AB_3 Proton NMR Using Tensor Algebra

Frank Rioux
Professor Emeritus of Chemistry
CSB|SJU

The purpose of this tutorial is to calculate the NMR spectrum of a four proton AB_3 system.

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

The following experimentally determined chemical shifts and coupling constant (all in Hz) are for the AB_3 proton system 1,1-dichloroethane at 60 MHz.

$\nu_A := 350.0$ $\nu_B := 120.0$ $Jab := 10.00$

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

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

Hamiltonian representing the nuclear spin-spin interaction in tensor format:

$$H_{spin} := Jab\cdot\left(\begin{matrix}kronecker(I_x, kronecker(I_x, kronecker(I, I))) + kronecker(I_y, kronecker(I_y, kronecker(I, I))) \ldots\\ + kronecker(I_z, kronecker(I_z, kronecker(I, I)))\end{matrix}\right) \ldots$$
$$+ Jab\cdot\left(\begin{matrix}kronecker(I_x, kronecker(I, kronecker(I_x, I))) + kronecker(I_y, kronecker(I, kronecker(I_y, I))) \ldots\\ + kronecker(I_z, kronecker(I, kronecker(I_z, I)))\end{matrix}\right) \ldots$$
$$+ Jab\cdot\left(\begin{matrix}kronecker(I_x, kronecker(I, kronecker(I, I_x))) + kronecker(I_y, kronecker(I, kronecker(I, I_y))) \ldots\\ + kronecker(I_z, kronecker(I, kronecker(I, I_z)))\end{matrix}\right)$$

Total Hamiltonian operator: $H := H_{mag} + H_{spin}$ $i := 1 .. 16$ $E := sort(eigenvals(H))$ $C^{\langle i\rangle} := eigenvec(H, E_i)$

The first half of the results matrix:

$augment(E, C^T)^T =$

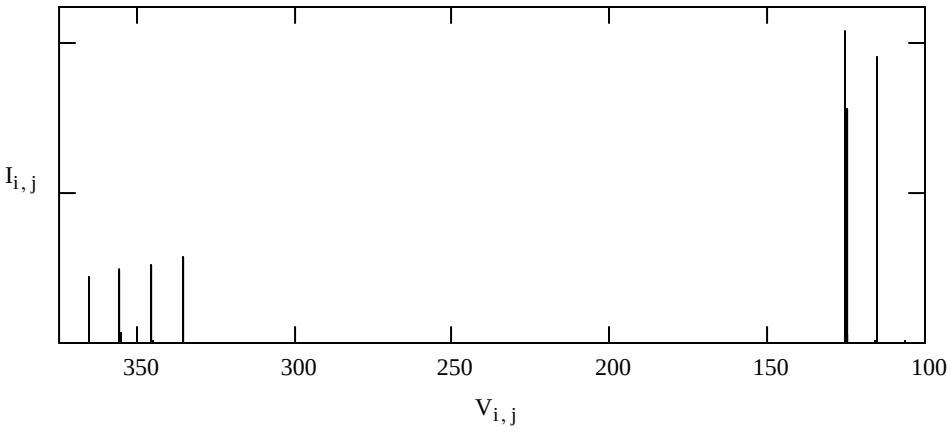
-347.5	-232.84	-232.5	-232.5	-117.93	-117.61	-117.61	-12.16	-2.81
1	0	0	0	0	0	0	0	0
0	0.58	-0.76	-0.76	0	0	0	0.02	0
0	0.58	0.11	0.11	0	0	0	0.02	0
0	0	0	0	0.58	-0.18	-0.18	0	0
0	0.58	0.64	0.64	0	0	0	0.02	0
0	0	0	0	0.58	-0.6	-0.6	0	0
0	0	0	0	0.58	0.78	0.78	0	0
0	0	0	0	0	0	0	0	1
0	-0.04	0	0	0	0	0	1	0
0	0	0	0	-0.03	0.02	0.02	0	0
0	0	0	0	-0.03	-0.01	-0.01	0	0
0	0	0	0	0	0	0	0	-0.02
0	0	0	0	-0.03	-0	-0	0	0
0	0	0	0	0	0	0	0	-0.02
0	0	0	0	0	0	0	0	-0.02

The nmr selection rule is that only one nuclear spin can flip during a transition. Therefore, the transition probability matrix for the four spin system is shown below. See the Appendix for detail on how this matrix is constructed.

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

Calculate the intensities and frequencies of the allowed transitions, and display the spectrum.

$i := 1 .. 16$ $\quad$ $j := 1 .. 16$ $\quad$ $I_{i,j} := \left[C^{\langle i \rangle} \cdot \left(T \cdot C^{\langle j \rangle}\right)\right]^2$ $\quad$ $V_{i,j} := \left|E_i - E_j\right|$



Appendix

The construction of the transition probability matrix requires the proper indexing of the 16 spin states of the four proton system. In tensor format the states are represented in this manner.

$$\begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} c \\ d \end{pmatrix} \otimes \begin{pmatrix} e \\ f \end{pmatrix} \otimes \begin{pmatrix} g \\ h \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} c \\ d \end{pmatrix} \otimes \begin{pmatrix} eg \\ eh \\ fg \\ fh \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \otimes \begin{pmatrix} ceg \\ ceh \\ cfg \\ cfh \\ deg \\ deh \\ dfg \\ dfh \end{pmatrix} = \begin{pmatrix} aceg \\ aceh \\ acfg \\ acfh \\ adeg \\ adeh \\ adfg \\ adfh \\ bceg \\ bceh \\ bcfg \\ bcfh \\ bdeg \\ bdeh \\ bdfg \\ bdfh \end{pmatrix}$$

Mathcad does not have a command for this type of vector tensor product, so it is necessary to develop a way of implementing it using *kronecker*, which requires square matrices. For this reason the spin vector is stored in the left column of a 2x2 matrix by augmenting the spin vector with the null vector. After all the matrix tensor products have been carried out using *kronecker* the final spin vector resides in the left column of the final square matrix. Next the *submatrix* cammand is used to save this column, discarding the rest of the matrix.

Spin-up in the z-direction: $\alpha := \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ Spin-down in the z-direction: $\beta := \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ Null vector: $N := \begin{pmatrix} 0 \\ 0 \end{pmatrix}$

The 16 possible spin states of a three-proton system are calculated as shown below.

$$\Psi(a,b,c,d) := \text{submatrix}(\text{kronecker}(\text{augment}(a,N),\text{kronecker}(\text{augment}(b,N),\text{kronecker}(\text{augment}(c,N),\text{augment}(d,N)))),1,16,1,1)$$

Representing the spin states in tensor format facillitates their proper indexing and the formation of the transition probability matrix.

$$\begin{pmatrix} \Psi(\alpha,\alpha,\alpha,\alpha)^T \\ \Psi(\alpha,\alpha,\alpha,\beta)^T \\ \Psi(\alpha,\alpha,\beta,\alpha)^T \\ \Psi(\alpha,\alpha,\beta,\beta)^T \\ \Psi(\alpha,\beta,\alpha,\alpha)^T \\ \Psi(\alpha,\beta,\alpha,\beta)^T \\ \Psi(\alpha,\beta,\beta,\alpha)^T \\ \Psi(\alpha,\beta,\beta,\beta)^T \\ \Psi(\beta,\alpha,\alpha,\alpha)^T \\ \Psi(\beta,\alpha,\alpha,\beta)^T \\ \Psi(\beta,\alpha,\beta,\alpha)^T \\ \Psi(\beta,\alpha,\beta,\beta)^T \\ \Psi(\beta,\beta,\alpha,\alpha)^T \\ \Psi(\beta,\beta,\alpha,\beta)^T \\ \Psi(\beta,\beta,\beta,\alpha)^T \\ \Psi(\beta,\beta,\beta,\beta)^T \end{pmatrix} = \begin{bmatrix} (1&0&0&0&0&0&0&0&0&0&0&0&0&0&0&0) \\ (0&1&0&0&0&0&0&0&0&0&0&0&0&0&0&0) \\ (0&0&1&0&0&0&0&0&0&0&0&0&0&0&0&0) \\ (0&0&0&1&0&0&0&0&0&0&0&0&0&0&0&0) \\ (0&0&0&0&1&0&0&0&0&0&0&0&0&0&0&0) \\ (0&0&0&0&0&1&0&0&0&0&0&0&0&0&0&0) \\ (0&0&0&0&0&0&1&0&0&0&0&0&0&0&0&0) \\ (0&0&0&0&0&0&0&1&0&0&0&0&0&0&0&0) \\ (0&0&0&0&0&0&0&0&1&0&0&0&0&0&0&0) \\ (0&0&0&0&0&0&0&0&0&1&0&0&0&0&0&0) \\ (0&0&0&0&0&0&0&0&0&0&1&0&0&0&0&0) \\ (0&0&0&0&0&0&0&0&0&0&0&1&0&0&0&0) \\ (0&0&0&0&0&0&0&0&0&0&0&0&1&0&0&0) \\ (0&0&0&0&0&0&0&0&0&0&0&0&0&1&0&0) \\ (0&0&0&0&0&0&0&0&0&0&0&0&0&0&1&0) \\ (0&0&0&0&0&0&0&0&0&0&0&0&0&0&0&1) \end{bmatrix}$$

'	αααα	αααβ	ααβα	ααββ	αβαα	αβαβ	αββα	αβββ	βααα	βααβ	βαβα	βαββ	ββαα	ββαβ	βββα	ββββ
αααα	0	1	1	0	1	0	0	0	1	0	0	0	0	0	0	0
αααβ	1	0	0	1	0	1	0	0	0	1	0	0	0	0	0	0
ααβα	1	0	0	1	0	0	1	0	0	0	1	0	0	0	0	0
ααββ	0	1	1	0	0	0	0	1	0	0	0	1	0	0	0	0
αβαα	1	0	0	0	0	1	1	0	0	0	0	0	1	0	0	0
αβαβ	0	1	0	0	1	0	0	1	0	0	0	0	0	1	0	0
αββα	0	0	1	0	1	0	0	1	0	0	0	0	0	0	1	0
αβββ	0	0	0	1	0	1	1	0	0	0	0	0	0	0	0	1
βααα	1	0	0	0	0	0	0	0	0	1	1	0	1	0	0	0
βααβ	0	1	0	0	0	0	0	0	1	0	0	1	0	1	0	0
βαβα	0	0	1	0	0	0	0	0	1	0	0	1	0	0	1	0
βαββ	0	0	0	1	0	0	0	0	0	1	1	0	0	0	0	1
ββαα	0	0	0	0	1	0	0	0	1	0	0	0	0	1	1	0
ββαβ	0	0	0	0	0	1	0	0	0	1	0	0	1	0	0	1
βββα	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	1
ββββ	0	0	0	0	0	0	0	1	0	0	0	1	0	1	1	0