4.21: Calculating the AB Proton NMR Using Tensor Algebra

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

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

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

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

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

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

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

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

Implementation of the operator in the Mathcad programming environment:

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

The total Hamiltonian spin operator is now calculated and displayed.

$$H = H_{mag} + H_{spin}$$

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

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

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

$$\mathrm{augment}(E,\ C^T)^T = \begin{pmatrix} -272.5 & -27.995 & 22.995 & 277.5 \\ 1 & 0 & 0 & 0 \\ 0 & -0.099 & 0.995 & 0 \\ 0 & 0.005 & 0.099 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{matrix} \alpha\alpha \\ \alpha\beta \\ \beta\alpha \\ \beta\beta \end{matrix}$$

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.

$$i = 1..4 \quad j = 1..4 \quad I_{i,j} = \left[C^{<i>}\left(TC^{<j>}\right)\right]^2 \quad V_{i,j} = \mathrm{if}\left(I_{i,j} > .001,\ |E_i - E_j|,\ 0\right)$$

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: $V = \begin{pmatrix} 0 & 244.5 & 295.5 & 0 \\ 244.5 & 0 & 0 & 244.5 \\ 295.5 & 0 & 0 & 254.5 \\ 0 & 305.5 & 254.5 & 0 \end{pmatrix}$

Display the calculated AB nmr spectrum: