# AB Proton NMR Using Tensor Algebra


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The purpose of this tutorial is to deviate from the traditional matrix mechanics approach to the AB proton nmr system in order to illustrate a related method of analysis which uses tensor algebra.

The nuclear magnetic energy operator for the AB system is given below.

$$\hat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B + J_{AB}\hat{I}^A \hat{I}^B \qquad \text{where} \qquad \nu_A = g_n \beta_n B_z (1-\sigma_A)\hat{I}_z^A \qquad \nu_B = g_n \beta_n B_z (1-\sigma_B)\hat{I}_z^B$$

$$\text{and} \qquad \hat{I}^A \cdot \hat{I}^B = \hat{I}_x^A \hat{I}_x^B + \hat{I}_y^A \hat{I}_y^B + \hat{I}_z^A \hat{I}_z^B$$

The customary matrix mechanics analysis requires the following mathematical structures.

- Nuclear spin wave function:

$$\left|\Psi_{mag}\right\rangle = c_1\left|\alpha_A\alpha_B\right\rangle + c_2\left|\alpha_A\beta_B\right\rangle + c_3\left|\beta_A\alpha_B\right\rangle + c_4\left|\beta_A\beta_B\right\rangle = c_1\left|\alpha_A\right\rangle\left|\alpha_B\right\rangle + c_2\left|\alpha_A\right\rangle\left|\beta_B\right\rangle + c_3\left|\beta_A\right\rangle\left|\alpha_B\right\rangle + c_4\left|\beta_A\right\rangle\left|\beta_B\right\rangle$$

- Spin operators (using atomic units, h = 2 π) in the x-, y- and z-directions, plus the identity operator (needed later):

$$I_x := \frac{1}{2}\cdot\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad I_y := \frac{1}{2}\cdot\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad I_z := \frac{1}{2}\cdot\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- Spin eigenfunctions in the x-, y- and z-directions:

$$\alpha_z := \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta_z := \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \alpha_x := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad \beta_x := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix} -1 \\ 1 \end{pmatrix} \qquad \alpha_y := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix} 1 \\ i \end{pmatrix} \qquad \beta_y := \frac{1}{\sqrt{2}}\cdot\begin{pmatrix} 1 \\ -i \end{pmatrix}$$

Note that while the spin wave function is a linear combination of four spin states, the operators are 2x2 matrices. This requires that special care is taken to insure that the operator is operating on the correct spin wave function component. This can be avoided by writing both the spin states and magnetic operator in tensor format.

First tensor vector multiplication is used to construct the nuclear spin states.

$$\left|\alpha\alpha\right\rangle = \left|\alpha\right\rangle\left|\alpha\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ 0\begin{pmatrix} 1 \\ 0 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \left|\alpha\beta\right\rangle = \left|\alpha\right\rangle\left|\beta\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 1\begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ 0\begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\left|\beta\alpha\right\rangle = \left|\beta\right\rangle\left|\alpha\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 0\begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ 1\begin{pmatrix} 1 \\ 0 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \qquad \left|\beta\beta\right\rangle = \left|\beta\right\rangle\left|\beta\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0\begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ 1\begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

We now write these spin states in Mathcad code.

$$\alpha\alpha := \begin{pmatrix}1\\0\\0\\0\end{pmatrix} \qquad \alpha\beta := \begin{pmatrix}0\\1\\0\\0\end{pmatrix} \qquad \beta\alpha := \begin{pmatrix}0\\0\\1\\0\end{pmatrix} \qquad \beta\beta := \begin{pmatrix}0\\0\\0\\1\end{pmatrix}$$

Next, tensor matrix multiplication is used to construct the magnetic energy operator.

$$-\nu_A \hat{I}_z^A \rightarrow -\nu_A \hat{I}_z^A \otimes \hat{I} = \frac{-\nu_A}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} = \frac{-\nu_A}{2}\begin{pmatrix}1\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} & 0\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\\0\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix} & -1\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\end{pmatrix} = \frac{-\nu_A}{2}\begin{pmatrix}1 & 0 & 0 & 0\\0 & 1 & 0 & 0\\0 & 0 & -1 & 0\\0 & 0 & 0 & -1\end{pmatrix}$$

$$-\nu_B \hat{I}_z^B \rightarrow \hat{I} \otimes -\nu_B \hat{I}_z^B = \begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}\otimes\frac{-\nu_B}{2}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} = \frac{-\nu_B}{2}\begin{pmatrix}1\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} & 0\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\\0\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} & 1\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\end{pmatrix} = \frac{-\nu_B}{2}\begin{pmatrix}1 & 0 & 0 & 0\\0 & -1 & 0 & 0\\0 & 0 & 1 & 0\\0 & 0 & 0 & -1\end{pmatrix}$$

$$J_{AB}\hat{I}_x^A \otimes \hat{I}_x^B = \frac{J_{AB}}{4}\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\otimes\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}0\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} & 1\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\\1\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix} & 0\begin{pmatrix}0 & 1\\1 & 0\end{pmatrix}\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}0 & 0 & 0 & 1\\0 & 0 & 1 & 0\\0 & 1 & 0 & 0\\1 & 0 & 0 & 0\end{pmatrix}$$

$$J_{AB}\hat{I}_y^A \otimes \hat{I}_y^B = \frac{J_{AB}}{4}\begin{pmatrix}0 & -i\\i & 0\end{pmatrix}\otimes\begin{pmatrix}0 & -i\\i & 0\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}0\begin{pmatrix}0 & -i\\i & 0\end{pmatrix} & -i\begin{pmatrix}0 & -i\\i & 0\end{pmatrix}\\i\begin{pmatrix}0 & -i\\i & 0\end{pmatrix} & 0\begin{pmatrix}0 & -i\\i & 0\end{pmatrix}\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}0 & 0 & 0 & -1\\0 & 0 & 1 & 0\\0 & 1 & 0 & 0\\-1 & 0 & 0 & 0\end{pmatrix}$$

$$J_{AB}\hat{I}_z^A \otimes \hat{I}_z^B = \frac{J_{AB}}{4}\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\otimes\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}1\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} & 0\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\\0\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix} & -1\begin{pmatrix}1 & 0\\0 & -1\end{pmatrix}\end{pmatrix} = \frac{J_{AB}}{4}\begin{pmatrix}1 & 0 & 0 & 0\\0 & -1 & 0 & 0\\0 & 0 & -1 & 0\\0 & 0 & 0 & 1\end{pmatrix}$$

$$J_{AB}\left(\hat{I}_x^A \otimes \hat{I}_x^B + \hat{I}_y^A \otimes \hat{I}_y^B + \hat{I}_z^A \otimes \hat{I}_z^B\right) = J_{AB}\hat{I}^A \otimes \hat{I}^B = \frac{J_{AB}}{4}\begin{pmatrix}1 & 0 & 0 & 0\\0 & -1 & 2 & 0\\0 & 2 & -1 & 0\\0 & 0 & 0 & 1\end{pmatrix}$$

The magnetic Hamiltonian can now be written in Mathcad code.

$$\text{IzAIzB} := \frac{-1}{2}\cdot\begin{pmatrix} \nu_A+\nu_B & 0 & 0 & 0 \\ 0 & \nu_A-\nu_B & 0 & 0 \\ 0 & 0 & -\nu_A+\nu_B & 0 \\ 0 & 0 & 0 & -\nu_A-\nu_B \end{pmatrix} \qquad \text{IAIB} := \frac{J_{AB}}{4}\cdot\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad H_{mag} := \text{IzAIzB} + \text{IAIB}$$

$$H_{mag} \rightarrow \begin{pmatrix} \frac{-1}{2}\cdot\nu_A - \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB} & 0 & 0 & 0 \\ 0 & \frac{-1}{2}\cdot\nu_A + \frac{1}{2}\cdot\nu_B - \frac{1}{4}\cdot J_{AB} & \frac{1}{2}\cdot J_{AB} & 0 \\ 0 & \frac{1}{2}\cdot J_{AB} & \frac{1}{2}\cdot\nu_A - \frac{1}{2}\cdot\nu_B - \frac{1}{4}\cdot J_{AB} & 0 \\ 0 & 0 & 0 & \frac{1}{2}\cdot\nu_A + \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB} \end{pmatrix}$$

The eigenvalues of the magnetic energy matrix can now be calculated.

$$\text{eigenvals}(H_{mag}) \rightarrow \begin{bmatrix} \frac{-1}{2}\cdot\nu_A - \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB} \\ \frac{1}{2}\cdot\nu_A + \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB} \\ \frac{-1}{4}\cdot J_{AB} + \frac{1}{2}\cdot\left(J_{AB}^{\;2} + \nu_A^{\;2} - 2\cdot\nu_A\cdot\nu_B + \nu_B^{\;2}\right)^{\frac{1}{2}} \\ \frac{-1}{4}\cdot J_{AB} - \frac{1}{2}\cdot\left(J_{AB}^{\;2} + \nu_A^{\;2} - 2\cdot\nu_A\cdot\nu_B + \nu_B^{\;2}\right)^{\frac{1}{2}} \end{bmatrix}$$

We can also calculate the magnetic energy matrix elements individually, as follows.

$\alpha\alpha^T\cdot H_{mag}\cdot\alpha\alpha \rightarrow \frac{-1}{2}\cdot\nu_A - \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB}$ $\quad \alpha\beta^T\cdot H_{mag}\cdot\alpha\alpha \rightarrow 0$ $\quad \beta\alpha^T\cdot H_{mag}\cdot\alpha\alpha \rightarrow 0$ $\quad \beta\beta^T\cdot H_{mag}\cdot\alpha\alpha \rightarrow 0$

$\alpha\beta^T\cdot H_{mag}\cdot\alpha\beta \rightarrow \frac{-1}{2}\cdot\nu_A + \frac{1}{2}\cdot\nu_B - \frac{1}{4}\cdot J_{AB}$ $\quad \beta\alpha^T\cdot H_{mag}\cdot\alpha\beta \rightarrow \frac{1}{2}\cdot J_{AB}$ $\quad \beta\beta^T\cdot H_{mag}\cdot\alpha\beta \rightarrow 0$

$\beta\alpha^T\cdot H_{mag}\cdot\beta\alpha \rightarrow \frac{1}{2}\cdot\nu_A - \frac{1}{2}\cdot\nu_B - \frac{1}{4}\cdot J_{AB}$ $\quad \alpha\beta^T\cdot H_{mag}\cdot\beta\alpha \rightarrow \frac{1}{2}\cdot J_{AB}$ $\quad \beta\beta^T\cdot H_{mag}\cdot\beta\alpha \rightarrow 0$

$\beta\beta^T\cdot H_{mag}\cdot\beta\beta \rightarrow \frac{1}{2}\cdot\nu_A + \frac{1}{2}\cdot\nu_B + \frac{1}{4}\cdot J_{AB}$