cos(\omega_L \tau) + L_Y \sin(\omega_L \tau)) \cos(\omega_L \tau) - \\ &\quad - (L_Y \cos(\omega_L \tau) - L_X \sin(\omega_L \tau)) \sin(\omega_L \tau) = \\ &= L_X (\cos^2(\omega_L \tau) + \sin^2(\omega_L \tau)) = L_X \end{aligned} \quad (297)$$

$$\begin{aligned} S_X \cos(\omega_S \tau) - S_Y \sin(\omega_S \tau) &\xrightarrow{\omega_L \hat{L}_Z + \omega_S \hat{S}_Z} (S_X \cos(\omega_S \tau) + S_Y \sin(\omega_S \tau)) \cos(\omega_S \tau) - \\ &\quad - (S_Y \cos(\omega_S \tau) - S_X \sin(\omega_S \tau)) \sin(\omega_S \tau) = \\ &= S_X (\cos^2(\omega_S \tau) + \sin^2(\omega_S \tau)) = S_X \end{aligned} \quad (298)$$

and we are again in the situation that existed at the end of the $\pi/2$ pulse in Equation (294) – the two spins have the same phase, and the system state is $\alpha L_X + \beta S_X$.

4.10.3 Evolution under spin-spin coupling Hamiltonians

In the general case of an arbitrary interaction tensor, the product operator formalism offers no cognitive or logistical advantages over Liouville - von Neumann equation; brute-force numerics is the best way forward. However, in the common case of a “weak” spin-spin coupling, simple and useful evolution diagrams do exist. The interaction Hamiltonian is:

$$\hat{H} = a\hat{L}_Z\hat{S}_Z \quad (299)$$

where $a = 2\pi J$ in the case of heteronuclear J -coupling. In the case of heteronuclear dipolar coupling, $a = -(\mu_0/4\pi)(\gamma_L\gamma_S\hbar/r_{LS}^3)[3(z_L - z_S)^2 - r_{LS}^2]$. Other cases may be found in Section [#.#](#).

The longitudinal magnetisation of both spins commutes with the Hamiltonian in Equation (299) and therefore remains invariant. The commutation relations for the transverse magnetisation are:

$$\begin{aligned} [\hat{L}_Z\hat{S}_Z, \hat{L}_X] &= [\hat{L}_Z, \hat{L}_X]\hat{S}_Z = +i\hat{L}_Y\hat{S}_Z, & [\hat{L}_Z\hat{S}_Z, \hat{L}_Y\hat{S}_Z] &= [\hat{L}_Z, \hat{L}_Y]\hat{S}_Z^2 = -(i/4)\hat{L}_X \\ [\hat{L}_Z\hat{S}_Z, \hat{L}_Y] &= [\hat{L}_Z, \hat{L}_Y]\hat{S}_Z = -i\hat{L}_X\hat{S}_Z, & [\hat{L}_Z\hat{S}_Z, \hat{L}_X\hat{S}_Z] &= [\hat{L}_Z, \hat{L}_X]\hat{S}_Z^2 = +(i/4)\hat{L}_Y \end{aligned} \quad (300)$$

where the factor of 4 in the denominators comes from $\hat{S}_Z^2 = 1/4$ for spin 1/2. For higher spin quantum numbers, the commutator would be different because \hat{S}_Z^2 would not be a multiple of the unit matrix. For spins 1/2, we get the following equations of motion:

$$\begin{cases} \frac{\partial}{\partial t}\langle L_X \rangle = -a\langle L_Y S_Z \rangle \\ \frac{\partial}{\partial t}\langle L_Y S_Z \rangle = +\frac{a}{4}\langle L_X \rangle \end{cases}, \quad \begin{cases} \frac{\partial}{\partial t}\langle L_Y \rangle = +a\langle L_X S_Z \rangle \\ \frac{\partial}{\partial t}\langle L_X S_Z \rangle = -\frac{a}{4}\langle L_Y \rangle \end{cases} \quad (301)$$

The dynamics is again rotational – the first system prescribes a rotation from the X axis onto the Y axis in the direction (clockwise or counterclockwise) that depends on the orientation of the partner spin. When the initial condition is pure single-spin order, we get elliptical trajectories:

$$\begin{cases} \langle L_X(t) \rangle = \cos\left(\frac{at}{2}\right) \\ \langle L_Y S_Z(t) \rangle = \frac{1}{2}\sin\left(\frac{at}{2}\right) \end{cases}, \quad \begin{cases} \langle L_Y(t) \rangle = \cos\left(\frac{at}{2}\right) \\ \langle L_X S_Z(t) \rangle = -\frac{1}{2}\sin\left(\frac{at}{2}\right) \end{cases} \quad (302)$$

Moving the factor of 2 into the definition of the two-spin order turns ellipses into circles:

$$\begin{cases} \langle L_X(t) \rangle = \cos\left(\frac{at}{2}\right) \\ \langle 2L_Y S_Z(t) \rangle = \sin\left(\frac{at}{2}\right) \end{cases}, \quad \begin{cases} \langle L_Y(t) \rangle = \cos\left(\frac{at}{2}\right) \\ \langle 2L_X S_Z(t) \rangle = -\sin\left(\frac{at}{2}\right) \end{cases} \quad (303)$$

Note that the frequency is $a/2$. The corresponding evolution diagrams are:

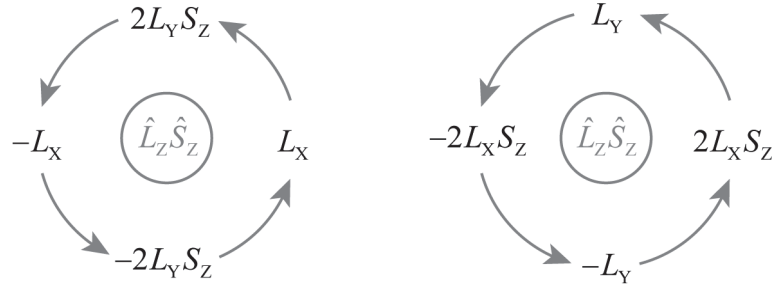
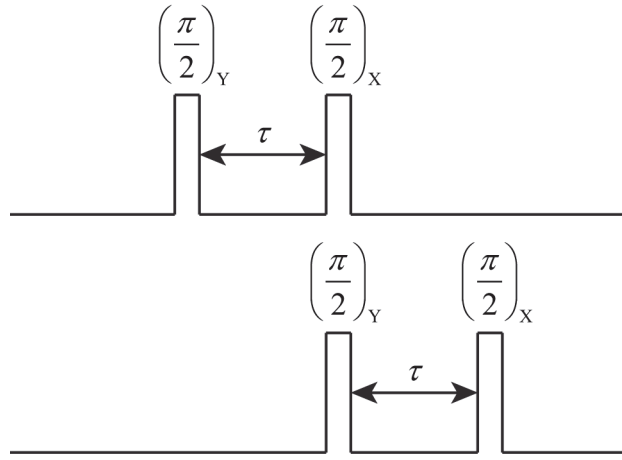


Figure 6. Spin state evolution diagrams under weak spin-spin coupling.

A practical example of using these diagrams is ^{15}N -enriched protein NMR spectroscopy, where a common magnetisation transfer stage is from the amide bond proton to its ^{15}N partner. When both ^1H and ^{15}N are on resonance with their rotating frames, the pulse sequence is:



When the initial condition is longitudinal proton magnetisation, the first pulse makes it transverse (middle diagram in Figure 5):

$$H_Z \xrightarrow{(\pi/2)_Y} H_X \quad (304)$$

The subsequent evolution under $a\hat{H}_z\hat{N}_z$ rotates the magnetisation towards the two-spin order (left diagram in Figure 6). Choosing a specific delay time τ such that $a\tau = \pi$ brings the magnetisation completely into the two-spin order:

$$H_X \xrightarrow{a\hat{H}_z\hat{N}_z} H_X \cos\left(\frac{a}{2}\tau\right) + 2H_Y N_Z \sin\left(\frac{a}{2}\tau\right) \xrightarrow{a\tau=\pi} 2H_Y N_Z \quad (305)$$

The next pair of pulses moves the situation where the proton is transverse and nitrogen longitudinal into the situation where the proton is longitudinal and the nitrogen is transverse:

$$2H_Y N_Z \xrightarrow{(\pi/2)_X \text{ on } H} 2H_Z N_Z \xrightarrow{(\pi/2)_Y \text{ on } N} 2H_Z N_X \quad (306)$$

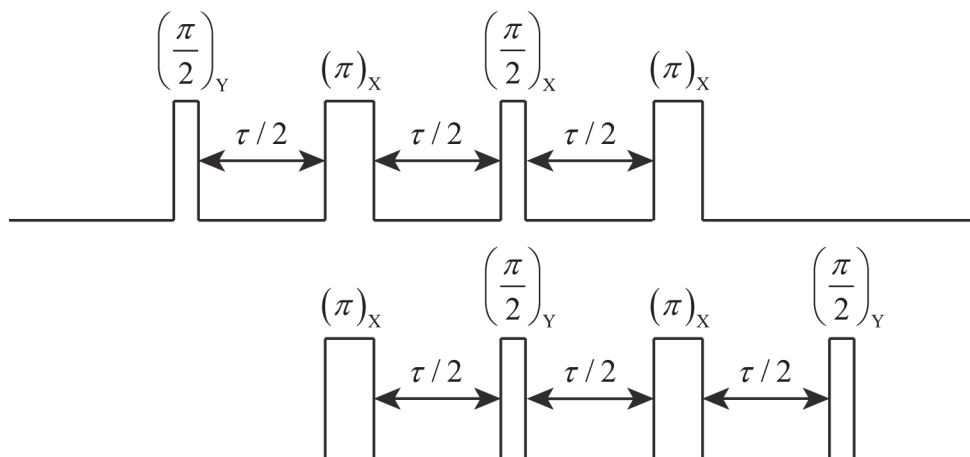
The next evolution period order (right diagram in Figure 6) rotates the resulting two-spin order towards transverse nitrogen magnetisation. Choosing the same evolution delay yields:

$$2H_Z N_X \xrightarrow{a\hat{H}_z\hat{N}_z} 2H_Z N_X \cos\left(\frac{a}{2}\tau\right) + N_Y \sin\left(\frac{a}{2}\tau\right) \xrightarrow{a\tau=\pi} N_Y \quad (307)$$

The optional last pulse (left diagram in Figure 5) makes nitrogen magnetisation longitudinal:

$$N_Y \xrightarrow{(\pi/2)_X \text{ on } N} N_Z \quad (308)$$

If the two nuclei are not on resonance with their rotating frames, spin echo stages must be inserted into the evolution periods to make sure that the offsets are refocused.



A similar analysis to the one presented above shows that this sequence accomplishes the same magnetisation transfer and is, at the same time, resilient to Zeeman frequency offsets on both spins. Because the coupling operator was assumed to be ZZ, this sequence only works in heteronuclear systems.