4.19: NMR - Quantum Mechanics of a Three Proton System

In this computer/spectroscopy lab the variational method is used to determine the nuclear spin states and allowed transitions in a three proton spin system. The theoretical procedure is essentially the same as that used in the other applications of the variational method that we have studied (LCAO-MO for H_2^+, Roothaan SCF, and various examples presented in class).

To prepare for this lab study the section on NMR in your textbook and review your class notes on the quantum mechanical treatment of the NMR spectroscopy of one- and two-proton systems. This lab will compare the low field NMR spectra of vinyl acetate and acrylonitrile. The high field (300 MHz) NMR spectrum of acrylonitrile will be measured and analyzed, and compared to the 60 MHz spectra of vinyl acetate and acrylonitrile.

The major steps in this exercise are listed below. Further detail is provided following the list. As you examine this sequence of steps you will see the similarities with previous variational calculations that we have looked at in class and lab.

1. Choose a trial nuclear spin wavefunction.
2. Write the energy operator for the three spin system which includes all the pertinent interactions.
3. Input parameters (in this case chemical shifts and coupling constants) and evaluate the matrix elements of the secular determinant for the system.
4. Solve the secular determinant for the energy eigenvalues and eigenfunctions.
5. Using the appropriate selection rule, $DI_z = \blacklozenge 1$, construct a transition probability matrix.
6. Using the results from parts 4 and 5 above, calculate the allowed transitions and their intensities and then generate a model spectrum.
7. Compare the theoretical generated spectrum with the experimentally determined NMR spectrum.

Fortunately for us, the computer does most of the work and certainly all the difficult math in this exercise.

1. A molecule with three protons can be in any of eight possible spin states. To determine these states we choose as our trial wavefunction the following linear combination.

$$|\Psi_{spin}\rangle = c_1|\alpha\alpha\alpha\rangle + c_2|\alpha\alpha\beta\rangle + c_3|\alpha\beta\alpha\rangle + c_4|\beta\alpha\alpha\rangle + c_5|\alpha\beta\beta\rangle + c_6|\beta\alpha\beta\rangle + c_7|\beta\beta\alpha\rangle + c_8|\beta\beta\beta\rangle$$

   In this particular notation, |aaa> stands for all three nuclear spins in the spin-up ($I_z = +\blacklozenge$) spin state, while |aba> indicates that nuclei 1 and 3 are in the spin-up state and nucleus 2 is in the spin-down state ($I_z = -\blacklozenge$). In the absence of an external magnetic field and any interaction between the protons, all eight states have the same energy.

2. The complete energy operator is the sum of equations (3) and (4). There is a term like (3) for each proton and there is a term like (4) for each distinct pair of protons. For a three proton system, ABC, we have,

$$\hat{H}_{mag} = -g_n\beta_n\hat{B}_z\left[(1-\sigma_a)\hat{I}_z(a) + (1-\sigma_b)\hat{I})_z(b) + (1-\sigma_c)\hat{I}_z(c)\right] + \hat{J}_{ab}\hat{I}_a\hat{I}_b + J_{ac}\hat{I}_a\hat{I}_c + J_{bc}\hat{I}_b\hat{I}_c$$

3. We are now ready to apply the variational method as outlined earlier in your text. The variational integral for this application is

$$E = \langle\Psi_{spin}|\hat{H}_{mag}|\Psi_{spin}\rangle$$

   Treatment of this integral by the usual techniques yields an 8 x 8 secular determinant of the form:

$$\begin{vmatrix} H_{11}-E & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & H_{22}-E & \frac{J_{bc}}{2} & \frac{J_{ac}}{2} & 0 & 0 & 0 & 0 \\ 0 & \frac{J_{bc}}{2} & H_{33}-E & \frac{J_{ab}}{b} & 0 & 0 & 0 & 0 \\ 0 & \frac{J_{ac}}{2} & \frac{J_{ab}}{2} & H_{44}-E & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & H_{55}-E & \frac{J_{ab}}{2} & \frac{J_{ac}}{2} & 0 \\ 0 & 0 & 0 & 0 & \frac{J_{ab}}{2} & H_{66}-E & \frac{J_{bc}}{2} & 0 \\ 0 & 0 & 0 & 0 & \frac{J_{ac}}{2} & \frac{J_{bc}}{2} & H_{\eta}-E & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & H_{88}-E \end{vmatrix} = 0$$

   where the diagonal matrix elements are, for example, of the form

$$H_{11} = \tfrac{1}{2}[v_a + v_b + v_c] + \tfrac{1}{4}[J_{ab} + J_{ac} + J_{bc}]$$

$$H_{22} = \tfrac{1}{2}[v_a + v_b - v_c] + \tfrac{1}{4}[J_{ab} - J_{ac} - J_{bc}]$$

$$\vdots$$

$$H_{88} = \tfrac{1}{2}[-v_a - v_b - v_c] + \tfrac{1}{4}[J_{ab} + J_{ac} + J_{bc}]$$

Here the n_i represent the terms $g_n\, b_n\, (1 - s_i)\, B_z$ which are the resonant frequencies of the protons in their respective chemical environments. The various matrix elements can be evaluated once the chemical shifts and coupling constants are supplied.

4. The Mathcad document which is appended solves the secular determinant (7) after chemical shifts and coupling constants are provided. It yields the nuclear spin energy levels, their associated wavefunctions, the allowed transitions between these levels, the frequencies at which the transitions occur and their intensities. It also generates a model spectrum. Study the Mathcad document to make certain you understand each of the steps in this quantum mechanical calculation.

5. The calculation of the allowed transitions deserves further comment. Because the three proton system has eight spin states, there are 28 potential transitions amongst these energy levels. How many transitions are actually observed and at what intensities is determined by the selection rule for NMR spectroscopy. This selection rule states that only one spin can be *flipped* in any given transition. In other words D I_z = � 1.
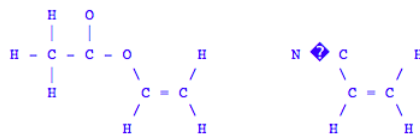
A transition is allowed if the product of the three matrices shown below is non-zero. The intensity of the transition is equal to the square of the product of these matrices.

$$
\begin{pmatrix} c_1 & c_2 & c_3 & c_4 & c_5 & c_6 & c_7 & c_8 \end{pmatrix}
\begin{pmatrix}
0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 \\
1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 \\
0 & 1 & 1 & 0 & 0 & 0 & 0 & 1 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 1 \\
0 & 0 & 1 & 1 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 1 & 1 & 1 & 0
\end{pmatrix}
\begin{pmatrix} c'_1 \\ c'_2 \\ c'_3 \\ c'_4 \\ c'_5 \\ c'_6 \\ c'_7 \\ c'_8 \end{pmatrix}
$$

For example this matrix determines whether the transition from state 1 to state 2 is allowed. The matrix on the left contains the coefficients of the wavefunction of state 1 written in row-matrix form, while the matrix on the right contains the coefficients of the wavefunction of state 2 written in column-matrix form. The center matrix is the transition matrix and is an 8x8 square matrix which summarizes the allowed transitions. For example, the (1,1) matrix element represents the |aaa> ---> |aaa> transition and is 0 because it violates the selection rule (no spins are flipped). However, the (1,2) matrix element is 1 because the transition |aaa> ---> |aab> is allowed (only one spin is flipped). Following the rules of matrix multiplication, Mathcad examines each possible transition. If its intensity is non-zero it makes a record of it and later displays the transition in tabular and graphical form. For example, the matrix product shown below indicates that the |aaa> ---> |bbb> transition is forbidden.

Experimental:

The 300 MHz NMR spectrum of acrylonitrile will be measured and compared to its 60 MHz NMR and also to the 60 MHz spectrum of vinyl acetate.
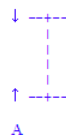

The methyl protons are not coupled to the vinyl protons so it is possible to treat the vinyl protons as an ABC system. The low field (60 MHz) NMR spectra of acrylonitrile and vinyl acetate are shown below.

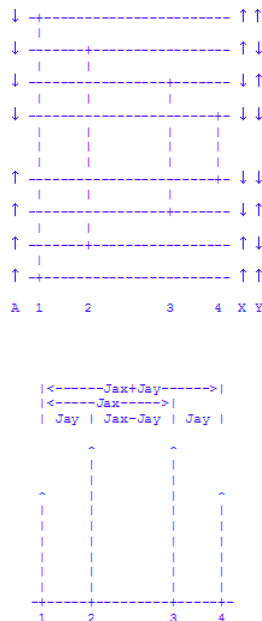**Interpretation of the Spectrum**

Acrylonitrile is a true ABC system while the vinyl protons of vinyl acetate behave like an ABC system because they are not coupled to the methyl protons. Vinyl acetate presents a classic ABC spectrum. Each proton has a distinct chemical shift and each proton's resonance is split by the two other protons. Thus what is observed is a spectrum which consists of three separate

resonances each of which is a quartet of peaks (a doublet of doublets). The chemical shifts are obtained by locating the center of the doublet of doublets. The determination of the coupling constants is described below.

In the absence of any coupling the resonance of an individual proton, A, would appear as a singlet.

```
↓ --+--
     |
     |
↑ --+--

A
```

The presence of two non-equivalent protons, X and Y , splits A's singlet into a quartet of peaks as shown in the diagram below. This occurs because there are four possible orientations of the non-equivalent protons (up-up, up-down, down-up, down-down) and, therefore, both the ground state and excited state of proton A are split into four levels.

```
↓ +--------------------- ↑↑
  |
↓ -------+--------------- ↑↓
  |      |
↓ ---------------------+------- ↓↑
  |      |           |
↓ ---------------------+--- ↓↓
  |      |      |     |
  |      |      |     |
  |      |      |     |
↑ ---------------------+--- ↓↓
  |      |      |
↑ ---------------------+------- ↓↑
  |      |
↑ -------+--------------- ↑↓
  |
↑ +--------------------- ↑↑

A   1    2        3     4  X Y
```

```
|<------Jax+Jay------>|
|<-----Jax---->|
| Jay | Jax-Jay | Jay |
       ^          ^
       |          |
 ^     |          |    ^
 |     |          |    |
 |     |          |    |
 |     |          |    |
 +-----+----------+----+-
 1     2          3    4
```
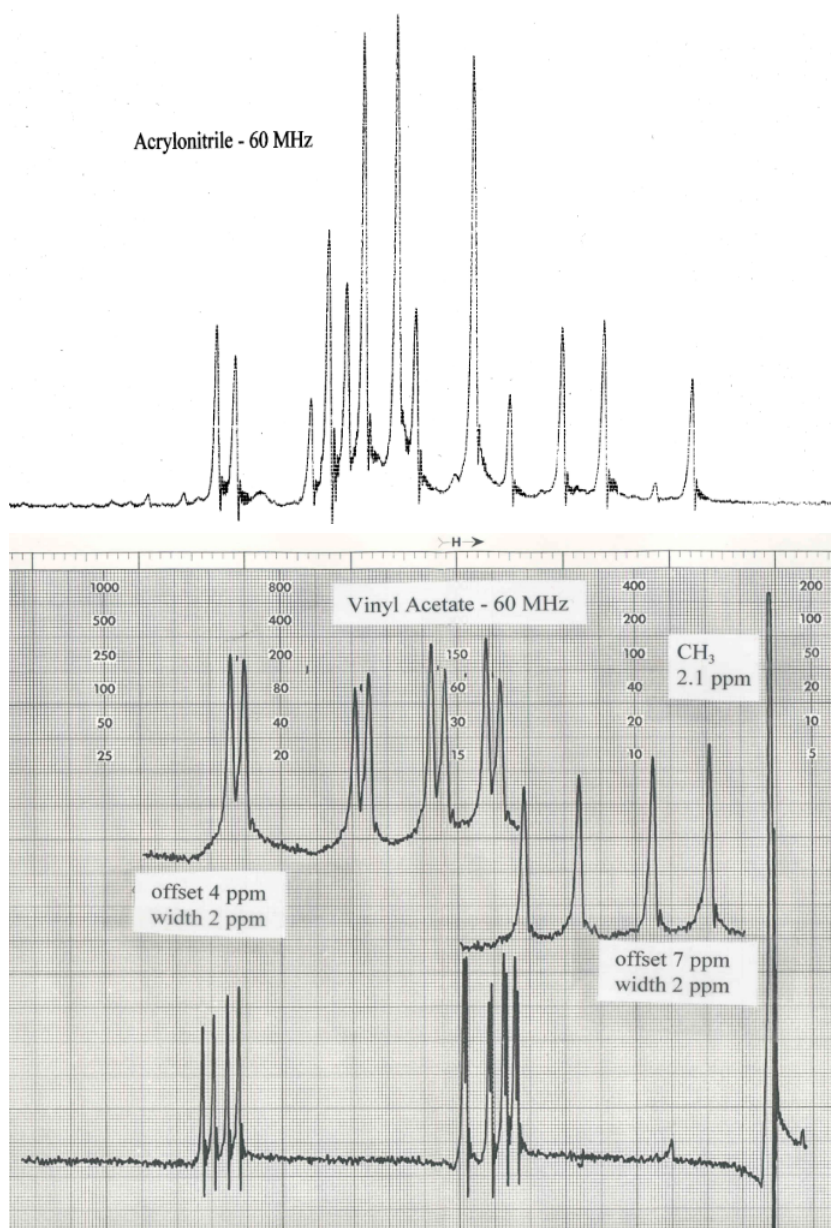
Remember that it is proton A that is undergoing the resonance and that the spins of X and Y don't flip during A's resonance. That is why there are only four transitions amongst these eight states. Note that the difference between transition 1 and 2 is the spin state of proton Y. Thus the frequency difference between these peaks is the coupling constant J_{ay} expressed in hertz. Similarly, the difference between 3 and 4 is J_{ay}, the difference between 1 and 3 is J_{ax}, the difference between 2 and 4 is J_{ax}, the difference between 1 and 4 is $J_{ax} + J_{ay}$, and the difference between 2 and 3 is $J_{ax} - J_{ay}$. Similar arguments would be used to discuss the resonances of protons B and C.

To obtain the three coupling constants for vinyl acetate use the following procedure. Label the doublet of doublets farthest down field "A", the middle one "B" and the last one "C". The analysis described above provides you with two direct measurements of two coupling constants. For example, J_{ab} and J_{ac} can be obtained from the analysis of the "A" resonance but you don't know which proton is "B" and which one is "C" at this point. However, the analysis of the "B" resonance provides determinations of J_{ab} and J_{bc}. Comparison of the results for "A" and "B" enable you to assign values to J_{ab}, J_{ac}, and J_{bc}. Use the average of the four values for J_{ab}, but hold off on J_{ac} and J_{bc} until you have analyzed the resonance of proton "C". This proceedure provides you with four determinations of J_{ac} and J_{bc}. Use the average values for each of these parameters.
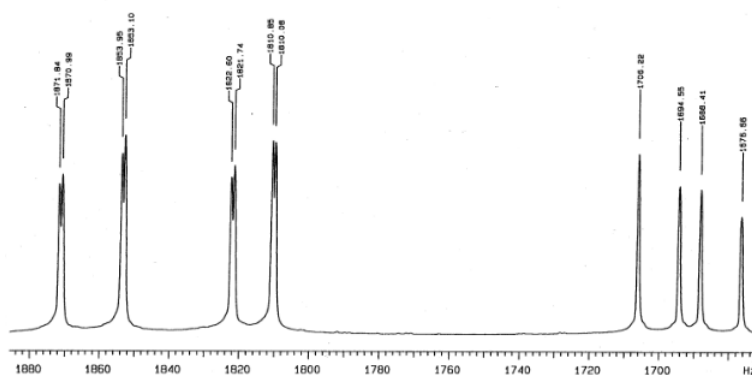
Assignment

1. First compare the 60 MHz NMR spectra of acrylonitrile and vinyl acetate shown below. Notice the difference in appearance of the spectra in spite of the fact that both spectra show the resonances of three vinyl protons.

Acrylonitrile - 60 MHz

Vinyl Acetate - 60 MHz

CH₃
2.1 ppm

offset 4 ppm
width 2 ppm

offset 7 ppm
width 2 ppm

2. Use the methods outlined above to obtain chemical shifts and coupling constants from the vinyl acetate NMR spectrum.

3. With assistance, obtain the 300 MHz spectrum of acrylonitile. Note its basic similarity to the low field vinyl acetate spectrum. Explain why increasing the magnetic field simplifies the acrylonitrile spectrum. Analyze the spectrum to obtain the chemical

Acrylonitrile - 300 MHz

shifts and coupling constants.

4. Run the Mathcad program supplied for the low field NMR spectrum of vinyl acetate.

   1. Use the eigenvalues and eigenvectors generated by Mathcad to construct an energy level diagram for the eight allowed spin states. Use the format indicated below for each energy level.

   E_8 .... Y_8

   E_7 .... Y_7

   E_6 .... Y_6

   E_5 .... Y_5

   E_4 .... Y_4

   E_3 .... Y_3

   E_2 .... Y_2

   E_1 .... Y_1

   2. Now use the intensity matrix generated by Mathcad to sketch in the allowed transitions on the diagram above.
   3. Also prepare a table which compares the experimental transition frequencies with the computer generated frequencies given in the frequency matrix. If you do not find a favorable comparison it means either that the theoretical model used in this exercise does not adequately represent the vinyl acetate nuclear spin system or that you have misread your spectrum.
   4. Qualitatively compare the appearance of the experimental spectrum with the model spectrum generated by Mathcad. In other words do you find satisfactory agreement for the relative values of the frequencies and intensities for each resonance. Explain.

5. Run the Mathcad program supplied for the high field NMR spectrum of acrylonitrile.

   1. Use the eigenvalues and eigenvectors generated by Mathcad to construct an energy level diagram for the eight allowed spin states. Use the format given in 4.1 for each energy level.
   2. Now use the intensity matrix generated by Mathcad to sketch in the allowed transitions on the diagram from part 4.1 above.
   3. Also prepare a table which compares the experimental transition frequencies with the computer generated frequencies given in the frequency matrix. If you do not find a favorable comparison it means either that the theoretical model used in this exercise does not adequately represent the acrylonitrile nuclear spin system or that you have misread your spectrum.
   4. Qualitatively compare the appearance of the experimental spectrum with the model spectrum generated by Mathcad. In other words do you find satisfactory agreement for the relative values of the frequencies and intensities for each resonance. Explain.

6. Run the Mathcad program to simulate the low field (60 MHz) spectrum of acrylonitrile. Do this by dividing the high field chemical shifts by 5 (60 = 300/5). Compare the Mathcad model spectrum with the experimental 60 MHz spectrum provided.

   1. Use the eigenvalues and eigenvectors generated by Mathcad to construct an energy level diagram for the eight allowed spin states. Use the format given in 4.1 for each energy level.
   2. Now use the intensity matrix generated by Mathcad to sketch in the allowed transitions on the diagram from part 4.1 above.

3. Qualitatively compare the appearance of the experimental spectrum with the model spectrum generated by Mathcad. In other words do you find satisfactory agreement for the relative values of the frequencies and intensities for each resonance. Explain.

4. Before the existence of high field nmr an analysis of the 60 MHz spectrum of acrylonitrile yielded the following chemical shifts and coupling constants in Hz: $s_a = 372.2$; $s_b = 364.4$; $s_c = 342.0$; $J_{ab} = 0.91$; $J_{ac} = 17.90$; $J_{bc} = 11.75$. Compare your values for the chemical shifts and coupling constants with these values.

7. The low-field acrylonitrile spectrom shows that 14 resonances are observed [a 15th resonance (see intensity matrix) is too weak to be seen experimentally]. The high-field acrylonitrile and low-field vinyl acetate spectra show 12 resonances. Examine the nuclear spin wave functions for all three cases and use the superposition principle to explain these differences.