How proton and carbon spectra arise from the density matrix

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I. INTRODUCTION

The MIT Junior Lab QIP labguide claims that a two-spin density matrix

$$\rho = \begin{bmatrix} a & 0 & 0 & 0 \\ 0 & b & 0 & 0 \\ 0 & 0 & c & 0 \\ 0 & 0 & 0 & d \end{bmatrix} \tag{1}$$

produces a proton spectrum with peak areas $a - c$ and $b - d$ for the $\omega_P - J/2$ and $\omega_P + J/2$ peaks, respectively, after a $R_x(\pi/2) \otimes I$ proton readout pulse is applied. The same density matrix also produces a carbon spectrum with peak areas $a - b$ and $c - d$ for the $\omega_C - J/2$ and $\omega_C + J/2$ peaks, respectively, after a $I \otimes R_x(\pi/2)$ carbon readout pulse is applied.

Here, we prove this claim, based on the fact that the voltage in the pick-up coil for spin k is given by

$$V(t) = -V_0 \text{tr} \left[e^{-iHt} \rho e^{iHt} (i\sigma_x^k + \sigma_y^k) \right] , \tag{2}$$

where H is the Hamiltonian for the two-spin system, σ_x^k and σ_y^k operate only on the kth spin, and V_0 is a constant factor dependent on coil geometry, quality factor, and maximum magnetic flux from the sample volume.

II. THE READOUT OPERATOR

Let $R_{xP} = R_x(\pi/2) \otimes I$ denote a $\pi/2$ readout pulse on the proton, and R_{xC} similarly for the carbon. Our goal is to compute

$$V_P(t) = -V_0 \text{tr} \left[e^{-iHt} R_{xP} \rho R_{xP}^\dagger e^{iHt} [(i\sigma_x + \sigma_y) \otimes I] \right] , \tag{3}$$

and similarly for the carbon. It is helpful first to move into the rotating frame of the proton and carbon, in which case nothing changes except we utilize the Hamiltonian

$$H = \frac{J}{4} \sigma_z \otimes \sigma_z , \tag{4}$$

representing the spin-spin coupling. Utilizing the cyclic property of the trace, $V_P(t)$ can be written as

$$V_P(t) = -V_0 \text{tr} \left[\rho R_{xP}^\dagger e^{iHt} [(i\sigma_x + \sigma_y) \otimes I] e^{-iHt} R_{xP} \right] , \tag{5}$$

at which point it is useful to define

$$\hat{M}_P = -R_{xP}^\dagger e^{iHt} \left[(i\sigma_x + \sigma_y) \otimes I \right] e^{-iHt} R_{xP} \tag{6}$$

as our proton magnetization "readout operator," such that $V_P(t) = V_0 \text{tr}\,(\rho \hat{M}_P)$. Explicitly working this out in terms of matrix products, we obtain:

$$\hat{M}_P = -R_{xP}^\dagger e^{iHt} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2\,i & 0 & 0 & 0 \\ 0 & 2\,i & 0 & 0 \end{bmatrix} e^{-iHt} R_{xP} \tag{7}$$

$$= -R_{xP}^{\dagger} \begin{bmatrix} e^{\frac{i}{4}Jt} & 0 & 0 & 0 \\ 0 & e^{\frac{-i}{4}Jt} & 0 & 0 \\ 0 & 0 & e^{\frac{-i}{4}Jt} & 0 \\ 0 & 0 & 0 & e^{\frac{i}{4}Jt} \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2i & 0 & 0 & 0 \\ 0 & 2i & 0 & 0 \end{bmatrix} \begin{bmatrix} e^{\frac{-i}{4}Jt} & 0 & 0 & 0 \\ 0 & e^{\frac{i}{4}Jt} & 0 & 0 \\ 0 & 0 & e^{\frac{i}{4}Jt} & 0 \\ 0 & 0 & 0 & e^{\frac{-i}{4}Jt} \end{bmatrix} R_{xP} \tag{8}$$

$$= -R_{xP}^{\dagger} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2\,ie^{-\frac{i}{2}Jt} & 0 & 0 & 0 \\ 0 & 2\,i\,e^{\frac{i}{2}Jt} & 0 & 0 \end{bmatrix} R_{xP} \tag{9}$$

$$= - \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} \\ \frac{i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2\,ie^{-\frac{i}{2}Jt} & 0 & 0 & 0 \\ 0 & 2\,i\,e^{\frac{i}{2}Jt} & 0 & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & \frac{-i}{\sqrt{2}} \\ \frac{-i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{-i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \end{bmatrix} \tag{10}$$

$$= \begin{bmatrix} e^{\frac{-i}{2}Jt} & 0 & -ie^{-\frac{i}{2}Jt} & 0 \\ 0 & e^{\frac{i}{2}Jt} & 0 & -i\,e^{\frac{i}{2}Jt} \\ -ie^{-\frac{i}{2}Jt} & 0 & -e^{\frac{-i}{2}Jt} & 0 \\ 0 & -i\,e^{\frac{i}{2}Jt} & 0 & -e^{\frac{i}{2}Jt} \end{bmatrix}. \tag{11}$$

Similarly, we find that the analogous carbon magnetization "readout operator" $\hat{M}_C$ is

$$\hat{M}_P = -R_{xC}^{\dagger} e^{iHt} \Big[I \otimes (i\sigma_x + \sigma_y) \Big] e^{-iHt} R_{xC} \tag{12}$$

$$= -R_{xC}^{\dagger} e^{iHt} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 2\,i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 2\,i & 0 \end{bmatrix} e^{-iHt} R_{xC} \tag{13}$$

$$= \begin{bmatrix} e^{\frac{-i}{2}Jt} & -ie^{-\frac{i}{2}Jt} & 0 & 0 \\ -ie^{-\frac{i}{2}Jt} & -e^{\frac{-i}{2}Jt} & 0 & 0 \\ 0 & 0 & e^{\frac{i}{2}Jt} & -i\,e^{\frac{i}{2}Jt} \\ 0 & 0 & -i\,e^{\frac{i}{2}Jt} & -e^{\frac{i}{2}Jt} \end{bmatrix}. \tag{14}$$

III. THE PROTON AND CARBON SPECTRA

$\hat{M}_P$ and $\hat{M}_C$ are very useful, because they now allows us to compute the free induction decay signal for the proton (centered in frequency around ω_P) and carbon (centered about ω_C) for any state ρ. For the state in Eq.(1), we obtain the proton FID

$$V_P(t) = V_0 \mathrm{tr}\,(\rho \hat{M}_P) \tag{15}$$

$$= V_0 \mathrm{tr} \left(\begin{bmatrix} a & 0 & 0 & 0 \\ 0 & b & 0 & 0 \\ 0 & 0 & c & 0 \\ 0 & 0 & 0 & d \end{bmatrix} \begin{bmatrix} e^{\frac{-i}{2}Jt} & 0 & -ie^{-\frac{i}{2}Jt} & 0 \\ 0 & e^{\frac{i}{2}Jt} & 0 & -i\,e^{\frac{i}{2}Jt} \\ -ie^{-\frac{i}{2}Jt} & 0 & -e^{\frac{-i}{2}Jt} & 0 \\ 0 & -i\,e^{\frac{i}{2}Jt} & 0 & -e^{\frac{i}{2}Jt} \end{bmatrix} \right) \tag{16}$$

$$= V_0 \Big[(a-c)e^{-iJt/2} + (b-d)e^{iJt/2} \Big]. \tag{17}$$

And for the carbon FID,

$$V_C(t) = V_0 \mathrm{tr}\,(\rho \hat{M}_C) = V_0 \Big[(a-b)e^{-iJt/2} + (c-d)e^{iJt/2} \Big]. \tag{18}$$