Visualizing Coherence Transfers in NMR Experiments
Density Vector Model for the Visualization of NMR Pulse Sequences
Huldrych Egli
Summary

The Density Vector Model Computer Program is available for Windows™ computers. Many scientists however use computers running the IOS™ operating systems. Although the calculations carried out by the DVM program use the Density Matrix Formalism and complex matrix algebra it is possible to derive equations yielding the same vectors as they are found in the matrix elements of the density matrix. These equations are suitable for calculations in an Excel™ spreadsheet and results can be displayed in diagrams in a way resembling the vector diagrams shown in the DVM computer program. Since Excel™ runs on Windows™ and IOS™ computers a spreadsheet has been created for the DVM. A selection of 10 pulse sequences demonstrates various ways of coherence transfers which can be viewed and visualized as density vectors. The density vectors extend the classical vector model for nmr to all coherences. The DVM computer program handles spin systems consisting of up to five atoms but the DVM spreadsheet is actually dealing with only two coupled nuclei. This is often good enough to enlighten the processes involved in pulse sequences but also may motivate scientists to raise their interest in the original DVM computer program.

In chapter 1 possible coherence transfers involving a $^1$H atom coupled to a $^{13}$C atom are shown. For every step in the pulse sequence, leading from the initial pulse applied to $^1$H via a time delay $\tau = 1/(2\times J)$ to the mixing pulse $\beta$, density vector diagrams are visualizing effects for sequences 1 and 6. For scientists familiar with the Product Operator Formalism the procedure of the DVM is explained using notations of the Product Operator Formalism. For a second pair of sequences 5 and 6 the density vector diagrams demonstrate how coherence is transferred if simultaneous pulses are applied to $^1$H and $^{13}$C.

In chapter 2 the effects of the sender phase are visualized by means of the DVM computer program and the pathways of density vectors associated with SQ, ZQ and DQ coherences are explained by viewing phase effects step by step. In addition the influence of the size of the spin systems is pictured by means of the DVM for the multiple quantum coherences if mixing pulses $\beta_x$ and $\beta_y$ are applied to the two atoms.

The spreadsheet for the calculation of the density vectors is available for free on www.eglinmr.com/wordpress.
Chapter 1: Typical examples of coherence transfers

The Density Vector Model (DVM) is a vector model used in NMR spectroscopy for the calculation of magnetizations vectors. The classical vector model is limited to the transverse magnetization. The DVM calculates vectors for transverse magnetizations of single quantum coherences and also extends the classical model to the vectors of zero and double quantum coherences. Ten model sequences 1 to 10 are presented below in this document in order to demonstrate the most important examples of coherence transfers. For each sequence equations have been derived by means of the DVM program. The equations are used in an Excel™ spreadsheet with the intention to let readers play with the vectors in a way close to the options offered by the DVM program.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Initial pulse</th>
<th>Mixing pulse</th>
<th>Atom 1</th>
<th>Atom 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\alpha_1 x$</td>
<td>$\beta_2 x$</td>
<td>active</td>
<td>passive</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha_2 x$</td>
<td>$\beta_1 x$</td>
<td>passive</td>
<td>active</td>
</tr>
<tr>
<td>3</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_2 x$</td>
<td>active</td>
<td>active</td>
</tr>
<tr>
<td>4</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_1 x$</td>
<td>active</td>
<td>active</td>
</tr>
<tr>
<td>5</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_1 x$, $\beta_2 x$</td>
<td>active</td>
<td>active</td>
</tr>
<tr>
<td>6</td>
<td>$\alpha_1 x$</td>
<td>$\beta_2 y$</td>
<td>active</td>
<td>passive</td>
</tr>
<tr>
<td>7</td>
<td>$\alpha_2 x$</td>
<td>$\beta_1 y$</td>
<td>passive</td>
<td>active</td>
</tr>
<tr>
<td>8</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_2 y$</td>
<td>active</td>
<td>active</td>
</tr>
<tr>
<td>9</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_1 y$</td>
<td>active</td>
<td>active</td>
</tr>
<tr>
<td>10</td>
<td>$\alpha_1 x$, $\alpha_2 x$</td>
<td>$\beta_1 y$, $\beta_2 y$</td>
<td>active</td>
<td>active</td>
</tr>
</tbody>
</table>

Table 1: Ten selected pulse sequences leading to coherence transfers. Between the initial pulse and the mixing pulse a delay of $\tau = 1/(2*J)$ leads to an antiphase arrangement of the transverse magnetizations.

Parameters

Resonance frequencies: $\nu(1) = 111$ Hz, $\nu(2) = 888$ Hz
Coupling constant: $J(1,2) = 120$ Hz

Atom 1 = $^1$H, initial density vector $I_z(1) = 4$
Atom 2 = $^{13}$C, initial density vector $I_z(2) = 1$

Comparing pulse sequences

Pulse sequence 1 is compared to pulse sequence 6 and pulse sequence 5 to sequence number 10 as given in table 1. The first two sequences start with an excitation pulse $\alpha_x$ applied to atom 1 and after a time delay of $\tau = 1/(2*J)$ coherence transfers are produced by mixing pulses to atom 2.

A second comparison of pulse sequences 5 and 10 is carried out with sequences in which simultaneous pulses $\alpha$ and $\beta$ are applied to both atoms.

The comparisons are carried out for a hetereonuclear two spin system. Calculations referring to rising and lowering operators are performed following the way described in the literature dealing with the Product Operator Formalism\(^1\). The goal is a correlation of the density vector model with the Product Operator Formalism.

\(^1\) Chapter 6 "Product Operators" © James Keeler, 1998 & 2002
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Correlation of DVM with Product Operator Formalism

During the time delay $\tau$ the transverse magnetization of the excited atom 1 evolves to an antiphase arrangement of the doublet spectrum of atom 1. The Product Operators of sequences 1 and 6 are given by the notations $2I_1xI_2z$, $2I_1yI_2z$. Atom 1 is the active spin and atom 2 the passive spin. Correlations for all possible combinations of Product Operators are presented in a blog on eglinmr.com/wordpress$^2$. This publication also shows how Product Operators change with coherence transfers induced by the mixing pulses. For sequences 1 and 6 the Product Operators are $2I_1xI_2x$, $2I_1xI_2y$, $2I_1yI_2x$ and $2I_1yI_2y$ as given in table 2 for sequence 1 and in table 3 for sequence 6.

**Sequence 1: $\alpha_1x - \tau - \beta_2x$**

<table>
<thead>
<tr>
<th>Initial pulses</th>
<th>$\alpha_1x$</th>
<th>$90^\circ$</th>
<th>$\alpha_2x$</th>
<th>$0^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_1 = 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho_2 = 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>0.00417</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixing pulses</th>
<th>$\beta_1x$</th>
<th>$0^\circ$</th>
<th>$\beta_2x$</th>
<th>$90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_+ / I_-$ Op</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I^+1B_2x$</td>
<td>$I^+1x$</td>
<td>$I^+1y$</td>
<td>SQ(1)</td>
<td>0.00</td>
</tr>
<tr>
<td>$I^-1B_2x$</td>
<td>$I^-1x$</td>
<td>$I^-1y$</td>
<td>SQ(1)</td>
<td>0.00</td>
</tr>
<tr>
<td>$I^+2B_2x$</td>
<td>$I^+2x$</td>
<td>$I^+2y$</td>
<td>SQ(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>$I^-2B_2x$</td>
<td>$I^-2x$</td>
<td>$I^-2y$</td>
<td>SQ(2)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MQ</th>
<th>$I_+ / I_-$ Operators</th>
<th>Product Operators</th>
<th>DVM $I_+x$</th>
<th>DVM $I_+y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DQ$x$</td>
<td>$\frac{1}{2}(I^+1x + I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y + I^-1y)$</td>
<td>3.89</td>
<td>2</td>
</tr>
<tr>
<td>DQ$y$</td>
<td>$\frac{1}{2}(I^+1x - I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y - I^-1y)$</td>
<td>-0.92</td>
<td>2</td>
</tr>
<tr>
<td>ZQ$x$</td>
<td>$\frac{1}{2}(I^+1x + I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y + I^-1y)$</td>
<td>-3.89</td>
<td>0</td>
</tr>
<tr>
<td>ZQ$y$</td>
<td>$\frac{1}{2}(I^+1x - I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y - I^-1y)$</td>
<td>0.93</td>
<td>0</td>
</tr>
<tr>
<td>ZQ$x$</td>
<td>$\frac{1}{2}(I^+1x + I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y + I^-1y)$</td>
<td>-3.89</td>
<td>0</td>
</tr>
<tr>
<td>ZQ$y$</td>
<td>$\frac{1}{2}(I^+1x - I^-1x)$</td>
<td>$\frac{1}{2}(I^+1y - I^-1y)$</td>
<td>0.93</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2: Correlation of Product Operators to Density vectors $I^+$, $I^-$ of SQ coherences and $ZQ$, $DQ$ of multiple quantum coherences (MQ) for sequence 1.

In Figure 1 the rising and lowering operators $I^+$ and $I^-$ are expressed by the density vectors $I_x$ and $I_y$. The vector diagram in the Excel™ spreadsheet corresponds to the

$^2$ Density Vector Model and Product Operator Formalism, Huldrych Egli 2018 to be published in eglinmr.com/wordpress
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representation given in the DVM computer program³ for the visualization of magnetizations and population differences by density vectors. Similar vector diagrams are presented for coherences created by the mixing pulses in Figure 2.

Equations for the calculation of $I^\tau(\tau)$ and $I(\tau)$ vectors

Initial parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{1x}$</td>
<td>4 if initial pulse $\alpha_{1x} = 90^\circ$</td>
</tr>
<tr>
<td>$I_{1y}$</td>
<td>0 if initial pulse $\alpha_{1x} = 90^\circ$</td>
</tr>
</tbody>
</table>

With $\omega_{01}$ = resonance frequency atom 1

$$\omega_{1}^+ = \omega_{01} + J_{1,2}$$
$$\omega_{1}^- = \omega_{01} - J_{1,2}$$

$$I_{1x}^+ = I_{1x} \times \cos(\omega_{1}^+ \tau)$$ (1)

$$I_{1y}^+ = I_{1y} \times \sin(\omega_{1}^+ \tau)$$ (2)

$$I_{1x}^- = I_{1x} \times \cos(\omega_{1}^- \tau)$$ (3)

$$I_{1y}^- = I_{1y} \times \sin(\omega_{1}^- \tau)$$ (4)

The vectors in Figure 1 are calculated by equations describing the rising $I^+$ and lowering $I^-$ vectors and correspond to the classical vectors. The classical vector model follows the mathematical rules for rotating vectors in the x,y-plane:

$$I_{1x}^+(\tau) = I_{1x} \times \cos(\omega_{1}^+ \tau) + I_{1y} \times \sin(\omega_{1}^+ \tau)$$

$$I_{1x}^-(\tau) = I_{1y} \times \cos(\omega_{1}^- \tau) + I_{1x} \times \sin(\omega_{1}^- \tau)$$

Figure 1: Transverse magnetizations $I_{1x}^+(\tau)$ (blue) and $I_{1x}^-(\tau)$ (red) in antiphase arrangement of density vectors belonging to doublet signals of nmr spectrum of atom 1 with $I_{1z} = 4$.

Equations for the calculation of SQ($\beta_{2x}$) vectors

$I^\tau_1$ and $I_1$ of SQ(1) of Atom 1

$$I_{1x}^+_{\beta_{2x}} = I_{1x}^+ \times \cos(\beta_{2x})$$ (5)

$$I_{1y}^+_{\beta_{2x}} = I_{1y}^+ \times \cos(\beta_{2x})$$ (6)

$$I_{1x}^-_{\beta_{2x}} = I_{1x}^- \times \cos(\beta_{2x})$$ (7)

$$I_{1y}^-_{\beta_{2x}} = I_{1y}^- \times \cos(\beta_{2x})$$ (8)

³ DVM computer program, Huldrych Egli, eglinmr.com/wordpress
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$I''_2$ and $I'_2$ of SQ(2) of Atom 2

Initial parameters

\[
\begin{align*}
I'_{2x} &= 1 \text{ if initial pulse } \beta_{2x} = 90° \\
I'_{2y} &= 0 \text{ if initial pulse } \beta_{2x} = 90° \\
\end{align*}
\]

With $\omega_{02} = \text{resonance frequency atom } i$

\[
\begin{align*}
\omega_{21}^+ &= \omega_{02} + J_{1,2} \\
\omega_{21}^- &= \omega_{02} - J_{1,2} \\
\end{align*}
\]

\[
\begin{align*}
I''_{2x}(\beta_{2x}) &= I_{2x} * \sin(\beta_{2x}) \\
I''_{2y}(\beta_{2x}) &= I_{2y} * \sin(\beta_{2x}) \\
I'_{2x}(\beta_{2x}) &= I_{2x} * \sin(\beta_{2x}) \\
I'_{2y}(\beta_{2x}) &= I_{2y} * \sin(\beta_{2x}) \\
\end{align*}
\]

Figure 2: Right: Vectors of multiple quantum coherence $DQ$ (blue) and $ZQ$ (red). The intensity of the SQ vectors $I'^1$ and $I'^1$ is transferred to the multiple quantum coherences. Left: Density vectors $I''^2$ and $I''^2$ as a result of the $\beta_{2x}$ pulse.

With sequence 1 the density vectors $I'^1$ and $I'^1$ can be transformed into the $DQ$ and $ZQ$ vectors by a rotation of 90° about the z-axis. The equations (13) – (16) are describing the coherence transfer from single quantum coherences to multiple quantum coherences.

Equations for the calculation of $DQ(\beta_{2x})$ and $ZQ(\beta_{2x})$ vectors

\[
\begin{align*}
DQ_x &= I'^1_y(\tau) * \sin(\beta_{2x}) \\
DQ_y &= I'^1_x(\tau) * \sin(\beta_{2x}) \\
ZQ_x &= I'^1_y(\tau) * \sin(\beta_{2x}) \\
ZQ_y &= I'^1_x(\tau) * \sin(\beta_{2x}) \\
\end{align*}
\]
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The equations 1-16 are applicable also for the case of initial parameters $I_{1x} = 1$ and $I_{1y} = 0$ if initial pulse $\alpha_{1x} = 90^\circ$. As a rule the active spin is with atom 1 and the initial pulse is $\alpha_{1x}$ which is applied to atom 1.

Sequence 6: $\alpha_{1x} - \tau - \beta_{2y}$

<table>
<thead>
<tr>
<th>Sequence</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pulses</td>
<td>$\alpha_{1x}$</td>
</tr>
<tr>
<td>$\beta_{1y}$</td>
<td>90°</td>
</tr>
<tr>
<td>$\beta_{2y}$</td>
<td>90°</td>
</tr>
<tr>
<td>$\phi_1 = 1$</td>
<td>$I_{1x}$</td>
</tr>
<tr>
<td>$\phi_2 = 1$</td>
<td>$I_{1y}$</td>
</tr>
</tbody>
</table>

Table 3: Correlation of Product Operators with density vectors $I^+, I^-$ of SQ coherences and $ZQ, DQ$ of multiple quantum coherences (MQ) for sequence 6.

The equations (1) – (4) for the calculation of $I^+(\tau)$ and $I^-(\tau)$ do also apply for sequence 6. The effects of the mixing pulse $\beta_{2y}$ is described by the equations given below.

Equations for the calculation of SQ($\beta_{2y}$) vectors

$I^+, I^-$ of SQ(1) of Atom 1

\[
\begin{align*}
I^+_{1x}(\beta_{2y}) &= I^+_{1x}(\tau) \times \cos(\beta_{2y}) \quad (17) \\
I^+_{1y}(\beta_{2y}) &= I^+_{1y}(\tau) \times \cos(\beta_{2y}) \quad (18) \\
I^-_{1x}(\beta_{2y}) &= I^-_{1x}(\tau) \times \cos(\beta_{2y}) \quad (19) \\
I^-_{1y}(\beta_{2y}) &= I^-_{1y}(\tau) \times \cos(\beta_{2y}) \quad (20)
\end{align*}
\]
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$I_x^2$ and $I_y^2$ of SQ(2) of Atom 2

Initial parameters

\[ I_{2x} = 0 \text{ if initial pulse } \beta_{2y} = 90^\circ \]
\[ I_{2y} = 1 \text{ if initial pulse } \beta_{2y} = 90^\circ \]

With $\omega_{02} = \text{resonance frequency atom } i$

\[
\omega_2^* = \omega_{02} + J_{1,2}
\]
\[
\omega_2 = \omega_{02} - J_{1,2}
\]

\[ I_{2x}(\beta_{2y}) = I_x^2 \sin(\beta_{2y}) \tag{21} \]
\[ I_{2y}(\beta_{2y}) = I_y^2 \sin(\beta_{2y}) \tag{22} \]
\[ I_{2x}(\beta_{2y}) = I_x^2 \sin(\beta_{2y}) \tag{23} \]
\[ I_{2y}(\beta_{2y}) = I_y^2 \sin(\beta_{2y}) \tag{24} \]

Equations for the calculation of $DQ(\beta_{2y})$ and $ZQ(\beta_{2y})$ vectors

\[ DQ_x = -I_x^1(\tau) \sin(\beta_{2y}) \tag{25} \]
\[ DQ_y = -I_y^1(\tau) \sin(\beta_{2y}) \tag{26} \]
\[ ZQ_x = I_x^1(\tau) \sin(\beta_{2y}) \tag{27} \]
\[ ZQ_y = I_y^1(\tau) \sin(\beta_{2y}) \tag{28} \]

Figure 3: Right: Vectors of multiple quantum coherence $DQ$ (blue) and $ZQ$ (red) for sequence 6. The intensity of the SQ vectors $I_1^1$ and $I_1^2$ is transferred to the multiple quantum coherences. Left: Density vectors $I_1^1$ and $I_1^2$ as a result of the $\beta_{2y}$ pulse.

Sequences 1 ($\alpha_{1x} - \tau - \beta_{2x}$) and 6 ($\alpha_{1x} - \tau - \beta_{2y}$) differ by a pulse of $90^\circ_{2z}$. The conversion of the SQ, ZQ and DQ vectors in sequence 1 to the vectors in sequence 6 can be visualized by means of the DVM. Examples are given in chapter 2 of this document.
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DVM for the description of sequences 5 and 10

Sequence 5: $\alpha_{1x} \alpha_{2x} - \tau - \beta_{1x} \beta_{2x}$

<table>
<thead>
<tr>
<th>Resulting $I_1x$ and $I_1y$ vectors</th>
<th>Sequence 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pulses</td>
<td>$\alpha_{1x}$</td>
</tr>
<tr>
<td>$P_1$ = 1</td>
<td></td>
</tr>
<tr>
<td>$P_2$ = 1</td>
<td>0.00417</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mixing pulses</th>
<th>$\beta_{1x}$</th>
<th>90 $^\circ$</th>
<th>$\beta_{2x}$</th>
<th>90 $^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I+ / I- Op</td>
<td>I+ I-</td>
<td>I+ I-</td>
<td>DVM Ix</td>
<td>DVM Iy</td>
</tr>
<tr>
<td>I+1(\tau)</td>
<td>2/1x:2z</td>
<td>SC(1)</td>
<td>-0.92</td>
<td>-3.89</td>
</tr>
<tr>
<td>I-1(\tau)</td>
<td>2/1y:2z</td>
<td>SC(1)</td>
<td>0.89</td>
<td>3.89</td>
</tr>
<tr>
<td>I+2(\tau)</td>
<td>2/1z:1x</td>
<td>SC(2)</td>
<td>0.96</td>
<td>-0.29</td>
</tr>
<tr>
<td>I-2(\tau)</td>
<td>2/1z:1y</td>
<td>SC(2)</td>
<td>-0.96</td>
<td>0.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MQ</th>
<th>I+ / I- Operators</th>
<th>Product Operators</th>
<th>DVM Ix</th>
<th>DVM Iy</th>
<th>Coherence order</th>
</tr>
</thead>
<tbody>
<tr>
<td>DQx</td>
<td>1/2 (I-1I+ + I-1I-)</td>
<td>1/2 (2I1xI2x - 2I1yI2y)</td>
<td>4.18</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>DQy</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>1/2 (2I1xI2y + 2I1yI2x)</td>
<td>0.00</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>ZQx</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>1/2 (2I1xI2x + 2I1yI2y)</td>
<td>3.60</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>ZQy</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>1/2 (2I1yI2x - 2I1xI2y)</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>DQx</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>-1/2 (2I1xI2x - 2I1yI2y)</td>
<td>-4.18</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>DQy</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>-1/2 (2I1yI2x - 2I1xI2y)</td>
<td>0.00</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>ZQx</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>-1/2 (2I1xI2x - 2I1yI2y)</td>
<td>3.60</td>
<td>-2</td>
<td></td>
</tr>
<tr>
<td>ZQy</td>
<td>1/4 (I+1I- - I+1I-)</td>
<td>-1/2 (2I1yI2x - 2I1xI2y)</td>
<td>0.00</td>
<td>-2</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: Density vectors $I^+$, $I^-$ of SQ coherences and $ZQ$, $DQ$ of multiple quantum coherences (MQ) for sequence 5.

Equations for the calculation of $I^+ (\tau)$ and $I^-(\tau)$ vectors

Initial parameters

\begin{align*}
I_{1x} &= 4 \text{ if initial pulse } \alpha_{1x} = 90^\circ \\
I_{1y} &= 0 \text{ if initial pulse } \alpha_{1x} = 90^\circ \\
I_{2x} &= 1 \text{ if initial pulse } \alpha_{2x} = 90^\circ \\
I_{2y} &= 0 \text{ if initial pulse } \alpha_{2x} = 90^\circ 
\end{align*}

With $\omega_{01} = \text{resonance frequency atom 1}$

\begin{align*}
\omega^{+}_{1} &= \omega_{01} + J_{1,2} \\
\omega^{-}_{1} &= \omega_{01} - J_{1,2} \\
\omega^{+}_{2} &= \omega_{01} + J_{1,2} \\
\omega^{-}_{2} &= \omega_{01} - J_{1,2}
\end{align*}

With $\omega_{02} = \text{resonance frequency atom 2}$
Visualizing Coherence transfer by the Density Vector Model

With $i = 1$ and 2 for atoms 1 and 2

\[
I^x_i(\tau) = I_i^x \cos(\omega^+_i \tau) \tag{29}
\]

\[
I^y_i(\tau) = I_i^y \sin(\omega^+_i \tau) \tag{30}
\]

\[
I^x_i(\tau) = I_i^x \cos(\omega^-_i \tau) \tag{31}
\]

\[
I^y_i(\tau) = I_i^y \sin(\omega^-_i \tau) \tag{32}
\]

Figure 4: Left: Transverse magnetizations $I^+ (\text{blue})$ and $I^- (\text{red})$ in antiphase arrangement of density vectors belonging to doublet signals of nmr spectrum of atom 1 with $\gamma = 4$. Right: Transverse magnetizations $I^+ (\text{blue})$ and $I^- (\text{red})$ in antiphase arrangement of density vectors belonging to doublet signals of nmr spectrum of atom 2 with $\gamma = 1$.

Equations for the calculation of SQ ($\beta_{1x} \beta_{2x}$) vectors

$I^*$, and $I^1$ of SQ(1) of Atom 1

\[
I^1_x(\beta_{1x} \beta_{2x}) = I^x_1(\tau) \cdot \cos^2(\beta_{1x}) - I^x_2(\tau) \cdot \cos^2(\beta_{2x}) \tag{33}
\]

\[
I^1_y(\beta_{1x} \beta_{2x}) = I^y_1(\tau) \cdot \cos(\beta_{1x}) \tag{34}
\]

\[
I^{1x}(\beta_{1x} \beta_{2x}) = I^x_1(\tau) \cdot \cos^2(\beta_{1x}) - I^x_2(\tau) \cdot \cos^2(\beta_{1x}) \tag{35}
\]

\[
I^{1y}(\beta_{1x} \beta_{2x}) = I^y_1(\tau) \cdot \cos(\beta_{1x}) \tag{36}
\]

Figure 5: Density vectors of SQ coherences of atom 1. The $I^*$ and $I^1$ vectors are aligned along the x-axis in the x,y-plane and produce pure absorption signals.
Visualizing Coherence transfer by the Density Vector Model

$I'^2$ and $I'^2$ of SQ(2) of Atom 2

**Initial parameters**

\[
\begin{align*}
I_{2x} &= 0 \text{ if initial pulse } \beta_{2y} = 90^\circ \\
I_{2y} &= 1 \text{ if initial pulse } \beta_{2y} = 90^\circ \\
\omega_{21} &= \omega_{02} + J_{1,2} \\
\omega_{21} &= \omega_{02} - J_{1,2}
\end{align*}
\]

With $\omega_{02} =$ resonance frequency atom $i$

\[
\begin{align*}
I'^2_{2x}(\beta_{1x}, \beta_{2x}) &= I'^2_{1x} \cos^2(\beta_{1x}) - I'^1_{1x} \sin^2(\beta_{2x}) \\
I'^2_{2y}(\beta_{1x}, \beta_{2x}) &= I'^2_{1y} \cos(\beta_{1x}) \\
I'^1_{2x}(\beta_{1x}, \beta_{2x}) &= I'^1_{1x} \cos^2(\beta_{1x}) - I'^1_{1x} \sin^2(\beta_{2x}) \\
I'^1_{2y}(\beta_{1x}, \beta_{2x}) &= I'^1_{1y} \cos(\beta_{1x})
\end{align*}
\]

**Equations for the calculation of DQ($\beta_{2y}$) and ZQ($\beta_{2y}$) vectors**

\[
\begin{align*}
DQ_x &= I'^1_y(\tau) \sin(\beta_{1x}) + I'^2_y(\tau) \sin(\beta_{2x}) \\
DQ_y &= I'^1_x(\tau) \sin(2\beta_{1x}) + I'^2_x(\tau) \sin(2\beta_{2x}) \\
ZQ_x &= I'^1_y(\tau) \sin(\beta_{1x}) - I'^2_y(\tau) \sin(\beta_{2x}) \\
ZQ_y &= I'^1_x(\tau) \sin(\beta_{2x}) + I'^2_x(\tau) \sin(\beta_{2x})
\end{align*}
\]

**Figure 6**: Density vectors of SQ coherences of atom 2. The $I'^2$ and $I'^2$ vectors are aligned along the x-axis in the x,y-plane and produce pure absorption signals.

**Figure 7**: Vectors of multiple quantum coherence $DQ$ (blue) and $ZQ$ (red) for sequence 5. The intensity of the SQ vectors $I'^1$ and $I'^1$ is transferred to the multiple quantum coherences.
Visualizing Coherence transfer by the Density Vector Model

Sequence 10: $\alpha_{1x}\alpha_{2x} - \tau - \beta_{1y}\beta_{2y}$

<table>
<thead>
<tr>
<th>Initial pulses</th>
<th>Resulting $\mathbf{dx}$ and $\mathbf{dy}$ vectors</th>
<th>Sequence 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_1 = 1$</td>
<td>$\alpha_{1x}$ 90° $\alpha_{2x}$</td>
<td>10</td>
</tr>
<tr>
<td>$p_2 = 1$</td>
<td>$\beta_{1y}$ 90° $\beta_{2y}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: Density vectors $\mathbf{I}_+^+$, $\mathbf{I}_-^-$ of SQ coherences and $\mathbf{ZQ}$, $\mathbf{DQ}$ of multiple quantum coherences (MQ) for sequence 10.

Sequences 5 and 10 as well as sequences 1 and 6 both can be interconverted by applying a phase angle $\phi_z = \pm 90°$.

Equations for the calculation of SQ ($\beta_{1y}\beta_{2y}$) vectors

$I^+ x (\beta_{1y} \beta_{2y}) = I^+ x (\tau) \times \cos(\beta_{1y}) \quad (45)$

$I^+ y (\beta_{1y} \beta_{2y}) = -I^+ y (\tau) \times \sin^2(\beta_{2y}) + I^+ y (\tau) \times \cos^2(\beta_{1y}) \quad (46)$

$I^- x (\beta_{1y} \beta_{2y}) = I^- x (\tau) \times \cos(\beta_{1y}) \quad (47)$

$I^- y (\beta_{1y} \beta_{2y}) = I^- y (\tau) \times \sin^2(\beta_{2y}) - I^- y (\tau) \times \cos^2(\beta_{1y}) \quad (48)$
Visualizing Coherence transfer by the Density Vector Model

\( I'_2 \) and \( I'_z \) of SQ(2) of Atom 2

**Initial parameters**

- \( I_{2x} = 0 \) if initial pulse \( \beta_{2y} = 90^\circ \)
- \( I_{2y} = 1 \) if initial pulse \( \beta_{2y} = 90^\circ \)

With \( \omega_{02} \) = resonance frequency atom i

\[ \omega^2 \zeta = \omega_{02} + J_{1,2} \]

\[ \omega^2 \zeta = \omega_{02} - J_{1,2} \]

\[ I'_2x(\beta_{1y} \beta_{2y}) = I^{+1}_x \cos(\beta_{2y}) \]  \hspace{1cm} (49)

\[ I'_2y(\beta_{1y} \beta_{2y}) = I^{+1}_y \cos^2(\beta_{2y}) - I^{+2}_y \sin^2(\beta_{1y}) \]  \hspace{1cm} (50)

\[ I'_2x(\beta_{1y} \beta_{2y}) = I^{-1}_x \cos(\beta_{2y}) \]  \hspace{1cm} (51)

\[ I'_2y(\beta_{1y} \beta_{2y}) = I^{-1}_y \cos^2(\beta_{2y}) - I^{-2}_y \sin^2(\beta_{2y}) \]  \hspace{1cm} (52)

**Equations for the calculation of DQ(\( \beta_{2y} \)) and ZQ(\( \beta_{2y} \)) vectors**

\[ DQ_x(\beta_{1y} \beta_{2y}) = -I^{+1}_x(t) \sin(\beta_{2y}) - I^{+2}_x(t) \sin(\beta_{1y}) \]  \hspace{1cm} (53)

\[ DQ_y(\beta_{1y} \beta_{2y}) = -\frac{1}{2} \{I^{+1}_y(t) \sin(2\beta_{2y}) + I^{+2}_y(t) \sin(2\beta_{1y})\} \]  \hspace{1cm} (54)

\[ ZQ_x(\beta_{1y} \beta_{2y}) = -I^{-1}_x(t) \sin(\beta_{2y}) + I^{-2}_x(t) \sin(\beta_{1y}) \]  \hspace{1cm} (55)

\[ ZQ_y(\beta_{1y} \beta_{2y}) = \frac{1}{2} \{I^{-1}_y(t) \sin(2\beta_{2y}) + I^{-2}_y(t) \sin(2\beta_{1y})\} \]  \hspace{1cm} (56)

Figure 8: Left: Density vectors of SQ coherence of atom 1. The vectors are aligned along the y-axis. Right: Polarization transfer of density vectors to signal of atom 2.

Figure 9: Only ZQ (red) coherence is created by sequence 10. The intensity of the SQ vectors \( I^{+2} \) and \( I^{-2} \) is transferred to ZQ coherences.
Chapter 2: Phases of density vectors of ZQ and DQ coherences

Transformation of sequence 1 into sequence 6

Figure 10: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of sequence 1 corresponding to \( \alpha_{1x} - \tau - \beta_{2x} = 90^\circ 1x - 1/(2^*J) - 0^\circ 2z \).

Vectors \( I_x \) and \( I_y \) of DQ \( p_1=+1, p_2=+1 \)

<table>
<thead>
<tr>
<th>Frequency</th>
<th>( I_x )</th>
<th>( I_y )</th>
<th>( i )</th>
<th>( j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>999</td>
<td>3.91</td>
<td>-0.85</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

Vectors \( I_x \) and \( I_y \) of ZQ \( p_1=+1, p_2=-1 \)

<table>
<thead>
<tr>
<th>Frequency</th>
<th>( I_x )</th>
<th>( I_y )</th>
<th>( i )</th>
<th>( j )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-777</td>
<td>-3.87</td>
<td>0.99</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 10. Coherence order of DQ is \( p = +2 \) and ZQ is \( p = 0 \).

Figure 11: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of phase shifted sequence 1 corresponding to \( \alpha_{1x} - \tau - \beta_{2x} = 90^\circ 1x - 1/(2^*J) - 10^\circ 2z \). \( i \) and \( j \) are indices of density matrix.
Vectors $I_x$ and $I_y$ of DQ $p_1=+1$, $p_2=+1$

<table>
<thead>
<tr>
<th>DQ Frequency</th>
<th>$I_x$</th>
<th>$I_y$</th>
<th>i</th>
<th>j</th>
</tr>
</thead>
<tbody>
<tr>
<td>999</td>
<td>3.99</td>
<td>-0.23</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

Vectors $I_x$ and $I_y$ of ZQ $p_1=+1$, $p_2=-1$

<table>
<thead>
<tr>
<th>ZQ Frequency</th>
<th>$I_x$</th>
<th>$I_y$</th>
<th>i</th>
<th>j</th>
</tr>
</thead>
<tbody>
<tr>
<td>-777</td>
<td>-3.67</td>
<td>1.58</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 7: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 11. Coherence order of DQ is $p = +2$ and ZQ is $p = 0$.

Vectors $I_x$ and $I_y$ of DQ $p_1=+1$, $p_2=+1$

<table>
<thead>
<tr>
<th>DQ Frequency</th>
<th>$I_x$</th>
<th>$I_y$</th>
<th>i</th>
<th>j</th>
</tr>
</thead>
<tbody>
<tr>
<td>999</td>
<td>1.58</td>
<td>3.67</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

Vectors $I_x$ and $I_y$ of ZQ $p_1=+1$, $p_2=-1$

<table>
<thead>
<tr>
<th>ZQ Frequency</th>
<th>$I_x$</th>
<th>$I_y$</th>
<th>i</th>
<th>j</th>
</tr>
</thead>
<tbody>
<tr>
<td>-777</td>
<td>0.23</td>
<td>3.99</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 8: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 12. Coherence order of DQ is $p = +2$ and ZQ is $p = 0$.

Figure 12: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of sequence 1 corresponding to $\alpha_{1x} - \tau - \beta_{2x} = 90^\circ x - 1/(2^*J) - 80^\circ z$. i and j are indices of density matrix.

Figure 13: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of sequence 1 corresponding to $\alpha_{1x} - \tau - \beta_{2x} = 90^\circ x - 1/(2^*J) - 90^\circ y$. i and j are indices of density matrix.
Visualizing Coherence transfer by the Density Vector Model

Vectors Ix and Iy of DQ p1=+1, p2=+1
DQ Frequency Ix  ly  i  j
999  0.92  3.89  4  1

Vectors Ix and Iy of ZQ p1=+1, p2=-1
ZQ Frequency Ix  ly  i  j
-777  0.92  3.89  3  2

Table 9: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 12. Coherence order of DQ is p = +2 and ZQ is p = 0.

Transformation of sequence 5 into sequence 10

Figure 14: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of sequence 5 corresponding to \( \alpha_1 x \alpha_2 x - \tau - \beta_1 x \beta_2 x = 90^\circ 1x 90^\circ 2x \).

Vectors Ix and Iy of DQ p1=+1, p2=-1
DQ Frequency Ix  ly  i  j
999  4.18  0.00  1  4

Vectors Ix and Iy of ZQ p1=+1, p2=-1
ZQ Frequency Ix  ly  i  j
-777  -3.60  0.00  2  3

Table 10: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 14. Coherence order of DQ is p = +2 and ZQ is p = 0.

Vectors Ix and Iy of DQ p1=-1, p2=-1
DQ Frequency Ix  ly  i  j
-999  -4.18  0.00  4  1

Vectors Ix and Iy of ZQ p1=-1, p2=-1
ZQ Frequency Ix  ly  i  j
777  3.60  0.00  2  3

Table 11: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 14. Coherence order of DQ is p = -2 and ZQ is p = 0.

Density Matrix

The lists containing frequencies and density vectors (intensities) are extracted from the complex density matrix. The DVM computer program provides access to the
density matrix. Comparing density vectors as shown in the lists with the density vectors as given in the density matrix may be helpful for the interpretation of data.

S: 1 K: 1 X: 90 K: 2 X: 90 D: 0.00417 S: 2 K: 1 X: 90 K: 2 X: 90

Density matrix. Real
0.93 -0.96 -4.18
-0.93 0.36 0.96
0.96 -3.60 -0.93
4.18 -0.96 0.93 0

Density matrix. Imaginary
0 0 0 0
0 0.01 0 0
0 0 0 0
0 0 0 -0.01

Figure 15: Density vectors of DQ (999 Hz) and ZQ (-777 Hz) coherences as the result of sequence 10 corresponding to $\alpha_1 x \alpha_2 x - \tau - \beta_1 x \beta_2 x = 90^\circ 1x 90^\circ 2x$.

Vectors $I_x$ and $I_y$ of DQ $p_1=+1$, $p_2=+1$
DQ Frequency $I_x$ $I_y$ $i$ $j$
999 -0.03 0.00 4 1

Vectors $I_x$ and $I_y$ of ZQ $p_1=+1$, $p_2=-1$
ZQ Frequency $I_x$ $I_y$ $i$ $j$
-777 1.89 0.00 3 2

Table 12: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 15. Coherence order of DQ is $p = +2$ and ZQ is $p = 0$.

Vectors $I_x$ and $I_y$ of DQ $p_1=-1$, $p_2=-1$
DQ Frequency $I_x$ $I_y$ $i$ $j$
-999 0.03 0.00 1 4

Vectors $I_x$ and $I_y$ of ZQ $p_1=-1$, $p_2=+1$
ZQ Frequency $I_x$ $I_y$ $i$ $j$
777 -1.89 0.00 2 3

Table 13: Frequencies and density vectors of DQ and ZQ coherences shown in Figure 15. Coherence order of DQ is $p = -2$ and ZQ is $p = 0$.

Density Matrix of sequence 10
Figure 16: Density vectors of sequence 10 shows polarization transfer from DQ coherence in sequence 5 to SQ coherence and experiences a phase shift of $\phi_z = 90^\circ$.

The polarization transfer to SQ coherence of atom 2 can also be seen in the imaginary part of the density matrix.

**Density Vectors for more than two atoms**

The effect of increasing the number of atoms involved in a spin system is shown by the vector diagrams produced by the DVM computer program. The examples are dealing with sequences 5 and 6 and show that in general the behaviour of vectors follows the pattern obtained with two spin systems also for larger spin systems.

**DVM for three atoms**
Visualizing Coherence transfer by the Density Vector Model

Figure 17: Density vectors of multiple quantum coherences of sequence 5.

HC 90°x – 0.00417 s – HC 90°y

Figure 18: Density vectors of multiple quantum coherences of sequence 10.
Visualizing Coherence transfer by the Density Vector Model

Figure 19: Density vectors of SQ coherence for atom 3 resulting from sequence 10 and showing coherence transfer from directly bonded atom 1 to atom 3.

**DVM for four atoms**

K 4 F 111 222 333 888 J 12 0 120 9 -7 M 4 4 1

HC 90% – 0.00417 s – HC 90%

Figure 20: Density vectors of multiple quantum coherences of sequence 5.
Visualizing Coherence transfer by the Density Vector Model

HC $90^\circ x - 0.00417$ s – HC $90^\circ y$

Figure 21: Density vectors of multiple quantum coherences of sequence 10.

Figure 22: Density vectors of SQ coherence for atom 4 resulting from sequence 10 and showing coherence transfer from directly bonded atom 1 to atom 4.