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.

\[
\begin{matrix}
\text{Nuclear spin and identity operators:} & I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} & I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
\text{Chemical shifts:} & \nu_A = 250 & \nu_B = 300 & \text{Coupling constant:} & \text{Jab} = 10
\end{matrix}
\]

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

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

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

\[
H_{mag} = - \nu_A \text{kronecker}(I_z, I) - \nu_B \text{kronecker}(I, I_z)
\]

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

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

Implementation of the operator in the Mathcad programming environment:

\[
H_{spin} = \text{Jab} \left( \text{kronecker}(I_x, I_x) + \text{kronecker}(I_y, I_y) + \text{kronecker}(I_z, I_z) \right)
\]

The total Hamiltonian spin operator is now calculated and displayed.

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

\[
\begin{array}
\alpha \alpha \alpha & \alpha \beta & \beta \alpha & \beta \beta \\
\begin{pmatrix}
-272.5 & 0 & 0 & 0 \\
0 & 22.5 & 5 & 0 \\
0 & 5 & -27.5 & 0 \\
0 & 0 & 0 & 277.5
\end{pmatrix}
\end{array}
\]

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

\[
i = 1 \ldots 4 & E = \text{sort(eigenvals(H))} & C^{<i>} = \text{eigenvec}(H, E_i) \end{matrix}
\]

\[
\begin{array}
\alpha \alpha \alpha & \alpha \beta & \beta \alpha & \beta \beta \\
\begin{pmatrix}
-272.5 & -27.995 & 22.995 & 277.5 \\
1 & 0 & 0 & 0 \\
0 & 0.099 & 0.995 & 0 \\
0 & 0.005 & 0.099 & 0
\end{pmatrix}
\end{array}
\]

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:

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

Calculate the intensities and frequencies of the allowed transitions.

\[
I_{i,j} = \left[ C^{<i>} \left( TC^{<j>} \right) \right]^2 \quad \text{and} \quad V_{i,j} = \begin{cases} 
\left| E_i - E_j \right|, & \text{if } I_{i,j} > 0.001 \\
0, & \text{otherwise}
\end{cases}
\]

Display the calculated AB nmr spectrum: