A Complete Product Operator Theory for $IS$ ($I = 1, S = 1$) Spin System and Application to 3D HMQC-COSY NMR Experiment

İrfan Şaka, Sedat Gümüş, and Azmi Gençten

Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayis University, 55139, Samsun, Turkey
Reprint requests to A. G.; Fax: +90 362 4576081; E-mail: gencten@omu.edu.tr

Z. Naturforsch. 64a, 377 – 386 (2009); received September 26, 2008 / revised February 25, 2009

There exist a variety of multi-pulse NMR experiments for spectral assignment of complex molecules in solution. The conventional heteronuclear multiple-quantum coherence (HMQC) NMR experiment provides correlation between weakly coupled hetero-nuclei. The COSY is one of the most popular two-dimensional NMR experiment which is used to correlate $J$-coupled homo-nuclei of spectral assignment. The combination of the conventional HMQC and COSY NMR experiments yields a new experiment called 3D HMQC-COSY NMR experiment. The product operator theory is widely used for the analytical descriptions of multi-pulse NMR experiments for weakly coupled spin systems in liquids. In this study, complete product operator theory for weakly coupled $IS$ ($I = 1, S = 1$) spin system is presented by obtaining the evolutions of the product operators under the scalar spin-spin coupling Hamiltonian. As an application and a verification, analytical descriptions of 3D HMQC-COSY NMR experiment are obtained for weakly coupled $IS, IS'$ ($I = I' = 1/2; S = S' = 1; n = 1, 2, 3; m = 1, 2$) multi-spin systems. Then the estimated spectra of this experiment for various multi-spin systems are explained in detail.

Key words: Product Operator Theory; Spin-1; 3D HMQC-COSY; NMR.

1. Introduction

It is well-known that the product operator theory as a quantum mechanical method is widely used for the analytical description of multi-pulse NMR experiments on weakly coupled spin systems in liquids having spin-1/2, spin-1 and spin-3/2 nuclei [1 – 16]. For weakly coupled two-spin-1 systems, evolutions of the $S_x, S_y, I_xS_y, I_yS_x, I_xS_y^2, I_yS_x^2, I_xS_y^2, I_yS_x^2$ and $I_xS_y^2$ product operators under the weak spin-spin coupling Hamiltonian and analytical descriptions of the INADEQUATE and DQC NMR experiments have been presented by Chandrakumar and co-workers [6, 10, 17, 18]. In our recent study, the complete product operator theory for the $IS$ ($I = 1/2, S = 1$) spin system and application to DEPT-HMQC and MAXY NMR experiments have been presented [19, 20]. By using product operator theory in NMR experiments, experimental results can be confirmed and also new experimental suggestions can be made.

The conventional HMQC NMR experiment provides correlation between weakly coupled hetero-nuclei [21, 22]. The COSY is one of the most popular two-dimensional NMR experiment which is used for the correlation of $J$-coupled homo-nuclei in order to make spectral assignment [11]. In COSY NMR experiment of complex molecules, the spin-spin coupling multiplets of different chemically shifted nuclei may overlap and then spectral assignment may become too difficult. In order to simplify COSY NMR spectra a new experiment called 3D HMQC-COSY was obtained [23, 24]. This experiment is the combination of HMQC and COSY NMR experiments. The spectrum of this experiment would contain H-H correlations in the F2 and F3 planes. Third dimension (F1) would separate the planes based on $^{13}$C chemical shifts of directly bounded $^{13}$C atoms.

In the present study, the complete product operator theory has been presented for weakly coupled $IS$ ($I = 1, S = 1$) spin system as it is presented before for weakly coupled $IS$ ($I = 1/2, S = 1$) spin system [19, 20]. First, the evolutions of all product operators under the scalar spin-spin coupling Hamiltonian have been obtained for the $IS$ ($I = 1, S = 1$) spin system. Then, for the first time in this study, the product operator descriptions of the 3D HMQC-COSY NMR experiment are obtained for weakly coupled $IS, IS'$ ($I = I' = 1/2; S = S' = 1; n = 1, 2, 3; m = 1, 2$) multi-spin systems. Then the estimated spectra of this experiment for various multi-spin systems are explained in detail.
spin systems. It is shown that this experiment can be used for spectral assignments of CD₃CD₃ groups in complex liquids. Therefore, after obtaining the complete product operator theory for IS (I = 1, S = 1) spin system an application and a verification of this theory is also presented.

2. Theory

The product operator formalism is the expansion of the density matrix operator in terms of matrix representation of angular momentum operators for individual spins. For the IS (I = 1, S = 1) spin system, the nine Cartesian spin angular momentum operators for I = 1 are E₁, Iₓ, Iᵧ, I₂, [Iₓ,Iᵧ] + , [Iₓ,I₁] + and (I₁² - I₂²) [19, 25]. Similarly, there are also nine Cartesian spin angular momentum operators for S = 1. So, 9 · 9 = 81 product operators are obtained with direct products of these spin angular momentum operators for the IS (I = 1, S = 1) spin system. Depending on the pulse experiment, the (I₁² - I₂²) Cartesian spin angular momentum operator is separated into two spin angular momentum operators as I₁² and I₂². In this case, there should be 10 · 10 = 100 product operators for this spin system. In this study they are used in separated form and the complete list of the product operators are given in Table 1.

In a liquid-state pulse NMR experiment of weakly coupled IS spin systems, the total Hamiltonian consists of the r.f. pulse, the chemical shift, and the spin-spin coupling Hamiltonians can be easily obtained [5–7, 10, 19].

For the IS (I = 1, S = 1) spin system the evolutions of some product operators under the weak spin-spin coupling Hamiltonian (J = 2πΩJ₁,J₂) are known and they are given in Table 2 [10, 17–20, 26]. In tables and equations, cₜ = cos(πJ₁t), sₜ = sin(πJ₁t), Iₓ = [Iₓ,I₁] +, Iᵧ = [Iₓ,I₂] +, Iₜ = [Sₓ,S₁] +, Iₛ = [Sₓ,S₂] +, Iₓy = [Sₓ,Sₘ] +, I₁² = (I₁² - I₂²) and S₂ = S₂(S₁ - S₂) short notations are used. For example for I₁² the product operator of IS (I = 1, S = 1) spin system can be found as

\[
\text{exp}(-i2\pi J₁lₓlₜ)I₁²\text{exp}(i2\pi J₁lₓlₜ) \frac{\mathcal{H}ₜ}{\frac{1}{2}I₁²(cₜ + 1) - \frac{1}{2}I₂²(cₜ - 1) + \frac{1}{2}I₁²SₓSₘ}. (5)
\]

The evolutions for the Iₓ, Iᵧ, Iₓz, Iᵧz, Iₓy, I₁², and I₂² product operators will be similar to those of Sₓ, Sᵧ, Sₓz, Sᵧz, Sₓy, S₂ = S₂(S₁ - S₂) product operators. For this spin system E, Iₓ, Iᵧ, I₁², I₂², Iₓz, Iᵧz, Iₓy, and I₁² I₂² product operators does not change under the spin-spin coupling Hamiltonian. Evolutions of all nine Cartesian spin angular momentum operators under the r.f. pulse and the chemical shift Hamiltonians have been presented in our previous work for spin-1 [19, 20].

At any time during the NMR experiments, the ensemble averaged expectation value of the spin angular momentum, e.g. for Iᵧ, is

\[
Mₜ(t) \approx \langle Iᵧ \rangle \equiv Tr[Iᵧ\sigma(t)], 
\]

where the time dependence of the density matrix is governed by Liouville-von Neumann equation:

\[
\frac{d\sigma}{dt} = -\frac{i}{\hbar}[\sigma,\mathcal{H}].
\]
Table 2. Evolutions of the product operators under the spin-spin coupling Hamiltonian (2π\(H_L, S_z\)) for weakly coupled IS (I = 1, S = 1) spin system [10, 17–20, 26].

<table>
<thead>
<tr>
<th>Product operator</th>
<th>Evolution of the product operator under the spin-spin coupling Hamiltonian ((H = 2\pi H_L, S_z))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_x)</td>
<td>(S_x + i\frac{J_1}{2}S_y(c_{2J} - 1) - iS y S_{2J})</td>
</tr>
<tr>
<td>(S_y)</td>
<td>(S_y + i\frac{J_1}{2}S_x(c_{2J} - 1) - iS x S_{2J})</td>
</tr>
<tr>
<td>(S_z)</td>
<td>(S_z + i\frac{J_1}{2}S_x(c_{2J} - 1) - iS y S_{2J})</td>
</tr>
<tr>
<td>(S_{x2})</td>
<td>(S_{x2} + i\frac{J_1}{2}S_{y2}(c_{4J} - 1) - iS_{y2}S_{4J})</td>
</tr>
<tr>
<td>(S_{y2})</td>
<td>(S_{y2} + i\frac{J_1}{2}S_{x2}(c_{4J} - 1) - iS_{x2}S_{4J})</td>
</tr>
<tr>
<td>(S_{z2})</td>
<td>(\frac{1}{2}iS_x(c_{2J} - 1) + \frac{1}{2}iS_y(c_{2J} - 1) + \frac{1}{2}(S_z S_y - S_y S_z)c_{2J})</td>
</tr>
<tr>
<td>(S_{xz})</td>
<td>(S_{xz} + i\frac{J_1}{2}S_{yz}(c_{4J} - 1) + i\frac{J_1}{2}S_{yz}S_{4J})</td>
</tr>
<tr>
<td>(S_{z1})</td>
<td>(S_{z1} + i\frac{J_1}{2}S_{x1}(c_{4J} - 1) - iS_{x1}S_{4J})</td>
</tr>
</tbody>
</table>

where \(\sigma(t)\) is the density matrix operator calculated from (4) at any time. Since \((I_\sigma)\) is proportional to the magnitude of the \(y\)-magnetization, it represents the signal detected on \(y\)-axis. So, in order to estimate the free induction decay (FID) signal of a multi-pulse NMR experiment, the density matrix operator should be obtained at the end of the experiment.

3. The Evolutions of Product Operators under the Spin-Spin Coupling Hamiltonian

As mentioned in section 2, there exist 100 product operators for IS \((I = 1, S = 1)\) spin system. None of them does not change under the spin-spin coupling Hamiltonian. The evolutions for 21 of them are known in the literature and are given in section 2. In this section the evolutions of 70 product operators under the spin-spin coupling Hamiltonian will be obtained. By using the Hausdorff formula given in (4), the evolutions of product operators under the spin-spin coupling Hamiltonian are derived for weakly coupled IS \((I = 1, S = 1)\) spin system. The weak spin-spin coupling Hamiltonian, which is the secular part of the scalar coupling, is \(H_J = 2\pi I J L, S_z\). As an example, evolution of \(I_\sigma S_{x2}\) product operator is obtained as follows, \(\langle I_\sigma S_{x2}\rangle = I_\sigma S_{x2}\) and \([S_{x2}, S_{x2}] = S_{x2}\):

\[
I_\sigma S_{x2} \xrightarrow{2\pi H_L, S_z} I_\sigma S_{x2} - (i2\pi J)\frac{1}{2}(I_s S_{x2} + I_{x2} S_s)
\]

\[
+ \left(\frac{(i2\pi J)^2}{2!}\right) - \frac{1}{2}(I_s S_{x2} - I_{x2} S_s)
\]

\[
- \left(\frac{(i2\pi J)^3}{3!}\right) \frac{i}{2}(I_s S_{x2} + I_{x2} S_s) + \cdots
\]

is obtained. In order to get the generalized form for the evolution of \(I_\sigma S_{x2}\) product operator under the spin-spin coupling Hamiltonian some additions and subtractions can be made as follows:

\[
I_\sigma S_{x2} \xrightarrow{2\pi H_L, S_z} I_\sigma S_{x2} - (i2\pi J)\frac{1}{2}(I_s S_{x2} + I_{x2} S_s)
\]

\[
+ \left(\frac{(i2\pi J)^2}{2!}\right) - \frac{1}{2}(I_s S_{x2} - I_{x2} S_s)
\]

\[
- \left(\frac{(i2\pi J)^3}{3!}\right) \frac{i}{2}(I_s S_{x2} + I_{x2} S_s) + \cdots
\]

\[
+ \frac{1}{2}(I_s S_{x2} - I_{x2} S_s) - \frac{1}{2}(I_s S_{x2} - I_{x2} S_s)
\]

Then, using sine and cosine series,

\[
I_\sigma S_{x2} \xrightarrow{2\pi H_L, S_z} \frac{1}{2}I_\sigma S_{x2}(c_{2J} + 1)
\]

\[
- \frac{1}{2}I_s S_{x2}(c_{2J} - 1) + \frac{1}{2}(I_s S_{x2} + I_{x2} S_s)c_{2J}
\]
Table 3. Evolution of the product operators under the spin-spin coupling Hamiltonian \((2\pi H_{IJS})\) for weakly coupled IS \((I = 1, S = 1)\) spin system.

<table>
<thead>
<tr>
<th>Product Operator</th>
<th>Evolution of the product operator under the spin-spin coupling Hamiltonian ((H = 2\pi H_{IJS}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_S c_2)</td>
<td>(\frac{1}{2}I_S c_1(I_S c_2 + 1) - \frac{1}{2}I_S c_1(I_S c_2 - 1) + \frac{1}{2}(I_S c_2 + I_S c_1) s_{2J})</td>
</tr>
<tr>
<td>(I_S c_2)</td>
<td>(\frac{1}{2}I_S c_1(I_S c_2 + 1) - \frac{1}{2}I_S c_1(I_S c_2 - 1) + \frac{1}{2}(I_S c_2 + I_S c_1) s_{2J})</td>
</tr>
<tr>
<td>(I_S c_2)</td>
<td>(\frac{1}{2}I_S c_1(I_S c_2 + 1) - \frac{1}{2}I_S c_1(I_S c_2 - 1) + \frac{1}{2}(I_S c_2 + I_S c_1) s_{2J})</td>
</tr>
<tr>
<td>(I_S c_2)</td>
<td>(\frac{1}{2}I_S c_1(I_S c_2 + 1) - \frac{1}{2}I_S c_1(I_S c_2 - 1) + \frac{1}{2}(I_S c_2 + I_S c_1) s_{2J})</td>
</tr>
<tr>
<td>(I_S c_2)</td>
<td>(\frac{1}{2}I_S c_1(I_S c_2 + 1) - \frac{1}{2}I_S c_1(I_S c_2 - 1) + \frac{1}{2}(I_S c_2 + I_S c_1) s_{2J})</td>
</tr>
</tbody>
</table>

is obtained. For the remainder, the same procedure is applied and the obtained results are presented in Table 3. The calculations are made only for the diagonal and upper terms of Table 1. Because of the symmetry, the evolutions for the lower terms can be written easily from the evolutions of the upper terms. As an example, evolution for \(I_S S_y^2\) as given in Table 2 is

\[
I_S S_y^2 \mapsto \frac{1}{2}I_S S_y^2(c_{2J} + 1) - \frac{1}{2}I_S S_y^2(c_{2J} - 1) + \frac{1}{2}(I_S S_y - I_S S_y) s_{2J}. \quad (17)
\]

Then, the evolution for \(I_S^2 S_y\) will be

\[
I_S^2 S_y \mapsto \frac{1}{2}I_S^2 S_y(c_{2J} + 1) - \frac{1}{2}I_S^2 S_y(c_{2J} - 1) + \frac{1}{2}(I_S S_y - I_S S_y) s_{2J}. \quad (18)
\]

4. 3D HMQC-COSY NMR Experiment for \(I_S S_y S'_y\) Multi-Spin Systems

For the analytical description of the 3D HMQC-COSY NMR experiment of \(I_S S_y S'_y\) multi-spin systems, the pulse sequence given in Figure 1 is used. As shown in this figure, the density matrix operator at each stage of the experiment is labelled with numbers where \(^{13}\)C is treated as spins \(I, I'\) and \(^{2}\)H as spins \(S, S'\).

In this pulse sequence, \(\tau\) is the evolution delay for hetero-nuclei and its optimum value is \(1/(2J_{IS})\). \(t_1\) is the chemical shift delay for both spins \(I\) and \(I'\). \(t_2\) is the homonuclear weak spin-spin coupling and chemical shift delay for both spins-\(S\) and \(S'\). \(t_3\) is the acquisition time for both spins \(S\) and \(S'\) along the x-axis. During the \(t_2\) and \(t_3\) homonuclear weak spin-spin coupling between \(S\) and \(S'\) takes place. Starting from the density matrix operator at thermal equilibrium, one should apply the required Hamiltonians during the pulse sequence and obtain the density matrix operator at the end of the experiment. For this experiment following r.f. pulse, chemical shift, and spin-spin coupling Hamiltonians are applied:

\[
\mathcal{H}_{rf}(I, I') = \omega_{rf} I \varphi + \omega_{rf} I' \varphi, \quad (\varphi = x, y) \quad (19)
\]

\[
\mathcal{H}_{rf}(S, S') = \omega_{rf} S \varphi + \omega_{rf} S' \varphi, \quad (\varphi = x, y) \quad (20)
\]

\[
\mathcal{H}_I(I, I') = \Omega I_z + \Omega I' z, \quad (21)
\]

\[
\mathcal{H}_C(S, S') = \Omega_S S_z + \Omega_S S'_z, \quad (22)
\]

\[
\mathcal{H}_{J}(I - S, I' - S') = 2\pi J_{IIS} I_z S_z + 2\pi J_{I'IS'} I'_z S'_z, \quad (J_{IS} = J_{I'S'}) \quad (23)
\]
For multi-spin systems, to follow these processes (applications of required Hamiltonians during the pulse sequence) by hand becomes too difficult. In order to overcome this problem a computer program was written in Mathematica for this study [27]. This program is used to obtain the density matrix operator at the end of the experiment for different multi-spin systems.

For IS'S' multi-spin system, the density matrix at thermal equilibrium is \( \sigma_0 = S_+ S'_- \). By using the computer program following density matrices are obtained for each labelled point:

\[
\begin{align*}
\sigma_0^{90_\circ(S,S')} &= -S_- S'_+ \equiv \sigma_1, \\
\sigma_1 &= \frac{\mathcal{H}_I(S{-}S') + \mathcal{H}_I'(S{-}S')}{2 J_I S_+ + 2J'_I S'_+}, \quad \text{where } \tau = 1/(2J_S), \\
\sigma_2^{90_\circ(I,F)} &= -2J_I S_- - 2J'_I S'_-, \\
\sigma_2 &= \frac{\mathcal{H}_C(I,F) + \mathcal{H}_C(I,F)}{2 I, S_+ - 2J'_I, S'_+}, \\
\sigma_6^{90_\circ(I,F)} &= -2J_I S_- \cos[\Omega t_I] + 2J_I S_+ \sin[\Omega t_I], \\
-2J'_I S'_- \cos[\Omega t'_I] + 2J'_I S'_+ \sin[\Omega t'_I], \\
\sigma_7 &= \frac{\mathcal{H}_I(S{-}S') + \mathcal{H}_I(S{-}S')}{2J_I S_- + 2J'_I S'_-}, \\
- S_- \cos[\Omega t_I] + 2J_I S_+ \sin[\Omega t_I], \\
- S'_- \cos[\Omega t'_I] + 2J'_I S'_+ \sin[\Omega t'_I], \\
\sigma_1 = \frac{\mathcal{H}_I(S{-}S') + \mathcal{H}_I(S{-}S')}{2 J_I S_+ + 2 J'_I S'_+}, \\
\sigma_10^{90_\circ(S,S')} &= -S_+ S'_- \equiv \sigma_{11}, \\
\mathcal{H}_I(S{-}S') &= 2\pi J_{SS'} S_+ S'_-.
\end{align*}
\]

Fig. 1. 3D HMQC-COBY NMR pulse sequence [23, 24].

In the last step, the density matrix consists of many product operator terms. So, for the simplification of the density matrix only the observable terms should be taken into account. As the acquisition is taken along the x-axes for spins-S and S', at the end of the experiment the following density matrix is obtained:

\[
\begin{align*}
\sigma_{11} &= \frac{1}{2} (2S_+ - S_+ S'_- - S_+ S'_-) c_I(t_1) c_S(t_2) s_S(t_3) \\
+ \frac{1}{2} (2S'_+ - S'_+ S'_- - S'_+ S'_-) c_I'(t_1) c'_S(t_2) s'_S(t_3) \\
+ \frac{1}{2} (S_+ S'_- + S_+ S'_-) c_{IJ}(t_2) c_I(t_1) c_S(t_2) s_S(t_3) \\
+ \frac{1}{2} (S'_+ S'_- - S'_+ S'_-) c_{IJ}(t_2) c'_I(t_1) c'_S(t_2) s'_S(t_3) \\
- \frac{1}{2} (S_+ S'_- - S_+ S'_-) (1 - c_{IJ}(t_2)) c_I(t_1) c'_I(t_1) c'_S(t_2) s'_S(t_3) \\
- \frac{1}{2} (S'_+ S'_- - S'_+ S'_-) (1 - c_{IJ}(t_2)) c_I(t_1) c'_I(t_1) c'_S(t_2) s'_S(t_3) \\
+ \frac{1}{2} (S_+ S'_- + S_+ S'_-) c_{IJ}(t_2) c_I(t_1) c'_S(t_1) s'_S(t_3) \\
+ \frac{1}{2} (S'_+ S'_- + S_+ S'_-) c_{IJ}(t_2) c'_I(t_1) c_S(t_1) s_S(t_3) \\
+ \frac{1}{2} (S_+ S'_- + S_+ S'_-) c_{IJ}(t_2) c_I(t_1) c'_S(t_1) s'_S(t_3) \\
+ \frac{1}{2} (S'_+ S'_- + S_+ S'_-) c_{IJ}(t_2) c'_I(t_1) c_S(t_1) s_S(t_3)
\end{align*}
\]

At above and in following equations, \( c_I(t_1) = \cos[\Omega t_I], \ c'_I(t_1) = \cos[\Omega t'_I], \ c_S(t_2) = \cos[\Omega t_S], \ c'_S(t_2) = \cos[\Omega t'_S], \ c_{IS}(t_3) = \cos[\Omega_{IS} t_3], \ c_{IS}(t_3) = \cos[\Omega_{IS} t_3], \ s_S(t_3) = \sin[\Omega t_S], \ s'_S(t_3) = \sin[\Omega t'_S], \ c_{IS}(t_2) = \cos[\pi J_{IS}], \ s_{IS}(t_2) = \sin[\pi J_{IS}], \ c_{IS}(t_3) = \cos[\pi J_{IS}], \ s_{IS}(t_3) = \sin[\pi J_{IS}]. \)

For IS'IS'' multi-spin systems the ensemble averaged expectation value of the spin angular momentum, \( \sum_{i=1}^{n} S_{ix} + \sum_{j=1}^{m} S'_{ix} \), is proportional to the magni-
Table 4. Results of the $\sum_{m=1}^{n} \text{Tr}[S_{m}O]$ calculations for the observable product operators of $ISf'S_{m}'$ multi-spin systems ($k = x, y, z; I = x, y, z; o = x, y, z$).

<table>
<thead>
<tr>
<th>Spin System</th>
<th>Product Operator ($O$)</th>
<th>$\sum_{m=1}^{n} \text{Tr}[S_{m}O]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t}$</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}'$</td>
<td>16</td>
</tr>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t} + S_{t}$</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>$S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}')$</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}S_{t}S_{t}' + S_{t}S_{t}S_{t}S_{t}'$</td>
<td>64</td>
</tr>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t} + S_{t}$</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>$S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}')$</td>
<td>1296</td>
</tr>
<tr>
<td></td>
<td>$S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}')$</td>
<td>1296</td>
</tr>
<tr>
<td></td>
<td>$S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}')$</td>
<td>1296</td>
</tr>
<tr>
<td></td>
<td>$S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}') + S_{t}(S_{t} + S_{t}')$</td>
<td>1296</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}S_{t}S_{t}' + S_{t}S_{t}S_{t}S_{t}'$</td>
<td>1296</td>
</tr>
</tbody>
</table>

Table 5. Results of the $\sum_{m=1}^{n} \text{Tr}[S_{m}'O]$ calculations for the observable product operators of $ISf'S_{m}'$ multi-spin systems ($k = x, y, z; I = x, y, z; o = x, y, z$).

<table>
<thead>
<tr>
<th>Spin System</th>
<th>Product Operator ($O'$)</th>
<th>$\sum_{j=1}^{m} \text{Tr}[S_{j}'O]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t}'$</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}'$</td>
<td>16</td>
</tr>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t}' + S_{t}'$</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>$(S_{t} + S_{t}')S_{t}'$</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}S_{t}'$</td>
<td>32</td>
</tr>
<tr>
<td>$ISf'S'$</td>
<td>$S_{t}'$</td>
<td>216</td>
</tr>
<tr>
<td></td>
<td>$(S_{t} + S_{t}')S_{t}'$</td>
<td>432</td>
</tr>
<tr>
<td></td>
<td>$(S_{t}S_{t}S_{t} + S_{t}S_{t})S_{t}'$</td>
<td>288</td>
</tr>
<tr>
<td></td>
<td>$S_{t}S_{t}S_{t}S_{t}'$</td>
<td>64</td>
</tr>
</tbody>
</table>

The saturation of the $x$-magnetization at any time during the experiment. So, the magnetization of 3D HMBC-COSY NMR experiment can be written as following:

$$M_{r}(t_{1}, t_{2}, t_{3}) \propto \sum_{i=1}^{n} \langle S_{i}\rangle + \sum_{j=1}^{m} \langle S_{j}' \rangle$$

$$= \sum_{i=1}^{n} \text{Tr}[S_{i}O_{11}] + \sum_{j=1}^{m} \text{Tr}[S_{j}'O_{11}].$$

Now it is necessary to obtain the $\sum_{i=1}^{n} \text{Tr}[S_{i}O]$ and $\sum_{j=1}^{m} \text{Tr}[S_{j}'O]$ values of the observable product operators indicated by $O$ and $O'$. The $\sum_{i=1}^{n} \text{Tr}[S_{i}O]$ and $\sum_{j=1}^{m} \text{Tr}[S_{j}'O]$ values are calculated by a computer program in Mathematica and the results for several multi-spin systems are given in Table 4 and Table 5, respectively. For example, the trace value for the observable product operator $S_{t}$ of $ISf'S'$ multi-spin systems is calculated as following:

$$\text{Tr}[S_{t}O] = \text{Tr}[S_{t}S_{t}] =$$

$$\text{Tr}[(E_{1} \otimes S_{t} \otimes E_{f}' \otimes E_{s}')(E_{1} \otimes S_{t} \otimes E_{f}' \otimes E_{s}')] = 24.$$

By using Table 4 and Table 5,

$$\langle S_{t} \rangle + \langle S_{t}' \rangle = \left\{ \begin{array}{ll} 8c_{2f}(t_{2}) + 8c_{2f}(t_{3}) & \text{if } c_{1}(t_{1})c_{5}(t_{2})s_{5}(t_{3}) + 8c_{2f}(t_{2})c_{2f}(t_{3}) \\ + 16c_{2f}(t_{2})c_{2f}(t_{3})c_{1}(t_{1})c_{5}(t_{2})s_{5}(t_{3}) & \text{if } c_{1}(t_{1})c_{5}(t_{2})s_{5}(t_{3}) + 16c_{2f}(t_{2})c_{2f}(t_{3})c_{1}(t_{1})c_{5}(t_{2})s_{5}(t_{3}) \end{array} \right.$$
signals will be in one plane. In this 3D HMQC-COSY NMR experiment these signals will be observed in two planes of $\Omega_1$ and $\Omega'_2$ frequencies in F1 dimension as shown in Figure 2. In this Figure 2D-2D correlations are shown in $F_2-F_3$ planes. Chemical shifts of $^{13}$C are in different planes. Intensity distributions for the diagonal peaks (1:2:1:2:0:2:1:2:0) and for the cross peaks (1:0:−1:0:0:0:−1:0:1) in two planes are in exact agreement with results predicted by Chandrakumar for COSY experiment [10].

For $I_S^1I_S^2$ multi-spin system, the density matrix at thermal equilibrium is $\sigma_0 = S_{1z} + S_{2z} + S'_y$. By using the computer program following density matrices are obtained for each labelled point:

$$\sigma_0 \xrightarrow{90^\circ(S_1, S_S, S'_y)} -S_{1y} - S_{2y} - S'_y \equiv \sigma_1,$$

(36)

$$\sigma_1 \xrightarrow{\mathcal{H}_{1z}(t-S_1)t+\mathcal{H}_{2z}(t-S_2)t+\mathcal{H}'_{1y}(t-S'_y)t} 2I_tS_{1x} + 2I'_tS_{2x} + 2I'_tS'_y,$$

(37)

$$\sigma_2 \xrightarrow{90^\circ(t,t')} -2I_tS_{1x} - 2I'_tS_{2x} - 2I'_tS'_y,$$

(38)

$$\sigma_3 \xrightarrow{\mathcal{H}_{c}(t,t')I_{1t}+180^\circ(S_1, S_S, S'_y)} -2I_tS_{1x}\cos[\Omega t t_1] + 2I'_tS_{1x}\sin[\Omega t t_1]$$

$$-2I_tS_{2x}\cos[\Omega t t_1] + 2I'_tS_{2x}\sin[\Omega t t_1]$$

(39)

$$-2I'_tS'_y\cos[\Omega t t_1] + 2I'_tS'_y\sin[\Omega t t_1].$$

As one can guess, after this step product operator calculations of $I_S^2I_S^2$ multi-spin system will be more complicated than those of $I_S^1I_S'$ multi-spin system. By using the trace values of the observable product operators in Table 4 and 5 we obtain following expression for the magnetization at the end of the experiment:

$$\sum_{i=1}^2 \langle S_{i\alpha} \rangle = \left\{ \begin{array}{l}
48c_{2j}(t_2) + 48c_{2j}(t_3) \\
+48c_{2j}(t_2)c_{2j}(t_3)
\end{array} \right\} c_{I_1}(t_1)c_{S}(t_2)sS(t_3)
+ \left\{ \begin{array}{l}
32s_{2j}(t_2)s_{2j}(t_3) \\
+64s_{2j}(t_2)s_{2j}(t_3)c_{2j}(t_3)
\end{array} \right\} c_{I_1}(t_1)c_{S}(t_2)s'_S(t_3)
+ \left\{ \begin{array}{l}
32s_{2j}(t_2)s_{2j}(t_3) \\
+64s_{2j}(t_2)c_{2j}(t_2)s_{2j}(t_3)
\end{array} \right\} c'_{I_1}(t_1)c'_{S}(t_2)sS(t_3)
+ \left\{ \begin{array}{l}
8c_{2j}^2(t_2) + 16c_{2j}c_{2j}(t_3) \\
+16c_{2j}c_{2j}(t_2)c_{2j}(t_3) + 8c_{2j}^2(t_3)
\end{array} \right\} c'_{I_1}(t_1)c'_{S}(t_2)s'_S(t_3)
+ \left\{ \begin{array}{l}
16c_{2j}^2(t_2)c_{2j}(t_3) + 8c_{2j}^2(t_3)
\end{array} \right\} c'_{I_1}(t_1)c'_{S}(t_2)s'_S(t_3).$$

(40)

This equation is also divided into four parts which represent the FID values of 8, 8 and 25 signals for 3D HMQC-COSY NMR experiment. The signal coordinates and intensity distribution of the expected 3D HMQC-COSY NMR spectrum are presented in Fig. 3 for $I_S^1I_S^2$ multi-spin system. 3D spectrum will be observed in two planes for $\Omega_1$ and $\Omega'_2$ frequencies in F1 dimension as indicated in this figure.
3D HMQC-COSY NMR experiment. The signal coordinates and intensity distribution of the expected 3D HMQC-COSY NMR spectrum are shown in Fig. 4 for the $IS_1S'_2$ multi-spin system. Again 3D spectrum will be observed in two planes for $\Omega_t$ and $\Omega'_t$ frequencies in F1 dimension. The calculations for the other multi-spin systems such as $IS_2S'_1$ and $IS_3S'_2$, can be also made.

5. Conclusion

As a result, a complete product operator theory for $IS (I = 1, S = 1)$ spin system has been presented and applied. For this spin system, first the evolutions of all the product operators under the spin-spin coupling Hamiltonian were obtained. This is the first complete presentation of product operator theory for this spin system in the literature. Therefore, it will be useful for the future studies on product operator theory and pulse NMR experiments. For example theoretical results found here can be used for the confirmation of experimental results in some pulse NMR experiments. Then, as an application and a verification, the product operator description of 3D HMQC-COSY NMR experiment was obtained for $IS_nI'S'_m (I = I' = 1/2; S = S' = 1; n = 1,2,3; m = 1,2)$ multi-spin systems. The spectra of 3D HMQC-COSY NMR experiment contain 2D-2D correlations in $F_2-F_3$ planes. Also the chemical shifts of different $CD_n$ groups will be in different planes. By presenting the estimated spectra of $IS_nI'S'_m$ groups, it is shown that NMR experiment can be used for the spectral assignments of $CD_nCD_m$ groups in complex liquids.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Schematic signal coordinates and intensity distributions of the 3D HMQC-COSY NMR spectrum for the $IS_2S'_1$ multi-spin system.}
\end{figure}

For the $IS_2S'_1$ multi-spin system, the FID values of 3D HMQC-COSY NMR experiment are obtained applying the same procedure as above. At the end of the experiment following FID values are obtained:

$$\sum_{i=1}^{3} \langle S_{ix} \rangle + \langle S'_{ix} \rangle = $$

\[
\begin{cases}
216c_2f(t_2) \\
+ 216c_2f(t_5) \\
+ 192c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
216c_2f(t_2) \\
+ 192c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
216c_2f(t_2) \\
+ 192c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
8c_2f(t_2) + 8c_2f(t_5) + 24c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
+ 24c_2f(t_2)c_2f(t_3) + 24c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
+ 24c_2f(t_2)c_2f(t_3) + 8c_2f(t_2)c_2f(t_5)
\end{cases}
\begin{cases}
+ 24c_2f(t_2)c_2f(t_3) + 24c_2f(t_2)c_2f(t_3)
\end{cases}
\begin{cases}
+ 24c_2f(t_2)c_2f(t_3) + 24c_2f(t_2)c_2f(t_3)
\end{cases}
\begin{cases}
+ 24c_2f(t_2)c_2f(t_3)
\end{cases}
\begin{cases}
\cdot c_1(t_1)c_2(t_2)c_2(t_5)
\end{cases}

This equation is also divided into four parts which represents the FID values of 8, 12, 12 and 49 signals for 3D HMQC-COSY NMR experiment. The signal coordinates and intensity distribution of the expected 3D HMQC-COSY NMR spectrum are obtained applying the same procedure as above. At the end of the experiment following FID values are obtained:

\[
\begin{array}{cccccc}
-1 & 0 & 1 & 1 & 4 & 6 & 4 & 1 \\
-1 & 0 & 1 & 4 & 8 & 8 & 4 \\
0 & 0 & 0 & 6 & 8 & 20 & 8 & 6 \\
1 & 0 & -1 & 4 & 8 & 8 & 4 \\
1 & 0 & -1 & 1 & 4 & 6 & 4 & 1 \\
\end{array}
\]

\[
\begin{array}{cccccc}
1 & 2 & 1 & -1 & -1 & 0 & 1 & 1 \\
2 & 0 & 2 & 0 & 0 & 0 & 0 & 0 \\
1 & 2 & 1 & 1 & 1 & 0 & -1 & -1 \\
\end{array}
\]

\[
\begin{array}{cccc}
\omega_t & -4\pi/ & -2\pi/ & -\omega'_t & 2\pi/ & 4\pi/ \\
\omega'_t & -2\pi/ & -\omega'_t & -2\pi/ & -4\pi/ \\
\omega_s & -2\pi/ & -\omega_s & -2\pi/ \\
\end{array}
\]
Appendix: Some New Relations between the Angular Momentum Operators for Spin-1

\[
\begin{align*}
S_x S_y &= \frac{1}{2} (S_z + i [S_x, S_y]_+) \\
S_x S_y &= \frac{1}{2} (S_z - i [S_x, S_y]_+) \\
S_y S_z &= \frac{1}{2} (S_z + i [S_x, S_y]_+) \\
(S_x^2 - S_y^2) S_z &= -i [S_x, S_y]_+ \\
[S_x, S_y]_+ &= -i (S_x^2 - S_y^2) \\
S_x S_z &= \frac{1}{2} ([S_x, S_z]_+ + i S_y) \\
S_y S_z &= \frac{1}{2} ([S_y, S_z]_+ - i S_x) \\
S_x S_y &= \frac{1}{2} ([S_x, S_y]_+ + i S_z) \\
S_y S_x &= \frac{1}{2} ([S_y, S_x]_+ - i S_z) \\
[S_y, S_z]_+ &= \frac{1}{2} (S_y - i [S_x, S_z]_+) \\
[S_x, S_z]_+ &= \frac{1}{2} (S_x + i [S_y, S_z]_+) \\
[S_y, S_x]_+ &= \frac{1}{2} (S_y + i [S_x, S_z]_+) \\
[S_x, S_y]_+ &= \frac{1}{2} (S_x - i [S_y, S_z]_+) \\
[S_y, S_x]_+ &= \frac{1}{2} (S_y - i [S_x, S_z]_+)
\end{align*}
\]