Product operators

Product operators provide us with a way to describe the behavior of complicated NMR experiments. The vector model, while informative, does not provide a means for predicting the outcomes of multi-pulsed coupled spin systems.

The product operator formalism gives a quantum mechanical description of spin systems in the form of the density matrix theory.

In this approach we use spin operators to describe spin magnetization along different axis and observe the effect pulses and delays have on the spin system.

Product operators vs. vector

Why involve ourselves with complex product operators when we can use the vector model?

The vector model, while useful for basic NMR experiments, fails when applied toward coupled spin systems (ie. COSY)

What makes the product operators so appealing is that it utilizes simple math to describe the complex quantum mechanics of multi-pulse NMR.

Spin operators

A mass in a circular orbit possesses angular momentum.

The x, y, and z components of the magnetization are represented by spin angular momentum operators:

$$I_x, I_y, \text{ and } I_z$$

At equilibrium (only z-magnetization is present) the density operator σ, which represents the state of the spin system, can be described:

$$\sigma_{eq} = I_z$$

Hamiltonians

In NMR the Hamiltonian is represented differently in different environments. There is one Hamiltonian for the spins in a static magnetic field, and another for a radio frequency pulse resulting in rotations about x and y-axes:

Free precession: Pulse about x-axis: Pulse about y-axis:

$$H_{free} = \Omega I_z \qquad H_{pulse,x} = \omega_1 I_x \qquad H_{pulse,y} = \omega_1 I_y$$

Ω represents the frequency of rotation about the z-axis, and ω represents the frequency of the Larmor precession (rad s^{-1})

Equation of motion

The density operator at a time *t*, σ(t), can be solved from time 0, σ(0), by the following:$\sigma(\mathrm{t}) =$

$$\sigma(\mathrm{t}) = \exp(-\mathrm{i}\mathcal{H}\mathrm{t})\sigma(0)\exp(\mathrm{i}\mathcal{H}\mathrm{t})$$

With some simple rules this equation is easily solved. For example consider a 90° x-pulse for duration τ_{p} is applied to equilibrium magnetization:

$$\sigma(0) = I_z$$

$$\mathcal{H} = \omega_1 I_x$$

$$\sigma\left(\tau_p\right) = \exp(-\mathrm{i}\omega_1 I_x \tau_p)\sigma(0)\exp(\mathrm{i}\omega_1 I_x \tau_p)$$

Rotation of operators

$$\sigma(\tau_p) = \exp(-\mathrm{i}\omega_1 I_x \tau_p)\sigma(0)\exp(\mathrm{i}\omega_1 I_x \tau_p)$$

By rewriting $\omega_1 \tau_p$ as an angle β, the equation becomes:

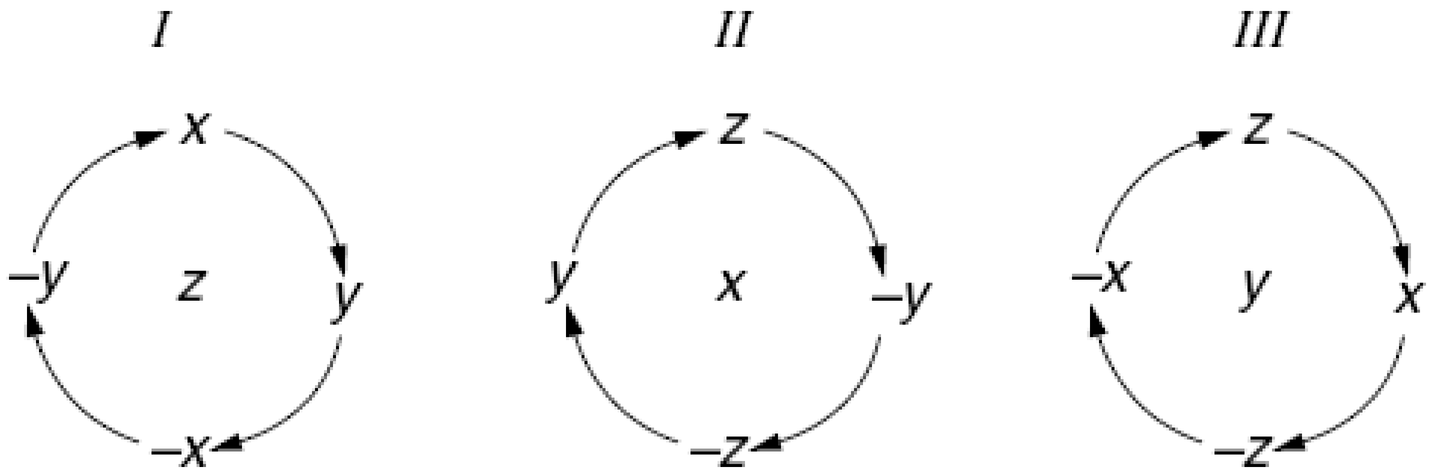
$$\sigma(\tau_p) = \exp(-\mathrm{i}\beta I_x)\sigma(0)\exp(\mathrm{i}\beta I_x)$$

We now need an identity to solve the equation. For a single spin system all identities have the same form:

$$\exp(-\mathrm{i}\theta I_a)\{\mathrm{old}\}\exp(\mathrm{i}\theta I_a) = \cos\theta\{old\} + \sin\theta\{new\}$$

where a = x, y or z. So how do we know what the new operator (magnetization vector) is? It is determined from the following rotation diagram, which is based on the information that we have already seen regarding how the various pulse operators will affect the spins.

Standard rotations



Angle of rotation = Ωt for offsets and $\omega_1 t_p$ for pulses

In our case the pulse is the about the x-axis. So the diagram shows that I_z (old operator) is rotated to I_{-y} (new operator).

Example: the π/2 pulse

I_z (old operator) and $-I_y$ (new operator)

We now need an identity to solve the equation. For a single spin system all identities have the same form:

$$\exp(-\mathrm{i}\pi I_x/2)\{\mathrm{old}\}\exp(\mathrm{i}\pi I_x/2) = \{new\}$$

$$\exp(-\mathrm{i}\pi I_x/2)I_z\exp(\mathrm{i}\pi I_x/2) = -I_y$$

We can construct a shorthand notation for this type of rotation:

$$I_z \xrightarrow{\omega_1 t_p I_x} -I_y$$