How proton and carbon spectra arise from the density matrix

I. Chuang
MIT Center for Bits and Atoms,
Media Laboratory
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I. INTRODUCTION

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

\[
\rho = \begin{bmatrix}
a & 0 & 0 & 0 \\
0 & b & 0 & 0 \\
0 & 0 & c & 0 \\
0 & 0 & 0 & d
\end{bmatrix}
\]

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 \( R_z(\pi/2) \otimes I \) 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 \( I \otimes R_z(\pi/2) \) 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

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

where \( H \) is the Hamiltonian for the two-spin system, \( \sigma_x^k \) and \( \sigma_y^k \) operate only on the \( k \)th 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 \( R_zP = R_z(\pi/2) \otimes I \) denote a \( \pi/2 \) readout pulse on the proton, and \( R_zC \) similarly for the carbon. Our goal is to compute

\[
V_P(t) = -V_0 \text{tr} \left[ e^{-iHt} R_zP \rho e^{iHt} (\sigma_x^P + \sigma_y^P) \otimes I \right],
\]

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

\[
H = \frac{J}{4} \sigma_z \otimes \sigma_z,
\]

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

\[
V_P(t) = -V_0 \text{tr} \left[ \rho \hat{R}_z^\dagger P e^{iHt} (\sigma_x^P + \sigma_y^P) \otimes I \right] e^{-iHt} R_zP
\]

at which point it is useful to define

\[
\hat{M}_P = -\hat{R}_z^\dagger P e^{iHt} \left( (\sigma_x^P + \sigma_y^P) \otimes I \right) e^{-iHt} R_zP
\]

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:

\[
\hat{M}_P = -\hat{R}_z^\dagger P e^{iHt} \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
2i & 0 & 0 & 0 \\
0 & 2i & 0 & 0
\end{bmatrix} e^{-iHt} R_zP
\]
\[ R_{xp} = \left[ \begin{array}{cccc} e^{\frac{i}{2}jt} & 0 & 0 & 0 \\ 0 & e^{\frac{i}{2}jt} & 0 & 0 \\ 0 & 0 & e^{\frac{i}{2}jt} & 0 \\ 0 & 0 & 0 & e^{\frac{i}{2}jt} \end{array} \right] \]

Similarly, we find that the analogous carbon magnetization “readout operator” \( M_C \) is

\[ M_C = -R_{xp}^T e^{iHt} \left[ I \otimes (i\sigma_x + \sigma_y) \right] e^{-iHt} R_{xc} \]

III. THE PROTON AND CARBON SPECTRA

\( \tilde{M}_P \) and \( \tilde{M}_C \) are very useful, because they now allow us to compute the free induction decay signal for the proton (centered in frequency around \( \omega_P \)) and carbon (centered about \( \omega_C \)) for any state \( \rho \). For the state in Eq.(1), we obtain the proton FID

\[ V_P(t) = V_0 \text{tr} (\rho \tilde{M}_P) \]

\[ = V_0 \text{tr} \left( \begin{array}{cccc} a & 0 & 0 & 0 \\ 0 & b & 0 & 0 \\ 0 & 0 & c & 0 \\ 0 & 0 & 0 & d \end{array} \right) \left[ \begin{array}{cccc} e^{\frac{i}{2}jt} & 0 & 0 & 0 \\ 0 & e^{\frac{i}{2}jt} & 0 & 0 \\ 0 & 0 & e^{\frac{i}{2}jt} & 0 \\ 0 & 0 & 0 & e^{\frac{i}{2}jt} \end{array} \right] \]

\[ = V_0 \left[ (a-c)e^{-iJt/2} + (b-d)e^{iJt/2} \right] . \]

And for the carbon FID,

\[ V_C(t) = V_0 \text{tr} (\rho \tilde{M}_C) = V_0 \left[ (a-b)e^{-iJt/2} + (c-d)e^{iJt/2} \right] . \]