**MATLAB® Program for Product Operator Formalism of Spin-1/2**

Kosuke Ohgo

URL: https://github.com/ohgo1977/ProductOperator

**Purpose**

This program is designed to handle the product operator formalism of spin-1/2 using MATLAB. The calculation is based on the cyclic commutation rules thus it is faster than the actual matrix calculation. The program can handle multiple-spin systems with a flexibility of labeling of spins. This program will be helpful for educational purpose, for example, showing how to calculate product operators and explaining how components of pulse sequences (Hahn-echo, INEPT etc.) work. Also, this program can be used to calculate an evolution of a density operator under your own pulse sequence including phase cycling. The code is written in the object-oriented programming (OOP) style.

**Requirement**

MATLAB and MATLAB Symbolic Math Toolbox are required to run this program. It is tested under the MATLAB R2020b environment. Basic knowledge of MATLAB programming and the toolbox is required.

**Limitation**

This program can only handle weakly coupled spin-1/2 systems as same as the product operator formalism.

**Design of the Programming and How to Use It**

With a manner of the OOP, parameters for constructing product operators and functions for NMR interactions are described as **properties** and **methods** of a **class** named **PO**, respectively.

**PO Class Properties**

Any product operator can be described by two properties, axis label (x, y or z) and a coefficient.

For example, in the case of -4IxSzKz\*cos(q), the axis labels are x, z and z for the 1st (I), 2nd (S) and 3rd (K) spins, respectively and the coefficient is -cos(q). Note that “4” is related to the number of spins in the system and thus it is not considered as an independent coefficient.

In the **PO** class, information on the axis label and coefficient are stored as **axis** and **coef** properties, respectively.

**axis**: This property stores axis labels of the product operators. It is a *M* x *N* matrix where *M* is a number of product operators in a system and *N* is a number of spin types. Each component in the matrix has a value of 0, 1, 2, 3 corresponding to 1-, x-, y- and z-operator, respectively. For example, Ix + Sx + Sy (*M* = 3) in the IS system (*N* = 2) has [1 0; 0 1; 0 2] as **axis**.

**coef**: This property stores coefficients including signs for the product operators. It is a *M* x 1 vector. Note that the 2*N* – 1 coefficient at the beginning of a product operator is stored in other property, **Ncoef**.

There are additional properties in the **PO** class.

**spin\_label**: This property defines labels of the spins in the current system such as, I,S,K, … or I1, I2, I3, … etc.. The default labels are I, S, K, L, M.

**Ncoef**: This property stores the 2*N* - 1 coefficients for the product operators in the system. It is automatically calculated from the axis property.

**txt**: This property stores a text output of the current system. It is automatically generated.

**M**: This property stores a matrix form of the current system. It is automatically generated.

**sqn**: This property stores a spin quantum number. As a default, it stores sym(1/2) for spin-1/2.

**disp**: This property stores a binary value to control the display of the applied method and result on the command window. The default value is 1 for display ON.

**coherence**: This property is a 2*N* x 2*N* matrix displaying populations of spin states on the diagonal and coherences between states off the diagonal. a and b means |α> and |β> states, respectively, and m and p means coherences of |α> => |β> and |β> => |α>, respectively.

**PO Class Methods**

**1. Creating an Initial State of a System (Class Constructor)**

An initial state of a system, i.e., a density operator at the beginning, is created from the class constructor **PO()**.

As an example, if you like to construct ρ = Ix\*cos(q) + 2IySz\*sin(q),

>> syms q;

>> rho = PO(2, {'Ix' 'IySz'},{cos(q) sin(q)},{'I' 'S'})

rho =

PO with properties:

axis: [2×2 double]

coef: [2×1 sym]

spin\_label: {'I' 'S'}

disp: 1

coherence : [4×4 sym]

Ncoef: [2×1 sym]

txt: 'Ix\*cos(q) + 2IySz\*sin(q)'

M: [4×4 sym]

sqn: [1×1 sym]

The general syntax of the constructor is

**obj = PO(spin\_no, sp\_cell, symcoef\_cell, spin\_label\_cell)**

where **obj** is a PO-class object, **spin\_no** is a number of spin types in the system, **sp\_cell** is a cell array for product operators (without 2*N* – 1 coefficients), **symcoef\_cell** is a cell array for coefficients (coefficients must be sym class) and **spin\_label\_cell** is a cell array for spin labels that will be used as the class property **spin\_label**.

There are some examples below how to use the constructor.

ρ = Ix + Sy

>> rho = PO(2, {'Ix' 'Sy'});

If only the first two parameters are set, the third, **symccoef\_cell**, is automatically set as {sym(1) sym(1)} and the fourth, **spin\_label\_cell**, is set as {'I' 'S' 'K' 'L' 'M'}.

ρ = I1x + I2y

>> rho = PO(2, {'I1x' 'I2y'},{sym(1) sym(1)},{'I1' 'I2'});

Since I1 and I2 will be used instead of I and S, it is necessary to input {'I1' 'I2'} as **spin\_label\_cell** in addition to {sym(1) sym(1)} as **symcoef\_cell**.

ρ = I1x in a 3-spin system (I1, I2 and I3)

>> rho = PO(3, {'I1x'},{sym(1) },{'I1' 'I2' 'I3'});

It is necessary to set the number of spins in the system by the constructor. Currently, it is not possible to increase the number of spins in the system later. Also, **spin\_label\_cell** should be assigned for this particular 3-spin system.

ρ = Ix + 4IxSyKz

>> rho = PO(3, {'Ix' 'IxSyKz'});

The 2*N* - 1 coefficient, 4 in 4IxSyKz, should not be included in both **sp\_cell** and **symcoef\_cell**.

As a special case,

>> rho = PO(1,{'1'});

creates a 1/2E operator with rho.axis = [0], rho.coef = [1], rho.Ncoef = [1/2] and rho.txt = '1/2E' and rho.M = [1/2 0; 0 1/2]. Actually, any types of characters not defined in spin\_label are used in sp\_cell, they are considered as 1/2E operator.

Values of the PO properties can be obtained by a syntax **obj.PropertyName**. For example,

>> rho\_matrix = rho.M;

In the current code, it is possible to rewrite many of properties directly from the command line, for example,

>> rho.axis = [1 2 3];

that is not an expected operation. In the future version, these properties will be only rewritable from the PO methods.

**2. Applying NMR Interactions to a System**

There are PO-class methods for NMR interactions i.e., RF pulse, chemical shift and *J*-coupling to apply a spin system.

**RF Pulses**

**Single Pulse**

A method to apply a single pulse is

**obj = pulse(obj, sp, ph, q)** or

**obj = obj.pulse(sp, ph, q)** .

where **obj** is a PO-class object, **sp** is a type of spin for the pulse, **ph** is a quadrature phase, and **q** is a flip angle in radian.

**sp** can be characters ('I', 'S', 'I1' or 'I2' etc. defined in **spin\_label**) or the order number of spin (1 for 'I', 2 for 'S' etc.).

**ph** can be characters such as 'x', 'X' or '-y' or numbers 0, 1, 2 or 3 for x, y, -x or -y, respectively.

**q** can be double or symbolic class, such as pi/2 (double) or syms q (symbolic). If q is double class, it is converted to symbolic class in the code.

Examples

>> rho = PO(1, {'Iz'});

>> rho = pulse(rho, 'I', 'x', pi/2);

or equivalently,

>> rho = rho.pulse(1, 0, pi/2);

**Simultaneous Pulses**

A method to apply simultaneous pulses is

**obj = simpulse(obj, sp\_cell, ph\_cell, q\_cell)** or

**obj = obj.simpulse(sp\_cell, ph\_cell, q\_cell)** .

**sp\_cell**, **ph\_cell** and **q\_cell** are cell arrays corresponding to **sp**, **ph** and **q** for **pulse()**.

>> rho = PO(2, {'Iz' 'Sz'});

>> rho = simpulse(rho, {'I' 'S'}, {'x' 'x'}, {pi/2 pi/2});

or equivalently,

>> rho = simpulse(rho, {1 2}, {0 0}, {pi/2 pi/2});

A wildcard character '\*' can be used for **sp\_cell** to make a code a bit simpler.

Let's consider a 4-spin system, I1, I2, I3 and S4.

>> rho = PO(4,{'I1z' 'I2z' 'I3z' 'S4z'},{sym(1) sym(1) sym(1) sym(1)},{'I1' 'I2' 'I3' 'S4'});

If applying a 90x pulse to all I spins, the wildcard character can be used as

>> rho = simpulse(rho, {'I\*'},{'x'},{pi/2});

If applying a 90x pulse to all spins,

>> rho = simpulse(rho, {'\*'},{'x'},{pi/2});

If applying a 90x pulse to all I spins and 180y pulse to S4 spin,

>> rho = simpulse(rho, {'I\*' 'S4'},{'x' 'y'},{pi/2 pi});

**Pulses with Phase Shift**

A method to apply a single pulse with a phase shift is

**obj = pulse\_phshift(obj, sp, ph, q)** or

**obj = obj.pulse\_phshift(sp, ph, q)** .

The difference from **pulse()** is that **ph** is an arbitrary phase in radian.

Accordingly, simultaneous pulses with phase shifts can be applied as

**obj = simpulse\_phshift(obj, sp\_cell, ph\_cell, q\_cell)** or

**obj = obj.simpulse\_phshift(sp\_cell, ph\_cell, q\_cell)** .

**Chemical Shift**

A method to apply a chemical shift evolution is

**obj = cs(obj, sp, q)** or

**obj = obj.cs(sp, q)** ,

where **sp** is a type of spin and **q** is a rotation angle in radian. Formats of **sp** and **q** are same as the ones used for **pulse()**.

It is possible to obtain chemical shift evolutions of multiple spins with

**obj = simcs(obj, sp\_cell, q\_cell)** or

**obj = obj.simcs(sp\_cell, q\_cell)**

where **sp\_cell** and **q\_cell** have safe formats as the one sued for **simpulse()**. The wildcard character '\*" also can be used for **sp\_cell**.

>> syms oI oS t

>> rho = PO(3, {'I1x' 'I2x' 'S3x'},{sym(1) sym(1) sym(1)},{'I1' 'I2' 'S3'});

>> rho = cs(rho,'I1',oI\*t);

>> rho = cs(rho,'I2',oI\*t);

>> rho = cs(rho,'S3',oS\*t);

or equivalently,

>> rho = simcs(rho,{1 2 3},{oI\*t oI\*t oS\*t});

or

>> rho = simcs(rho,{'I\*' 'S3'},{oI\*t oS\*t});

***J*-coupling**

A method to apply a *J*-coupling evolution is

**obj = jc(obj, sp, q)** or

**obj = obj.jc(sp, q)** ,

where **sp** is labels of a spin pair and **q** is a rotation angle in radian.

**sp** can be characters 'IS', 'I1I3' etc. or a 1 x 2 vector showing the index of spins such as [1 2] or [1 3].

>> rho = PO(2, {'Ix'});

>> syms J12 t

>> rho = jc(rho,'IS',pi\*J12\*t);

It is possible to obtain *J*-coupling evolutions of multiple spin-pairs with

**obj = simjc(obj, sp\_cell, q\_cell)** or

**obj = obj.simjc(sp\_cell, q\_cell)** ,

where **sp\_cell** is a cell array of spin pairs. Note that the wildcard character '\*' is not accepted for **sp\_cell** in this method. The spin pairs must be explicitly given in **sp\_cell**.

>> rho = PO(3,{'I1x' 'I2x'},{sym(1) sym(1)},{'I1' 'I2' 'S3'});

>> syms J13 J23 t

>> rho = simjc(rho,{'I1S3' 'I2S3'},{pi\*J13\*t pi\*J23\*t});

**Pulse Field Gradients**

A method to apply a pulse field gradient is

**obj = pfg(obj, G, gamma\_cell)** or **obj = obj.pfg(G, gamma\_cell)**.

(if **gamma\_cell** is stored as property, **obj = pfg(obj, G)** or **obj = obj.pfg(G)** might be possible)

**G** is a strength of the gradient field and **gamma\_cell** is a cell array to store gyromagnetic ratio of spins in the system.

**G** can be double or symbolic class. Components of **gamma\_cell** can be also double or symbolic class.

>> syms G gH gC

>> rho = PO(3,{'I1x' 'I2x' 'S3x'},{sym(1) sym(1) sym(1)},{'I1' 'I2' 'S3'});

>> rho = pfg(rho, G, {gH gH gC});

Internally, angles are calculated from **G** and **gamma\_cell** and they are used as an input of **simcs()**. In the case above, the angles are {G\*gH G\*gH G\*gC}. Note that a length of the gradient pulse is not counted in the calculation (and generally speaking, it is not necessary to do that). If necessary, multiply a time constant to **G**. This method was inspired by a reference (Güntert, 2006).

**Applying multiple methods in one time**

Since the program is written in the OOP style, you can apply multiple methods in one time using '.' like this;

>> rho = rho.pulse('I','y',pi/2).cs('I',q).jc('IS',pi\*J12\*t);

that is equivalent to

>> rho = rho.pulse('I','y',pi/2);

>> rho = rho.cs('I',q);

>> rho = rho.jc('IS',pi\*J12\*t);

Note that the order is left to right (**pulse()** => **cs()** => **jc()**) but not right to left (**jc()** => **cs()** => **pulse()**).

**3. Utilities**

There are several methods as utilities. Some of them are static methods, i.e., they are called by **PO.MethodName()**. These utilities can be used when a pulse sequence is emulated.

**phout = PO.phmod(phx,ii)**

Read a phase value, **phout**, from a phase table (vector), **phx**.

If **ii** is smaller or equal to length(phx), phout = phx(ii) otherwise phout = phx(mod(ii,length(phx)).

This method can be used in cases where there are phase tables with different lengths and phase-cycle them together.

**dispPOtxt(obj)** or

**obj.dispPOtxt()**

displays the **txt** property of **obj** to the Command Window.

**dispPO(obj)** or

**obj.dispPO()**

displays terms in **obj** in the following manner.

ID Product-Operator Coefficient

For example, in the case of ρ = Ix\*cosθ + Iy\* sinθ

>> syms q; rho = PO(1,{'Ix' 'Iy'},{cos(q) sin(q)});

>> dispPO(rho)

1 Ix cos(q)

2 Iy sin(q)

**id\_vec = findcoef (obj, coef\_in\_cell)** or

**id\_vec = obj. findcoef (coef\_in\_cell)**

finds particular terms that includes coefficients defined in **coef\_in\_cell** and returns ID numbers for these terms as **id\_vec**.

**obj = delPO(obj,id\_in)** or

**obj = obj.delPO(id\_in)**

Delete particular terms from **obj** using the information given by **id\_in**.

If **id\_in** is a vector including numbers, these numbers are ID for terms to be deleted. The ID number of each term can be found by **obj.dispPO()** or be obtained from **obj.findcoef()**. The example is

>> rho = PO(3,{'Ix' 'Sx' 'Kx'});

>> rho.dispPO()

1 Ix 1

2 Sx 1

3 Kx 1

>> rho = delPO(rho,[1 2])

>> rho.dispPO()

1 Kx 1

If **id\_in** is a cell array with product operators, terms including these operators are deleted.

There are some examples.

>> rho = delPO(rho,{'Ix'}); % delete Ix term

>> rho = delPO(rho,{'IzSz'}) % delete 2IzSz term

>> rho = delPO(rho,{'Ix' 'IzSz'})% delete Ix and 2IzSz term

A wildcard character '\*' can be used at choose all three phases.

>> rho = delPO(rho,{'IxS\*'})% delete 2IxSx, 2IxSy and 2IxSz if they exist

>> rho = delPO(rho,{'I\*S\*' 'I\*S\*K\*'})% delete any terms including 2I\*S\* and 4I\*S\*K\*

**obj = selPO(obj,id\_in)** or

**obj = obj.delPO(id\_in)**

Select particular terms from **obj** using the information given by **id\_in**. The format of **id\_in** is same as in **delPO()**.

**dispRaiseLower(obj)** or

**obj.dispRaiseLower()**

displays ρ with raising/lowering operator basis. (Güntert, 2006). This method will be available in the future version.

**[a0\_V,rho\_V] = SigAmp(obj,sp,phR)** or

**[a0\_V,rho\_V] = obj.SigAmp(sp,phR)**

Calculation of the initial signal amplitudes s(0) corresponding to (-1) quantum coherences in the equation

s(t) = 2\*i\*ρ[-](t) \*exp(-i\*φrec)

in Spin Dynamics, p. 288 (eq. 11.48).

For example, in the case of homonuclear 2-spin system, the equation is

s(t) = 2\*i\*(ρ[-β](t) + ρ[-α](t) + ρ[β-](t) + ρ[α-](t))\*exp(-i\*φrec)

shown in p. 379.

Related topics: Spin Dynamics (2nd Ed.), p.262, p. 287, p. 371, p.379, pp.608-610.

**sp** describes spin types to be observed (e.g., 'I', 'IS', [1], [1 2]). **phR** is a quadrature receiver phase (e.g. 'x', 'y', 0, 1).

**a0\_V** is a vector corresponding to 2i\*[ρ[-β…](0) ρ[-α…](0) ρ[β-…](0) ρ[α-…](0) …] \*exp(-i\*φrec).

**rho\_V** is a vector describing which component of a0\_V comes from which coherence in the density operator (e.g., 'ma' for '-α', 'bm' for 'β-').

**Technical Details**

**Description of a product operator in the code**

In the code, a product operator is described as a 1 x *N* vector where *N* is a number of spins in a system. The axis label of a product operator is described as 1 for x, 2 for y, and 3 for z, and 0 for 1/2\**E*. For example, Ix and IzSz in the IS system are described as [1 0] and [3 3], respectively. The intrinsic coefficient 2(*N* - 1) (e.g., 2 for 2IzSz) is automatically calculated from the vector size and stored separately. In the case of multiple terms, 1 x *N* vectors are combined to a *M* x *N* matrix where *M* is a number of terms. A coefficient of each term is stored separately.

**Cyclic commutation rules**

If the operators *A*, *B*, and *C* shows [*A*, *B*] = i*C*, [*B*, *C*] = i*A* and [*C*, *A*] = i*B* (cyclic commutation) then

exp(-iθ*A*) *B* exp(iθ*A*) = *B* cosθ + *C* sinθ,

exp(-iθ*B*) *C* exp(iθ*B*) = *C* cosθ + *A* sinθ, and

exp(-iθ*C*) *A* exp(iθ*C*) = *A* cosθ + *B* sinθ

It is known that Ix, Iy, Iz are in the cyclic commutation ([Iz, Ix] = iIy) and the formula above can be used to describe an evolution of a density operator under a Hamiltonian. For example, a density operator ρ(0) = Ix evolves under a chemical shift Hamiltonian *H* = ωIz during a time period of t as

ρ(t) = exp(-i*H*t) ρ(0) exp(i*H*t) = exp(-iωtIz) Ix exp(iωtIz) = Ix cos(ωt) + Iy sin(ωt)

**Use of the master table to accelerate calculation**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  | B |  |
|  |  |  | x | y | z |
|  |  |  | 1 | 2 | 3 |
|  | x | 1 | **0** | **3** | **-2** |
| A | y | 2 | **-3** | **0** | **1** |
|  | z | 3 | **2** | **1** | **0** |
|  |  |  |  | C |  |

The cyclic commutation rules can be summarized as a table (master table) using the equation exp(-iθ*A*) *B* exp(iθ*A*) = *B* cosθ + *C* sinθ above and Ix, Iy and Iz. For example, in the case of exp(-iθIz) Ix exp(iθIz) = Ix cosθ + Iy sinθ, the axis numbers of the *A* and *B* positions are 3 (z) and 1 (x), respectively. Then the axis number for *C* is the (3, 1) component in the table, i.e., 2 meaning Iy.

If the value for *C* is 0 for given *A* and *B*, then *A* and *B* are not in the cyclic commutation (e.g., *A* = *B* = Ix). If the value for *C* is negative, then -*C* sinθ is used instead of +*C* sinθ.

This is the basic idea of the calculation in the code, and it is not necessary to handle a matrix calculation which usually has a high calculation cost.

**When can the master table be used for the calculation?**

If the two rules below are satisfied, an evolution of ρ under *H* can be calculated with using the master table. Otherwise ρ does not evolve under *H*.

**Rule 1**. There should be at least one spin type matching between *H* and ρ.

AND

**Rule 2**. Only one spin type in the matching spin types has different axis labels between *H* and ρ.

These rules can be used for spin-1/2 with *H* that is a product of up to two spin operators (e.g. *H* = 2IzSz but not like 4IzSzKz). The rule 1 is obvious but how about the rule 2. Here is the analysis.

Suppose *H* = 2IaSb and ρ = 8IbSbKL where K, L are product operators which are different types each other in addition to I and S. Suppose [Ia, Ib] = iIc in the cyclic commutation. There are two spin-types matching between *H* and ρ (thus satisfying the Rule 1) and only one of them (I spin) has different labels between *H* and ρ (thus satisfying the Rule 2).

Then [*H*, ρ] = 2IaSb 8IbSbKL – 8IbSbKL 2IaSb = 16 IaIbSb2KL - 16IbIaSb2KL

= 16 (IaIb – IbIa)Sb2KL = 4(IaIb – IbIa)KL = i4IcKL. Note that Sb2 = 1/4E for spin-1/2.

[4IcKL, *H*] = 4IcKL 2IaSb - 2IaSb 4IcKL = 8IcIaSbKL - 8IaIcSbKL = 8(IcIa – IaIc)SbKL = i8IbSbKL = iρ.

[ρ, 4IcKL] = 8IbSbKL 4IcKL - 4IcKL 8IbSbKL = 32IbIcSbK2L2 – 32IcIbSbK2L2 = 2(IbIc – IcIb)Sb = i2IaSb = i*H*. Note that K2 = L2 = 1/4E for spin-1/2.

Thus, *H* and ρ are in the cyclic commutation.

What if the Rule 2 is not satisfied?

In the case of *H* = 2IbSb and ρ = 8IbSbKL,

[*H*, ρ] = 2IbSb 8IbSbKL – 8IbSbKL 2IbSb = 16 Ib2Sb2KL - 16Ib2Sb2KL = 0

thus, *H* and ρ are not in the cyclic commutation.

In the case of *H* = 2IaSb and ρ = 8IbScKL, [*H*, ρ] is calculated as 0 from the fact [2IaSb, 2IbSc] = 0 that can be calculated from the matrix representation.

[*H*, ρ] = 2IaSb 8IbScKL - 8IbScKL 2IaSb = 2IaSb 2IbSc 4KL - 2IbSc 4KL 2IaSb = 2IaSb 2IbSc 4KL - 2IbSc 2IaSb 4KL = [2IaSb, 2IbSc]\*4KL = 0 (Read Spin Dynamics (2nd Ed.) p.403, Eq. 15.24 and p. 407, Note 3).

Examples for these rules

ρ = Iy and *H* = Iz

Both ρ and *H* include I-spin (Rule 1: yes) and they have different axis labels (Iy vs. Iz) (Rule 2: yes). 🡺 Master Table: Yes

ρ = Sy and *H* = Iz

ρ and *H* don't have a same type of spin (Rule 1: No) 🡺 Master Table: No

ρ = Iy and *H* = Iy

Both ρ and *H* include I-spin (Rule 1: yes) but they have same axis labels (Iy) (Rule 2: no). 🡺 Master Table: no

ρ = 2IzSy and *H* = Iz

Both ρ and *H* include I-spin (Rule 1: yes) but I-spins have same axis labels (Iz) (Rule 2: no). 🡺 Master Table: no

ρ = 2IzSy and *H* = 2IzSz

Both ρ and *H* include I- and S-type product operators (Rule 1: yes) and only S-spins have different axis labels (Sy vs. Sz) (Rule 2: yes). 🡺 Master Table: yes

ρ = 2IxSx and *H* = Iz

Both ρ and *H* include I-spin (Rule 1: yes) and they have different axis labels (Ix vs. Iz) (Rule 2: yes). 🡺 Master Table: Yes

ρ = 2IxSx and *H* = 2IzSz

Both ρ and *H* include I- and S-type product operators (Rule 1: yes) but both spin types have different axis labels (Ix vs. Iz and Sx vs. Sz) (Rule 2: no). 🡺 Master Table: No

**Special cases for *J*-coupling evolutions**

According to p. 483 of *Spin Dynamics*, there are four cases where a product operator does not evolve under *J*-coupling Hamiltonian *I*jz*I*kz.

1. If both spin *I*j and *I*k are missing in the product operator.

2. If only one spin *I*j or *I*k is present, and that spin carries a z label.

3. If both spins *I*j and *I*k are present, but both spins carry a z label.

4. If both spins *I*j and *I*k are present, but neither spin carries a z label.

These four cases are excluded by the two rules above.

Case 1. Rule 1 is not satisfied.

Case 2. Rule 1 is satisfied but Rule 2 is not satisfied.

Case 3. Rule 1 is satisfied but Rule 2 is not satisfied.

Case 4. Rule 1 is satisfied but Rule 2 is not satisfied.

**Implementation of the two rules in the programing code**

The two rules above can be evaluated in the programming code as shown below.

type\_mask\_vec = (rho\_axis.\*H\_axis)~=0;

% Check how many spin types get matched, matched: 1, unmatched: 0

axis\_diff\_vec = rho\_axis ~= H\_axis;

% Check the difference of the direction of each spin type, unmatched: 1, matched: 0

axis\_mask\_vec = type\_mask\_vec.\*axis\_diff\_vec;

% Comparing the spin-type matching and spin-label unmatching.

axis\_mask = sum(axis\_mask\_vec);

axis\_mask becomes 1 ONLY when the two rules are satisfied.

If axis\_mask is 1, then

H\_axis = [h1 h2 h3 …] corresponding to *A*

rho\_axis = [r1 r2 r3 …] corresponding to *B*

are used to calculate a product operator

axis\_tmp = [a1 a2 a3 …] corresponding to *C*.

if both rn and hn are not 0, an takes an absolute value of the (hnth row, rnth column) component of the master table. If the value from the master table is negative, the sign of the coefficient is inverted.

if rn is not 0 but hn is 0, an is same as rn. This is for cases such as ρ = 2IzSz and *H* = Ix 🡺 *C*: 2IySz

if rn is 0 but hn is not 0, an is same as hn. This is for cases such as ρ = 2Ix and *H* = 2IzSz 🡺 *C*: 2IySz

Note that the sign of *H* (i.e., Ix vs. -Ix) is not reflected in the calculation above. Instead, the sign of *H* is considered in the coefficient calculation of *C*.

**References**

Levitt, M. H., *Spin Dynamics*, 2nd Edition, Wiley, 2008.

Keeler, J., *Understanding NMR Spectroscopy*, 1st Edition, Wiley, 2005.

Güntert, P., *Symbolic NMR Product Operator Calculations*, *Int. J. Quant. Chem.* **2006**, *106*, 344 – 350.

Hassan, J., Nabulsi, A. A., *A New Graphical User Interface for Teaching NMR*, *Am. J. Educ. Res.* 2014, 2, 240 – 244.