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

Chemical shifts: $\nu_A := 250$ $\nu_B := 300$ Coupling constant: $Jab := 10$

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

$$\hat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B = -\nu_A \hat{I}_z^A \otimes \hat{I} + \hat{I} \otimes \left(-\nu_B \hat{I}_z^B\right)$$ 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, *kronecker*, is as follows.

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

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

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

Implementation of the operator in the Mathcad programming environment:

$$H_{spin} := Jab \cdot \left(\text{kronecker}(I_x, I_x) + \text{kronecker}(I_y, I_y) + \text{kronecker}(I_z, I_z)\right)$$

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

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

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

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

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

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:

$$T = \begin{pmatrix} ' & \alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\ \alpha\alpha & 0 & 1 & 1 & 0 \\ \alpha\beta & 1 & 0 & 0 & 1 \\ \beta\alpha & 1 & 0 & 0 & 1 \\ \beta\beta & 0 & 1 & 1 & 0 \end{pmatrix} \qquad T := \begin{pmatrix} 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \end{pmatrix}$$

Calculate the intensities and frequencies of the allowed transitions.

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

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: