Problem Set #5
Rad 226

1. Two-spin Operators

For a single spin-1/2 nucleus, matrices corresponding to the spin operators are identity plus the 2x2 Pauli matrices:

\[
I_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad I_y = \frac{1}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
\]

If we now consider pairs of spins, e.g. \(I\) and \(S\), the two-spin operators needed to describe the system correspond to 4 x 4 matrices are calculated using the matrix direct product (also known as the Kronecker product, tensor product, or outer product):

\[
\begin{bmatrix} a & b \\ c & d \end{bmatrix} \otimes \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix} = \begin{bmatrix} a\alpha & a\beta & b\alpha & b\beta \\ a\gamma & a\delta & b\gamma & b\delta \\ c\alpha & c\beta & d\alpha & d\beta \\ c\gamma & c\delta & d\gamma & d\delta \end{bmatrix}
\]

Direct product

a. Find the matrices corresponding to these two-spin operators:

\[
I_x = \frac{1}{2} I_x \otimes E = ? \quad S_x = ?
\]

\[
2I_x S_z = ? \quad 2I_y S_z = ?
\]

b. Show \(2\hat{I}_z \hat{S}_z\), \(\hat{I}_x\), and \(2\hat{I}_y \hat{S}_z\) cyclically commute.
2. The Steady-State Density Matrix $\sigma_0$

Given a time independent Hamiltonian, $\hat{H}$ with non-degenerate eigenvalues $e_i$ and eigenkets $|i\rangle$, i.e.

$$\hat{H}|i\rangle = e_i|i\rangle,$$

a) Show that in steady-state conditions, the diagonal elements of $\sigma_0$ (expressed in terms of the eigenkets of $\hat{H}$) are constants.

b) Show that in steady-state conditions the off-diagonal elements of $\sigma_0$ (expressed in terms of the eigenkets of $\hat{H}$) are zero.

c) For a two-spin system of spin 1/2 nuclei I and S, the steady-state density operator, $\hat{\sigma}_0$, can be expressed as a linear combination of the following four product operators:

$$\hat{E}, \hat{I}_z, \hat{S}_z,$$ and $2\hat{I}_z\hat{S}_z$

Why don’t we need any of the other twelve 2-spin product operators?
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d. Given: \( \hat{H}_0 = -\gamma_I B_0 \hat{I}_z - \gamma_S B_0 \hat{S}_z + 2\pi J (\hat{I} \cdot \hat{S}) \),

the Boltzmann distribution yields the follow expression for \( \hat{\sigma}_0 \):

\[
\hat{\sigma}_0 = \frac{1}{Z} e^{\frac{-\hbar \hat{H}_0}{kT}} \quad \text{and} \quad Z = \text{Tr}\left( e^{\frac{-\hbar \hat{H}_0}{kT}} \right).
\]

Ignoring the standard high temperature approximation, show

\[
\hat{\sigma}_0 = \alpha_0 \frac{1}{2} \hat{E} + \alpha_1 \hat{I}_z + \alpha_2 \hat{S}_z + \alpha_3 2 \hat{I}_z \hat{S}_z
\]

where

\[
\alpha_0 = \frac{1}{2}
\]

\[
\alpha_1 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma_I B_0}{2kT} \right)
\]

\[
\alpha_2 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma_S B_0}{2kT} \right)
\]

\[
\alpha_3 \approx \frac{1}{2} \tanh \left( \frac{\hbar \gamma_I B_0}{2kT} \right) \tanh \left( \frac{\hbar \gamma_S B_0}{2kT} \right)
\]

Hint: you may safely assume \( \gamma_I B_0, \gamma_S B_0 \gg J \).
3. **J-coupling**

Consider a homonuclear two-spin system with a J-coupling of $J=16 \text{ Hz}$, $T_2=100 \text{ ms}$, and chemical shift difference between the two spins equal to $\Delta \Omega$. Using the full density matrix, simulate (e.g. using Matlab) the series of spectra generated by the 90-acquire sequence shown below with $\Delta \Omega / J$ ranging from 0 to 10. Account for the effect of $T_2$ by assuming the signal following the $90^0$ excitation is weighted by a factor of $e^{-t/T_2}$.

![90y acquire t](image)

4. **Dipolar-coupling**

Consider a homonuclear two-spin system from an anisotropic material with $J=0$ but a residual dipole coupling of $d=16 \text{ Hz}$. Assume a $T_2=100 \text{ ms}$ and a chemical shift difference between the two spins equal to $\Delta \Omega$. Using the full density matrix, simulate (e.g. using Matlab) the series of spectra generated by the 90-acquire sequence shown above with $\Delta \Omega / d$ ranging from 0 to 10. Use the secular approximation to the dipolar coupling spin Hamiltonian. Account for the effect of $T_2$ by assuming the signal following the $90^0$ excitation is weighted by a factor of $e^{-t/T_2}$.

Comments on the differences between the results found in Problems 2 and 3.