

What is product operator formalism?

Product operator formalism is a part of every NMR class, but often it is reduced to memorization. The familiar forms being:

$$\begin{array}{lll}
 I_z \xrightarrow{\phi I_z} I_z & I_x \xrightarrow{\phi I_z} I_x \cos \phi + I_y \sin \phi & I_y \xrightarrow{\phi I_z} I_y \cos \phi - I_x \sin \phi \\
 I_z \xrightarrow{\phi I_x} I_z \cos \phi - I_y \sin \phi & I_x \xrightarrow{\phi I_x} I_x & I_y \xrightarrow{\phi I_x} I_y \cos \phi + I_z \sin \phi \\
 I_z \xrightarrow{\phi I_y} I_z \cos \phi + I_x \sin \phi & I_x \xrightarrow{\phi I_y} I_x \cos \phi - I_z \sin \phi & I_y \xrightarrow{\phi I_y} I_y \\
 I_z \xrightarrow{2\phi I_z S_z} I_z & I_x \xrightarrow{2\phi I_z S_z} I_x \cos \phi + 2I_y S_z \sin \phi & I_y \xrightarrow{2\phi I_z S_z} I_y \cos \phi - 2I_x S_z \sin \phi \\
 2I_z S_z \xrightarrow{2\phi I_z S_z} 2I_z S_z & 2I_x S_z \xrightarrow{2\phi I_z S_z} 2I_x S_z \cos \phi + I_y \sin \phi & 2I_y S_z \xrightarrow{2\phi I_z S_z} 2I_y S_z \cos \phi - I_z \sin \phi
 \end{array}$$

A product operators is actually a short-hand for a mathematical relationship of the general form:

$$A \xrightarrow{B} f(\phi) \equiv \exp[-i\phi B] A \exp[i\phi B] = f(\phi)$$

How do these equations get these forms?

These equations are rotations, and to prove these are the correct solutions first consider the following:

$$\begin{aligned}
 f(\phi) &= \exp[-i\phi B] A \exp[i\phi B] \\
 \frac{d}{d\phi} f(\phi) &= -iB \exp[-i\phi B] A \exp[i\phi B] + \exp[-i\phi B] A iB \exp[i\phi B] \\
 &= i \exp[-i\phi B] (-BA + AB) \exp[i\phi B] \\
 &= i \exp[-i\phi B] [A, B] \exp[i\phi B] \\
 &= i \exp[-i\phi B] iC \exp[i\phi B] \\
 \frac{d}{d\phi} f(\phi) &= - \exp[-i\phi B] C \exp[i\phi B] \\
 \frac{d^2}{d\phi^2} f(\phi) &= iB \exp[-i\phi B] C \exp[i\phi B] - \exp[-i\phi B] C iB \exp[i\phi B] \\
 &= i \exp[-i\phi B] (BC - CB) \exp[i\phi B] \\
 &= i \exp[-i\phi B] [B, C] \exp[i\phi B] \\
 &= i \exp[-i\phi B] iA \exp[i\phi B] \\
 \frac{d^2}{d\phi^2} f(\phi) &= - \exp[-i\phi B] A \exp[i\phi B] = -f(\phi)
 \end{aligned}$$

Where a cyclic commutation relationship ($[I_i, I_j] = i\epsilon_{ijk} I_k$) is essential. The final differential equation ($\frac{d^2 f}{d\phi^2} = -f$) is the famous harmonic oscillator, with solution $f(\phi) = a \cos \phi + b \sin \phi = \exp[-i\phi B] A \exp[i\phi B]$. Allowing $\phi = 0$ identifies a as A . Finally, to determine b it is easiest to use a little horse sense, as it depends on the A and B but must be an element of the Lie algebra. For example, if $A = B$ then $b = 0$ is the only satisfactory conclusion, as there would be no reason for one member of the algebra to spontaneously evolve into another member. Another consideration is sign; for example, if $A = I_x$ and $B = I_z$ then

either I_y or $-I_y$ would be a valid choice for b . For consistency, the choice of sign is based on the “right-handed” solution, so thumb along \hat{z} , fingers starting along \hat{x} , and the fingers wrap towards $+\hat{y}$. (To be more precise, the choice of handedness is dependent on the sign of the nucleus’ gyromagnetic ratio).

How do I deal with these bilinear operators?

This is something that often gets skipped, I’m not sure why. For example, a two spin system may have a terms similar $I_x S_z$ and S_y in its product operators. The truth is that the notation is just lazy, what we really mean is $I_x \otimes S_z$ and $1 \otimes S_y$, so there is never a mismatch in matrix size. Also note that the order does matter; in other words, $I_x S_z \neq S_z I_x$.

How do I evaluate $\exp[A]$

Use the exponential series:

$$\exp[A] = \sum_{n=0}^{\infty} \frac{1}{n!} A^n$$

So where does the Hamiltonian fit into all of this?

In the equations above, A is the magnetization, which (because NMR is a soft measurement) may be described using just the spin operator even though it is a bulk property. And B is the Hamiltonian (or part of it) that is affecting the magnetization. In fact, the product operator $A \xrightarrow{B} f(\phi)$ is read A evolved under B goes to $f(\phi)$. Because all the components here are state functions, you may choose your own order of operators - just be sure to do them all before you’re done. In other words, if you want to do all the chemical shift terms first and then the coupling terms - that’s fine.

Why are product operators useful in NMR?

Under the approximations of perfect, ideal pulses and no relaxation product operators may be used to describe the magnetization evolution during a pulse sequence that involves spin- $\frac{1}{2}$ nuclei. (A perfect pulse applies exactly the correct flip angle to only the signals it should and creates no artifacts. An ideal pulse requires no time and does not change the hardware or sample in any way. No real pulse is ever perfect or ideal, much less both).

So what does it mean when someone says “That commutes with I_z ”?

Literally, the person means $[A, I_z] = AI_z - I_z A = 0$. What the person is conveying is that as time progresses, the magnetization of the A term is not changing. That means the A magnetization is along the \hat{z} -axis. For example, in the inversion-recovery T_1 experiment the equilibrium magnetization is first flipped along the $-\hat{z}$ -axis, where it sits for a delay time. During that delay time all the chemical shift and scalar coupling Hamiltonians “commute with I_z ”, so as far as product operator formalism is concerned the system will sit there forever until something is done to change the state. This means you don’t usually have to decouple a liquid sample during that delay time, as there are no surviving coupling terms to worry about. (A solid sample you often do have to decouple some because of spin-diffusion, which comes about from the direct dipole coupling being so much stronger than the scalar (indirect dipolar) coupling).