AB Proton NMR Using Tensor Algebra

Frank Rioux
Professor Emeritus of Chemistry
CSB|SJU

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:

\[
I_x := \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad I_y := \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad I_z := \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad I := \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

Chemical shifts:

\[
\nu_A := 250, \quad \nu_B := 300
\]

Coupling constant:

\[
J_{ab} := 10
\]

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

\[
\hat{H}_{mag} = -\nu_A \hat{I}_z^A - \nu_B \hat{I}_z^B = -\nu_A \hat{I}_z^A \otimes \hat{I} + \hat{I} \otimes (-\nu_B \hat{I}_z^B)
\]

where for example,

\[
\nu_A = g_n \beta_n B \left(1 - \sigma_A \right)
\]

Implementing the operator using Mathcad's command for the tensor product, \texttt{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:

\[
H_{spin} := J_{ab} \cdot \left( \text{kronecker}(I_x, I_x) + \text{kronecker}(I_y, I_y) + \text{kronecker}(I_z, I_z) \right)
\]

The total Hamiltonian spin operator is now calculated and displayed.

\[
H := H_{mag} + H_{spin}
\]

\[
H = \begin{pmatrix}
-272.5 & 0 & 0 & 0 \\
0 & 22.5 & 5 & 0 \\
0 & 5 & -27.5 & 0 \\
0 & 0 & 0 & 277.5 \\
\end{pmatrix}
\]

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

\[
i := 1..4 \quad E := \text{sort(eigvals}(H)) \quad C^{(i)} := \text{eigvec}(H, E_i)
\]
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:

\[
T = \begin{pmatrix}
\alpha\alpha & \alpha\beta & \beta\alpha & \beta\beta \\
\alpha\alpha & 0 & 1 & 1 \\
\alpha\beta & 1 & 0 & 0 \\
\beta\alpha & 1 & 0 & 0 \\
\beta\beta & 0 & 1 & 1
\end{pmatrix}
\]

\[
T := \begin{pmatrix}
0 & 1 & 1 & 0 \\
1 & 0 & 0 & 1 \\
1 & 0 & 0 & 1 \\
0 & 1 & 1 & 0
\end{pmatrix}
\]

Calculate the intensities and frequencies of the allowed transitions.

\[
i := 1, 4 \quad j := 1, 4 \quad I_{i,j} := \left[ C_i \cdot (T \cdot C_j) \right]^2 \quad V_{i,j} := \text{if}(I_{i,j} > .001, \vert E_i - E_j \vert, 0)
\]

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: