

AB₂ Proton NMR Using Tensor Algebra

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The purpose of this tutorial is to deviate from the usual matrix mechanics approach to proton nmr in order to illustrate a related method of analysis which uses tensor algebra. For a discussion of the traditional approach visit <http://www.users.csbsju.edu/~frioux/nmr/SpecLab4.htm>. This site also provides general information on the quantum mechanics of nmr spectroscopy.

Nuclear spin operators and identity: $I_x := \frac{1}{2} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ $I_y := \frac{1}{2} \cdot \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$ $I_z := \frac{1}{2} \cdot \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ $I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

The following experimentally determined chemical shifts and coupling constant (all in Hz) are for the AB₂ proton system 1,1,2-trichloroethane at 60 MHz.

Chemical shifts and coupling constant: $\nu_A := 345.6$ $\nu_B := 237.6$ $J_{AB} := 6.1$

Hamiltonian representing the interaction of nuclear spins with the external magnetic field in tensor format:

$$\widehat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B - \nu_C \hat{I}_z^C = -\nu_A \hat{I}_z^A \otimes \hat{I} \otimes \hat{I} + \hat{I} \otimes (-\nu_B \hat{I}_z^B) \otimes \hat{I} + \hat{I} \otimes \hat{I} \otimes (-\nu_B \hat{I}_z^B)$$

where for example, $\nu_A = g_n \beta_n B_z (1 - \sigma_A)$

Implementing the operator using Mathcad's command for the tensor product, *kroncker*, is as follows.

$$H_{mag} := -\nu_A \cdot \text{kroncker}(I_z, \text{kroncker}(I, I)) - \nu_B \cdot \text{kroncker}(I, \text{kroncker}(I_z, I)) - \nu_B \cdot \text{kroncker}(I, \text{kroncker}(I, I_z))$$

Hamiltonian representing the interaction of nuclear spins with each other in tensor format:

$$\begin{aligned} \widehat{H}_{spin} &= J_{AB} \left(\hat{I}_x^A \otimes \hat{I}_x^B \otimes \hat{I} + \hat{I}_y^A \otimes \hat{I}_y^B \otimes \hat{I} + \hat{I}_z^A \otimes \hat{I}_z^B \otimes \hat{I} \right) \\ &+ J_{AB} \left(\hat{I}_x^A \otimes \hat{I} \otimes \hat{I}_x^B + \hat{I}_y^A \otimes \hat{I} \otimes \hat{I}_y^B + \hat{I}_z^A \otimes \hat{I} \otimes \hat{I}_z^B \right) \end{aligned}$$

Implementation of the operator in the Mathcad programming environment:

$$H_{spin} := J_{AB} \cdot \left(\text{kroncker}(I_x, \text{kroncker}(I_x, I)) + \text{kroncker}(I_y, \text{kroncker}(I_y, I)) + \text{kroncker}(I_z, \text{kroncker}(I_z, I)) \right) \dots \\ + \left[J_{AB} \cdot \left(\text{kroncker}(I_x, \text{kroncker}(I, I_x)) + \text{kroncker}(I_y, \text{kroncker}(I, I_y)) + \text{kroncker}(I_z, \text{kroncker}(I, I_z)) \right) \right]$$

The total Hamiltonian spin operator is now calculated and displayed. $H := H_{mag} + H_{spin}$

The indexing of the matrix elements of the Hamiltonian spin operator is discussed in the Appendix.

$$H = \begin{pmatrix} -407.35 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -172.8 & 0 & 0 & 3.05 & 0 & 0 & 0 \\ 0 & 0 & -172.8 & 0 & 3.05 & 0 & 0 & 0 \\ 0 & 0 & 0 & 61.75 & 0 & 3.05 & 3.05 & 0 \\ 0 & 3.05 & 3.05 & 0 & -67.85 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3.05 & 0 & 172.8 & 0 & 0 \\ 0 & 0 & 0 & 3.05 & 0 & 0 & 172.8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 413.45 \end{pmatrix}$$

Calculate and display the energy eigenvalues and associated eigenvectors of the Hamiltonian.

$$E := \text{sort}(\text{eigenvals}(H)) \quad C^{(i)} := \text{eigenvec}(H, E_i)$$

$$\text{augment}(E, C^T)^T = \begin{pmatrix} -407.35 & -172.977 & -172.8 & -67.673 & 61.583 & 172.8 & 172.967 & 413.45 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.707 & -0.707 & 0.029 & 0 & 0 & 0 & 0 \\ 0 & 0.707 & 0.707 & 0.029 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.999 & 0 & 0.039 & 0 \\ 0 & -0.041 & 0 & 0.999 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -0.027 & -0.707 & 0.707 & 0 \\ 0 & 0 & 0 & 0 & -0.027 & 0.707 & 0.707 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{matrix} \alpha\alpha\alpha \\ \alpha\alpha\beta \\ \alpha\beta\alpha \\ \alpha\beta\beta \\ \beta\alpha\alpha \\ \beta\alpha\beta \\ \beta\beta\alpha \\ \beta\beta\beta \end{matrix}$$

Notice that the ground state $|\alpha\alpha\alpha\rangle$ and the highest excited state $|\beta\beta\beta\rangle$ are pure states. The other six states are strictly speaking superpositions.

The nmr selection rule is that only one nuclear spin can flip during a transition. Therefore, the transition probability matrix for the ABC spin system is:

$$T := \begin{matrix} & \alpha\alpha\alpha & \alpha\alpha\beta & \alpha\beta\alpha & \alpha\beta\beta & \beta\alpha\alpha & \beta\alpha\beta & \beta\beta\alpha & \beta\beta\beta \\ \begin{pmatrix} 0 & 1.00 & 1.00 & 0 & 1.00 & 0 & 0 & 0 \\ 1.00 & 0 & 0 & 1.00 & 0 & 1.00 & 0 & 0 \\ 1.00 & 0 & 0 & 1.00 & 0 & 0 & 1.00 & 0 \\ 0 & 1.00 & 1.00 & 0 & 0 & 0 & 0 & 1.00 \\ 1.00 & 0 & 0 & 0 & 0 & 1.00 & 1.00 & 0 \\ 0 & 1.00 & 0 & 0 & 1.00 & 0 & 0 & 1.00 \\ 0 & 0 & 1.00 & 0 & 1.00 & 0 & 0 & 1.00 \\ 0 & 0 & 0 & 1.00 & 0 & 1.00 & 1.00 & 0 \end{pmatrix} & \alpha\alpha\alpha \\ & \alpha\alpha\beta \\ & \alpha\beta\alpha \\ & \alpha\beta\beta \\ & \beta\alpha\alpha \\ & \beta\alpha\beta \\ & \beta\beta\alpha \\ & \beta\beta\beta \end{matrix}$$

Calculate the intensities and frequencies of the allowed transitions.

$$i := 1..8 \quad j := 1..8 \quad I_{i,j} := [C^{(i)} \cdot (T \cdot C^{(j)})]^2 \quad V_{i,j} := |E_i - E_j|$$

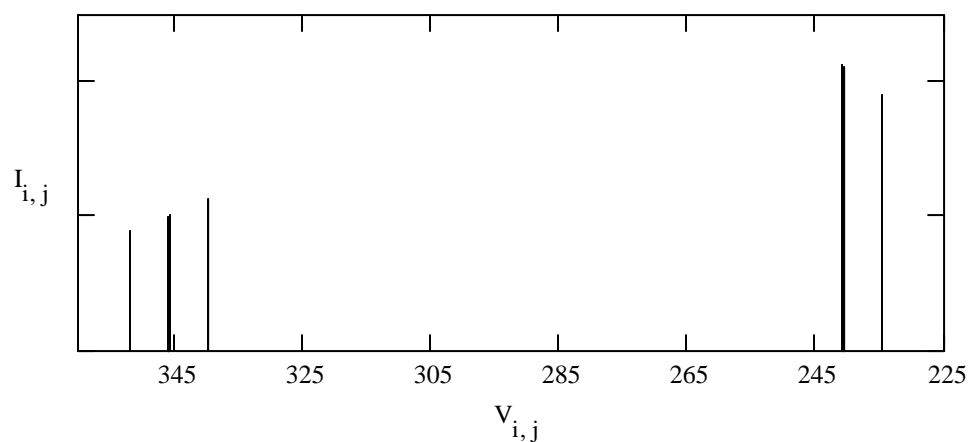
Intensity matrix:

$$I = \begin{pmatrix} 0 & 1.88 & 0 & 1.12 & 0 & 0 & 0 & 0 \\ 1.88 & 0 & 0 & 0 & 1.89 & 0 & 0.99 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1.12 & 0 & 0 & 0 & 0 & 0 & 2.12 & 0 \\ 0 & 1.89 & 0 & 0 & 0 & 0 & 0 & 0.89 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.99 & 0 & 2.12 & 0 & 0 & 0 & 2.11 \\ 0 & 0 & 0 & 0 & 0.89 & 0 & 2.11 & 0 \end{pmatrix}$$

Frequency matrix:

$$V = \begin{pmatrix} 0 & 234.37 & 234.55 & 339.68 & 468.93 & 580.15 & 580.32 & 820.8 \\ 234.37 & 0 & 0.18 & 105.3 & 234.56 & 345.78 & 345.94 & 586.43 \\ 234.55 & 0.18 & 0 & 105.13 & 234.38 & 345.6 & 345.77 & 586.25 \\ 339.68 & 105.3 & 105.13 & 0 & 129.26 & 240.47 & 240.64 & 481.12 \\ 468.93 & 234.56 & 234.38 & 129.26 & 0 & 111.22 & 111.38 & 351.87 \\ 580.15 & 345.78 & 345.6 & 240.47 & 111.22 & 0 & 0.17 & 240.65 \\ 580.32 & 345.94 & 345.77 & 240.64 & 111.38 & 0.17 & 0 & 240.48 \\ 820.8 & 586.43 & 586.25 & 481.12 & 351.87 & 240.65 & 240.48 & 0 \end{pmatrix}$$

Display the calculated vinyl acetate nmr spectrum:



The calculated spectrum compares favorably with experimental spectrum, indicating that the spin Hamiltonian used adequately represents the magnetic interaction of the protons in 1,1,2-trichloroethane at 60 MHz.

Appendix

The tensor product of three spinors is shown below.

$$\begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} c \\ d \end{pmatrix} \otimes \begin{pmatrix} e \\ f \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} ce \\ cf \\ de \\ df \end{pmatrix} = \begin{pmatrix} ace \\ acf \\ ade \\ adf \\ bce \\ bcf \\ bde \\ bdf \end{pmatrix}$$

Mathcad does not have a command for this type of vector tensor product, so it is necessary to develop a way of implementing it using *kroncker*, which requires square matrices. For this reason the spin vector is stored in the left column of a 2x2 matrix by augmenting the spin vector with the null vector. After all the matrix tensor products have been carried out using *kroncker* the final spin vector resides in the left column of the final square matrix. Next the *submatrix* command is used to save this column, discarding the rest of the matrix.

Spin-up in the z-direction: $\alpha := \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ Spin-down in the z-direction: $\beta := \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ Null vector: $N := \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

The eight possible spin states of a three-proton system are calculated as shown below.

$$\Psi(a, b, c) := \text{submatrix}(\text{kroncker}(\text{augment}(a, N), \text{kroncker}(\text{augment}(b, N), \text{augment}(c, N))), 1, 8, 1, 1)$$

$$\begin{aligned} \Psi(\alpha, \alpha, \alpha)^T &= (1 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0) & \Psi(\alpha, \alpha, \beta)^T &= (0 \ 1 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0) \\ \Psi(\alpha, \beta, \alpha)^T &= (0 \ 0 \ 1 \ 0 \ 0 \ 0 \ 0 \ 0) & \Psi(\alpha, \beta, \beta)^T &= (0 \ 0 \ 0 \ 1 \ 0 \ 0 \ 0 \ 0) \\ \Psi(\beta, \alpha, \alpha)^T &= (0 \ 0 \ 0 \ 0 \ 1 \ 0 \ 0 \ 0) & \Psi(\beta, \alpha, \beta)^T &= (0 \ 0 \ 0 \ 0 \ 0 \ 1 \ 0 \ 0) \\ \Psi(\beta, \beta, \alpha)^T &= (0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 1 \ 0) & \Psi(\beta, \beta, \beta)^T &= (0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 0 \ 1) \end{aligned}$$

Thus the indexing in Hamiltonian matrix is: $|\alpha\alpha\alpha\rangle, |\alpha\alpha\beta\rangle, |\alpha\beta\alpha\rangle, |\alpha\beta\beta\rangle, |\beta\alpha\alpha\rangle, |\beta\alpha\beta\rangle, |\beta\beta\alpha\rangle, |\beta\beta\beta\rangle$.