

AB Proton NMR Using Tensor Algebra

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The purpose of this tutorial is to deviate from the usual matrix mechanics approach to the ABC proton nmr system in order to illustrate a related method of analysis which uses tensor algebra. For a discussion of the traditional approach for the ABC system 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 and identity operators:
$$I_x := \frac{1}{2} \cdot \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y := \frac{1}{2} \cdot \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad I_z := \frac{1}{2} \cdot \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Chemical shifts: $\nu_A := 250$ $\nu_B := 300$ Coupling constant: $J_{AB} := 10$

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

$$\widehat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B = -\nu_A \hat{I}_z^A \otimes \hat{I} + \hat{I} \otimes (-\nu_B \hat{I}_z^B) \quad \text{where for example,} \quad \nu_A = g_n \beta_n B_z (1 - \sigma_A)$$

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

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

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

$$\widehat{H}_{spin} = J_{AB} (\hat{I}_x^A \otimes \hat{I}_x^B + \hat{I}_y^A \otimes \hat{I}_y^B + \hat{I}_z^A \otimes \hat{I}_z^B)$$

Implementation of the operator in the Mathcad programming environment:

$$H_{spin} := J_{AB} \cdot (\text{kroncker}(I_x, I_x) + \text{kroncker}(I_y, I_y) + \text{kroncker}(I_z, I_z))$$

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

$$H = \begin{matrix} & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ \begin{pmatrix} -272.5 & 0 & 0 & 0 \\ 0 & 22.5 & 5 & 0 \\ 0 & 5 & -27.5 & 0 \\ 0 & 0 & 0 & 277.5 \end{pmatrix} & \alpha\alpha \\ & \alpha\beta \\ & \beta\alpha \\ & \beta\beta \end{matrix}$$

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

$$i := 1..4 \quad E := \text{sort}(\text{eigenvals}(H)) \quad C^{(i)} := \text{eigenvec}(H, E_i)$$

$$\text{augment}(E, C^T)^T = \begin{pmatrix} -272.5 & -27.995 & 22.995 & 277.5 \\ 1 & 0 & 0 & 0 \\ 0 & -0.099 & 0.995 & 0 \\ 0 & 0.995 & 0.099 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{matrix} \alpha\alpha \\ \alpha\beta \\ \beta\alpha \\ \beta\beta \end{matrix}$$

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

$$T = \begin{pmatrix} & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ \alpha\alpha & 0 & 1 & 1 & 0 \\ \alpha\beta & 1 & 0 & 0 & 1 \\ \beta\alpha & 1 & 0 & 0 & 1 \\ \beta\beta & 0 & 1 & 1 & 0 \end{pmatrix} \quad T := \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

Calculate the intensities and frequencies of the allowed transitions.

$$i := 1..4 \quad j := 1..4 \quad I_{i,j} := [C^{(i)} \cdot (T \cdot C^{(j)})]^2 \quad V_{i,j} := \text{if}(I_{i,j} > .001, |E_i - E_j|, 0)$$

Intensity matrix: $I = \begin{pmatrix} 0 & 0.8 & 1.2 & 0 \\ 0.8 & 0 & 0 & 0.8 \\ 1.2 & 0 & 0 & 1.2 \\ 0 & 0.8 & 1.2 & 0 \end{pmatrix}$ Frequency matrix: $V = \begin{pmatrix} 0 & 244.5 & 295.5 & 0 \\ 244.5 & 0 & 0 & 305.5 \\ 295.5 & 0 & 0 & 254.5 \\ 0 & 305.5 & 254.5 & 0 \end{pmatrix}$

Display the calculated AB nmr spectrum:

