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# Subspectral Editing with a Multiple Quantum Trap of $IS_n$ Spin Systems by Using Product Operator Theory

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Product operator theory was often used to describe analytically multi-pulse NMR experiments for weakly coupled spin systems. In this study first we introduce the descriptions of subspectral editing with a multiple quantum trap NMR spectra for $IS_n$ ($I = 1/2$, $S = 5/2$ with $n = 1, 2, 3$) spin systems by using product operator formalism. These theoretical investigations lead us to form the general expressions for the intensities of the spin $-1/2$ nuclei coupled to the nuclei with spin $\geq 5/2$. The obtained results can be used for the spectral editing in both liquid-state and solid-state NMR experiments. Furthermore, in order to satisfy the obtained analytical expressions for signal intensities we add the presentation of analytically description of subspectral editing with a multiple quantum trap sequence for weakly coupled $IS$ ($I = 1/2$, $S = 7/2$) spin system.

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## 1. Introduction

Subspectral editing using a multiple quantum trap (namely SEMUT sequence) has been proposed as an alternative method for subspectral editing of $^{13}$C NMR spectra [1]. This pulse sequence has mainly two advantages. Firstly, it contains fewer pulses than polarization technique distortionless enhancement polarization transfer (DEPT) and SEMUT sequence includes quaternaries for the determination of proton multiplicities in $^{13}C$ NMR while DEPT can produce only CH, $CH_2$, and $CH_3$ subspectra [2]. Secondly, it is most convenient experiment to be analyzed by using product operator theory as a simple quantum mechanical method [3, 4]. In this framework recently, SEMUT sequence has been described analytically for weakly coupled $IS_n$ ($I = 1/2$, $S = 1$ and $3/2$ with $n = 1, 2, 3$) spin systems by using product operator formalism [5, 6].

On the other hand, it is a well known fact that approximately 74% of NMR active nuclei in the periodic table have a spin greater than 1/2. For this reason a somewhat unusual two-spin system involving a spin $S = 5/2$ (or $\geq 5/2$) could be interesting for some spectral editing experiments in particular when one considers the solid-state analogue of the SEMUT experiment [7].

In the present work first we introduce the analytical descriptions of SEMUT sequence for weakly coupled $IS_n$ ($I = 1/2$, $S = 5/2$ with $n = 1, 2, 3$) spin systems by using product operator theory. Furthermore, we resume the similar results for weakly coupled $IS_n$ ($I = 1/2$, $S \geq 1/2$; $n = 1, 2, 3$) spin systems in Table which includes the earlier obtained results for $IS_n$ ($I = 1/2$, $S = 1/2$ and $3/2$; $n = 1, 2, 3$) spin systems in the mentioned pulse sequence. Later we present the description of SEMUT sequence for another weakly coupled spin system $IS$ ($I = 1/2$, $S = 7/2$) in Appendix for the purpose of confirming the signal intensity in formed Table.

## 2. The evolutions of product operators under spin–spin coupling Hamiltonian for $IS_n$ ($I = 1/2$, $S = 5/2$) spin system and application to SEMUT sequence

For the analysis of multipulse experiments by using product operator formalism when a spin $I = 1/2$ is coupled to a spin $S = 5/2$, under scalar coupling it is convenient to consider the decomposition of $I = 1/2$ spin multiplicity into in-phase and anti-phase coherence with the inner and outer transitions of multiplet [4, 8–10]. This leads us to consider the operators $I_x$, $I_y$, $I_xS_z$ and $I_yS_z$ as some of the product operators for $IS$ ($I = 1/2$, $S = 5/2$) spin system. By considering the Hausdorff formula for the evolutions of the mentioned product operators under spin–spin coupling Hamiltonian a shorthand notation can be obtained as follows [9]:

$$I_x \xrightarrow{2\pi J I_z S_z t} I_x E_s(\pm\tfrac{5}{2})\cos(5\pi Jt) + \tfrac{2}{5} I_y S_z E_s(\pm\tfrac{5}{2})\sin(5\pi Jt)$$

$$+ I_x E_s(\pm\tfrac{3}{2})\cos(3\pi Jt) + \tfrac{2}{3} I_y S_z E_s(\pm\tfrac{3}{2})\sin(3\pi Jt)$$

$$+ I_x E_s(\pm\tfrac{1}{2})\cos(\pi Jt) + 2 I_y S_z E_s(\pm\tfrac{1}{2})\sin(\pi Jt), \tag{1a}$$

$$I_y \xrightarrow{2\pi J I_z S_z t} I_y E_s(\pm\tfrac{5}{2})\cos(5\pi J t) - \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2})\sin(5\pi J t)$$
$$+I_y E_s(\pm\tfrac{3}{2})\cos(3\pi J t) - \tfrac{2}{3} I_x S_z E_s(\pm\tfrac{3}{2})\sin(3\pi J t)$$
$$+I_y E_s(\pm\tfrac{1}{2})\cos(\pi J t) - 2 I_x S_z E_s(\pm\tfrac{1}{2})\sin(\pi J t), \tag{1b}$$

$$I_x S_z \xrightarrow{2\pi J I_z S_z t} I_x S_z E_s(\pm\tfrac{5}{2})\cos(5\pi J t) + \tfrac{5}{2} I_y E_s(\pm\tfrac{5}{2})\sin(5\pi J t)$$
$$+I_x S_z E_s(\pm\tfrac{3}{2})\cos(3\pi J t) + \tfrac{3}{2} I_y E_s(\pm\tfrac{3}{2})\sin(3\pi J t)$$
$$+I_x S_z E_s(\pm\tfrac{1}{2})\cos(\pi J t) + \tfrac{1}{2} I_y E_s(\pm\tfrac{1}{2})\sin(\pi J t), \tag{1c}$$

$$I_y S_z \xrightarrow{2\pi J I_z S_z t} I_y S_z E_s(\pm\tfrac{5}{2})\cos(5\pi J t) - \tfrac{5}{2} I_x E_s(\pm\tfrac{5}{2})\sin(5\pi J t)$$
$$+I_y S_z E_s(\pm\tfrac{3}{2})\cos(3\pi J t) - \tfrac{3}{2} I_x E_s(\pm\tfrac{3}{2})\sin(3\pi J t)$$
$$+I_y S_z E_s(\pm\tfrac{1}{2})\cos(\pi J t) - \tfrac{1}{2} I_x E_s(\pm\tfrac{1}{2})\sin(\pi J t), \tag{1d}$$

We used these expressions for the analytical description of SEMUT sequence within the framework of product operator formalism. SEMUT sequence is shown in Fig. 1. The numbers labelled in Fig. 1 indicate all single stages of the density matrix operators in SEMUT pulse sequences.

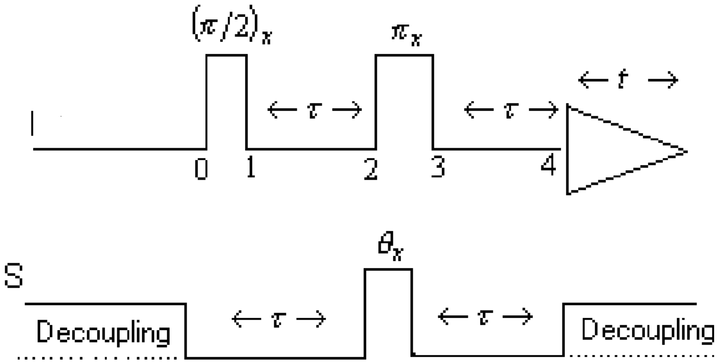


Fig. 1. SEMUT pulse sequence ($\tau = 1/(2J)$).

For $IS$ ($I = 1/2,\ S = 5/2$) weakly coupled spin system the density matrix operators are as follows: in equilibrium state we have $\sigma_0 = I_z$ and after the first pulse $\sigma_1 = -I_y$. During $\tau$ interval, the density matrix operator is

$$\sigma_2 = -I_y E_s(\pm\tfrac{5}{2}) C_{5J} + \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2}) S_{5J}$$
$$-I_y E_s(\pm\tfrac{3}{2}) C_{3J} + \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{3}{2}) S_{3J}$$
$$-I_y E_s(\pm\tfrac{1}{2}) C_{J} + \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{1}{2}) S_{J},$$

where $C_{nJ} = \cos(n\pi J\tau)$ and $S_{nJ} = \sin(n\pi J\tau)$. For $\tau = 1/(2J)$ we take the values $C_J = C_{3J} = C_{5J} = 0$ and $S_J = S_{5J} = 1$, $S_{3J} = -1$ and thus $\sigma_2$ becomes

$$\sigma_2 = \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2}) - \tfrac{2}{3} I_x S_z E_s(\pm\tfrac{3}{2}) + 2 I_x S_z E_s(\pm\tfrac{1}{2}). \tag{2}$$

Then, after the applications of $(180°)_x$ and $(\theta)_x$ pulses we obtain

$$\sigma_3 = \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2}) C_\theta - \tfrac{2}{3} I_x S_z E_s(\pm\tfrac{3}{2}) C_\theta + 2 I_x S_z E_s(\pm\tfrac{1}{2}) C_\theta, \tag{3}$$

where $C_\theta = \cos\theta$. During $\tau$ evolution time, we get

$$\sigma \xrightarrow{2\pi J I_z S_z} \sigma_4,$$

$$\begin{aligned}\sigma_4 = {} & \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2}) C_\theta C_{5J} + I_y E_s(\pm\tfrac{5}{2}) C_\theta S_{5J} \\ & - \tfrac{2}{3} I_x S_z E_s(\pm\tfrac{3}{2}) C_\theta C_{3J} - I_y E_s(\pm\tfrac{3}{2}) C_\theta S_{3J} \\ & + 2 I_x S_z E_s(\pm\tfrac{1}{2}) C_\theta C_J + I_y E_s(\pm\tfrac{1}{2}) C_\theta S_J.\end{aligned} \tag{4}$$

By taking the values $C_J = C_{3J} = C_{5J} = 0$, $S_J = S_{5J} = 1$ and $S_{3J} = -1$ for $\tau = 1/(2J)$ we get

$$\sigma_4 = I_y E_s(\pm\tfrac{5}{2}) C_\theta + I_y E_s(\pm\tfrac{3}{2}) C_\theta + I_y E_s(\pm\tfrac{1}{2}) C_\theta. \tag{5}$$

During $\tau$ between stages 3 and 4 in Fig. 1, relaxation and effect of chemical shift Hamiltonian on the evolutions of product operators can be disregarded. But during detection time, $t$, the chemical shift effect exists. As a matter of fact, the calculation can be stopped at point four because of the density operator at this point. On the other hand, the signal is detected from $y$-axis and since the contributions to the observable signals becomes only including $I_y$ product operator terms, the magnetization is proportional to $\langle I_y \rangle$, that is,

$$M_y(t) \sim \langle I_y \rangle = \mathrm{Tr}[I_y \sigma_4]. \tag{6}$$

For $IS$ ($I = 1/2$, $S = 5/2$) spin system by substituting Eq. (7) into Eq. (8) we have the coefficients

$$\mathrm{Tr}[I_y I_y E_s(\pm\tfrac{5}{2})] = \mathrm{Tr}[I_y I_y E_s(\pm\tfrac{3}{2})] = \mathrm{Tr}[I_y I_y E_s(\pm\tfrac{1}{2})] = 1. \tag{7}$$

Thus we obtain

$$\langle I_y \rangle (IS) = 3 C_\theta. \tag{8}$$

For $IS_2$ ($I = 1/2$, $S = 5/2$) spin systems by following the same calculations steps we obtain the observable signal as

$$\langle I_y \rangle (IS_2) = 18 C_\theta^2. \tag{9}$$

In a similar way, for $IS_3$ ($I = 1/2$, $S = 5/2$) spin system the observable signal becomes

$$\langle I_y \rangle (IS_3) = 4 \times 27 C_\theta^3. \tag{10}$$

## 3. Discussion and conclusions

Considering Eqs. (8)–(10) we can study the dependencies of observable signal intensities on the pulse angle $\theta$ (Fig. 2). In Fig. 2 the unnormalized values are used and if we denote the $IS_n$ ($I = 1/2,\ S = 5/2$) spin systems as $XY_n$ (for instance, $X = {}^{13}$C), the relative intensities of $^{13}$C SEMUT NMR spectra can be observed separately for every single group. In the case of $\theta = 90°$ or $270°$ only quaternary carbons are observed. From Fig. 2 it is easily seen that the relative intensities for CY, $CY_2$, and $CY_3$ groups are the same at the angle 180°.

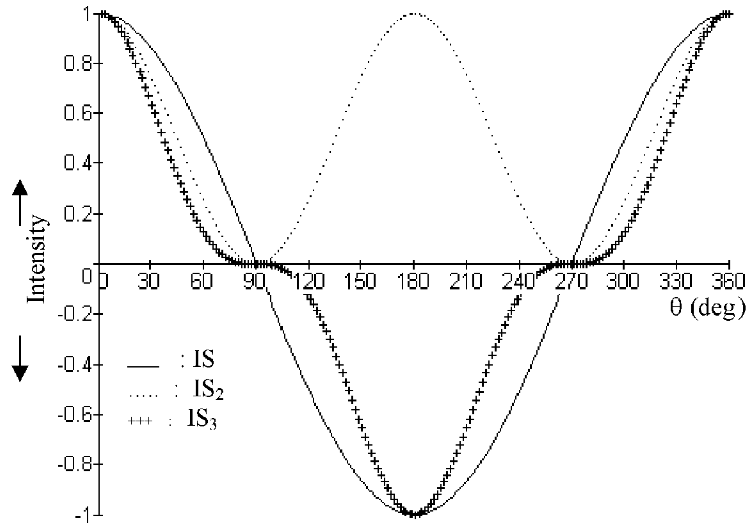


Fig. 2. The plot of the signal intensities as a function of the pulse angle $\theta$.

On the other hand, the obtained intensity values exhibit a significant proportionality to the results of weakly coupled $IS$ ($I = 1/2$, $S = 1/2$ and $3/2$; $n = 1$, 2, 3) spin systems by using product operator formalism in the subspectral editing $^{13}$C NMR SEMUT spectra [1, 6]. Based on this proportionality, the intensities of the observable signals for weakly coupled half-integer spin systems are listed in Table.

From Table, we can derive an expression between the total signal intensities and the dimensions in the matrix representations of $S$ spin operators as

$$I = n\left(\frac{N}{2}\right)^n \cos^n\theta \qquad \text{for } n = 1, 2 \tag{11}$$

and

$$I = (n+1)\left(\frac{N}{2}\right)^n \cos^n\theta \qquad \text{for } n = 3, \tag{12}$$

where $N$ is the dimension of the matrix representation of $S$ spin operator.

TABLE

The obtained signal intensities in the analytical descriptions of SEMUT sequence by using product operator theory for weakly coupled $IS_n$ ($I = 1/2$, $S = 1/2$, $3/2$, $5/2$, $7/2$, and $9/2$; $n = 1$, 2, 3) spin systems.

| Spin system | Coefficients | $S = 1/2^a$ | $S = 3/2^b$ | $S = 5/2$ | $S = 7/2$ | $S = 9/2$ |
|---|---|---|---|---|---|---|
| $IS$ | $\cos\theta$ | 1 | 2(=1.2) | 3(=1.3) | 4(=1.4) | 5(=1.5) |
| $IS_2$ | $\cos^2\theta$ | 2 | $8(=2.2^2)$ | $18(=2.3^2)$ | $32(=2.4^2)$ | $50(=2.5^2)$ |
| $IS_3$ | $\cos^3\theta$ | 4 | $32(=4.2^3)$ | $108(=4.3^3)$ | $256(=4.4^3)$ | $500(=4.5^3)$ |

[a]Taken from Ref. [1] and [b]taken from Ref. [6].

As the conclusion we can express that although the spin systems involving the spin $S \geq 5/2$ are rather unusual for the spectral editing experiments the product operator formalism became a crucial method to describe analytically multidimensional and multipulse sequences for scalar coupled spin systems in both solvent and dilute-solids NMR.

## Appendix

## The analytical description of SEMUT sequence for weakly coupled $IS$ ($I = 1/2$, $S = 7/2$) spin system by using product operator theory

According to the decomposition mentioned in Sec. 1, the unitary matrix representation of $S = 7/2$ spin operator can be written as

$$E_s = E_s(\pm\tfrac{7}{2}) + E_s(\pm\tfrac{5}{2}) + E_s(\pm\tfrac{3}{2}) + E_s(\pm\tfrac{1}{2}), \tag{A.1}$$

where

$$E_s(\pm\tfrac{7}{2}) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix},$$

$$E_s(\pm\tfrac{5}{2}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

$$E_s(\pm\tfrac{3}{2}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix},$$

and

$$E_s(\pm\tfrac{1}{2}) = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \tag{A.2}$$

Thus the product operator $I_x$ can be defined as

$$\begin{aligned} I_x &= I_x \otimes E_s \\ &= I_x \otimes E_s(\pm\tfrac{7}{2}) + I_x \otimes E_s(\pm\tfrac{5}{2}) + I_x \otimes E_s(\pm\tfrac{3}{2}) + I_x \otimes E_s(\pm\tfrac{1}{2}). \end{aligned} \tag{A.3}$$

In order to express the evolutions of operator $I_x$ under spin–spin coupling Hamiltonian, $H_J = 2\pi J I_z S_z$, we should use the Hausdorff formula and the conditions

$$\begin{aligned} S_z^n E_s(\pm\tfrac{7}{2}) &= \tfrac{49}{4} S_z^{n-2} E_s(\pm\tfrac{7}{2}), \qquad n \geq 2, \\ S_z^n E_s(\pm\tfrac{5}{2}) &= \tfrac{25}{4} S_z^{n-2} E_s(\pm\tfrac{5}{2}), \qquad n \geq 2, \\ S_z^n E_s(\pm\tfrac{3}{2}) &= \tfrac{9}{4} S_z^{n-2} E_s(\pm\tfrac{3}{2}), \qquad n \geq 2, \\ S_z^n E_s(\pm\tfrac{1}{2}) &= \tfrac{1}{4} S_z^{n-2} E_s(\pm\tfrac{1}{2}), \qquad n \geq 2, \end{aligned} \tag{A.4}$$

and we have

$$\begin{aligned} I_x \xrightarrow{2\pi J I_z S_z t}\ & I_x E_s(\pm\tfrac{7}{2}) \cos(7\pi J t) + \tfrac{2}{7} I_y S_z E_s(\pm\tfrac{7}{2}) \sin(7\pi J t) \\ & + I_x E_s(\pm\tfrac{5}{2}) \cos(5\pi J t) + \tfrac{2}{5} I_y S_z E_s(\pm\tfrac{5}{2}) \sin(5\pi J t) \\ & + I_x E_s(\pm\tfrac{3}{2}) \cos(3\pi J t) + \tfrac{2}{3} I_y S_z E_s(\pm\tfrac{3}{2}) \sin(3\pi J t) \\ & + I_x E_s(\pm\tfrac{1}{2}) \cos(\pi J t) + 2 I_y S_z E_s(\pm\tfrac{1}{2}) \sin(\pi J t), \end{aligned} \tag{A.5a}$$

$$I_y \xrightarrow{2\pi J I_z S_z t} I_y E_s(\pm\tfrac{7}{2})\cos(7\pi Jt) - \tfrac{2}{7} I_x S_z E_s(\pm\tfrac{7}{2})\sin(7\pi Jt)$$
$$+I_y E_s(\pm\tfrac{5}{2})\cos(5\pi Jt) - \tfrac{2}{5} I_x S_z E_s(\pm\tfrac{5}{2})\sin(5\pi Jt)$$
$$+I_y E_s(\pm\tfrac{3}{2})\cos(3\pi Jt) - \tfrac{2}{3} I_x S_z E_s(\pm\tfrac{3}{2})\sin(3\pi Jt)$$
$$+I_y E_s(\pm\tfrac{1}{2})\cos(\pi Jt) - 2 I_x S_z E_s(\pm\tfrac{1}{2})\sin(\pi Jt), \tag{A.5b}$$
$$I_x S_z \xrightarrow{2\pi J I_z S_z t} I_x S_z E_s(\pm\tfrac{7}{2})\cos(7\pi Jt) + \tfrac{7}{2} I_y E_s(\pm\tfrac{7}{2})\sin(7\pi Jt)$$
$$+I_x S_z E_s(\pm\tfrac{5}{2})\cos(5\pi Jt) + \tfrac{5}{2} I_y E_s(\pm\tfrac{5}{2})\sin(5\pi Jt)$$
$$+I_x S_z E_s(\pm\tfrac{3}{2})\cos(3\pi Jt) + \tfrac{3}{2} I_y E_s(\pm\tfrac{3}{2})\sin(3\pi Jt)$$
$$+I_x S_z E_s(\pm\tfrac{1}{2})\cos(\pi Jt) + \tfrac{1}{2} I_y E_s(\pm\tfrac{1}{2})\sin(\pi Jt), \tag{A.5c}$$
$$I_y S_z \xrightarrow{2\pi J I_z S_z t} I_y S_z E_s(\pm\tfrac{7}{2})\cos(7\pi Jt) - \tfrac{7}{2} I_x E_s(\pm\tfrac{7}{2})\sin(7\pi Jt)$$
$$+I_y S_z E_s(\pm\tfrac{5}{2})\cos(5\pi Jt) - \tfrac{5}{2} I_x E_s(\pm\tfrac{5}{2})\sin(5\pi Jt)$$
$$+I_y S_z E_s(\pm\tfrac{3}{2})\cos(3\pi Jt) - \tfrac{3}{2} I_x E_s(\pm\tfrac{3}{2})\sin(3\pi Jt)$$
$$+I_y S_z E_s(\pm\tfrac{1}{2})\cos(\pi Jt) - \tfrac{1}{2} I_x E_s(\pm\tfrac{1}{2})\sin(\pi Jt). \tag{A.5d}$$

By following the same procedure within the text we obtain the observable signal as

$$\langle I_y\rangle(IS) = 4C_\theta. \tag{A.6}$$

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