

NMR Analyzer v. 3.0

A proton NMR spin system analyzer

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1. INTRODUCTION

NMR Analyzer was born after testing the program NMR Calc, written by Milton D. Johnson Jr., University of Tampa, Florida. I found the program very interesting, useful but annoying, and very slow. The package included the source code in basic, so I recompiled the code with PowerBASIC, an excellent BASIC compiler which can create code using the maths-coprocessor. After modifying two or three minor details, I obtained a very quick NMR Calc. I modified also the plotting routines to include a scale below the spectrum, something that surprisingly Johnson had not made.

I thought then about programming a new interface, more comfortable, and also some analysis routines for complex spin systems: AB, ABX, etc... This program is the result of that work. It offers common characteristics for this kind of programs: calculation of the theoretical ¹H-NMR spectrum and the frequencies and intensities of the spectral lines. But it also offers some small routines for the analysis of AB, ABX, AB2 and AA'XX' spin systems, using the standard Windows interface. This makes the program slower but useful, and allows also a on-line help.

I think some users, specially those who are making his graduate and undergraduate studies, could use this program as a very quick tool for test NMR assignments. I have included some examples in the package to probe this. See section 13, Examples, for more details.

2. CONTENTS

The package contains the following files:

NMR.EXE	The program itselfs
NMR.HLP	The help file
CMDIALOG.VBX	A library for the program
NMR.WRI	This file
README	A short explanation file
EXAMPLE1.NMR	Methyl acrylate parameters file
EXAMPLE2.NMR	Isopropyl bromide parameters file
EXAMPLE3.NMR	β-d-glucose pentaacetate parameters file
EXAMPLE4.NMR	Not published compound parameters file
AB.DAT	Analysis data for 4-(6,7-dihydro-5H-[1]pyrindin-2-yl)-butyronitrile
ABX.DAT	Analysis data for (4S)-4-bromo-3-t-butylcyclopent-2-enone
AB2.DAT	Analysis data for 2,6-dibromopyridine
AAXX.DAT	Analysis data for furan

The program also needs the file VBRUN100.DLL, which can be easily found in many FTP sites.

3. INSTALLING THE PROGRAM

Copy the files included in the package to a directory. That directory can be named as you want. Start Windows, and create a new item in any group, using File/New. Choose Program item, and introduce the program's path. In the Work Directory text box, introduce also the program's path. This is a very important point. *If you don't do that, the program will not find the help's file.* When finish, click Ok. A new icon will appear in the group. If you save configuration, the NMR.INI file will be created into the Windows directory. Remember to delete this file when you desinstall the program.

4. GETTING STARTED

This section tries to be the program's manual. Explains all program features, operations, and problems you can found using the program.

To start NMR Analyzer , double click on the NMR Analyzer. When the program starts you will see a single main window. At the top of the window is the menu bar. The contents of the menu bar are File, Parameters, Calculations, Display, Analysis and Help. The menu bar is 'Windows-like' as far as is possible.

Below the menu bar is the status bar, containing the Spectrometer Frequency Box, and the Work Files Name Box. These box will display the current work frequency in MHz, and the name of the files to be saved or loaded. These two initial parameters can be changed by saving configuration, or by editing directly the NMR.INI file.

In the bottom of the window, is the messages bar. Between this bar and the status bar is the Graphic Box, where spectrum and levels diagrams will be plotted.

5. CALCULATING A THEORETICAL SPECTRUM

To calculate a theoretical spectrum, you must introduce the following parameters:

- The number of spins (nuclei) that compose the system
- The chemical shifts for that nuclei
- The coupling constants between then considered nuclei

Before initiate calculations, you must also choose the frequency for the spectrometer (also called the magnet field), and the name of the files where parameters and calculations will be stored. You can do this operation before introduce the parameters, but once you have started calculations, *don't change the frequency or the name*. To change these two values, type in the Work Frequency Text Box the value in MHz for the field, and type in the Work Files Name Text Box a name, which must be between 1 and 8 characters long.

Now, click Parameters/Number of spins. The Number of spins Dialog Box will appear on the screen. Type in the text box the number of nuclei. The maximum number is seven. If the number is lesser or larger than seven, the program will display an error message, and will prompt you to change the value.

Second, click Parameters/Chemical shifts. The Chemical shifts Dialog Box will appear on the screen. You must introduce the *chemical shifts* for the nuclei in ppm. To serve you as guide, only will be enabled so many text boxes as nuclei. If you are working with *chemically equivalent* nuclei, you must introduce so many chemical shifts as chemically equivalent nuclei. This means, for a methyl group with a chemical shift of 3 ppm, you must type three times that shift.

Third, click Parameters/Coupling constants. The Coupling constant matrix Dialog Box will appear on the screen. Only the necessary quadratic matrix will be enabled. Introduce the coupling constant of the nucleus i with the nucleus j. The program will automatically assume that value as the coupling constant of the nucleus j with the nucleus i. All coupling constants must be in Hz.

You can also introduce a title and comments for the spectrum if you want. To do this, choose Parameters/Parameters Info. In the Title Text Box type the title (255 characters max.). In the Comments Text Box type the comments you want. You can type also carriage returns, and special characters. Click Ok when finish.

NMR Analyzer version 3.0 presents a new feature: additional signals which will not be incorporated to the calculations, but will be appear in the spectrum. This feature allows the

simulation of more complicated spectra, avoiding the seven nuclei limit. For example, a *tert*-butyl group (nine nuclei) can be easily introduced. For introducing that kind of groups, choose Parameters/Additional signals. Select the desired type: you can choose between signals going from singlets to heptaplets. If type selected is different from none (it means, you are going to introduce an additional signal), three text boxes will be enabled. Use them to type the chemical shift, the coupling constant (if necessary) and the number of protons for that signal.

You are ready to initiate calculations. These are divided in four steps:

First, choose Calculations/Generate basis functions. This will generate the spin basis functions for the considered spin system, the Fz values, and will store all the parameters in a file, using the name in the Work Files Name Text Box, and the extension NMR. You can open this file using the Open command. Generate the basis functions is the only way to store the parameters. It's a very fast operation, so don't worry about having to generate the spin basis functions every time you want to save the parameters for a spin system. One point deserves special attention: *when the file was stored, it will replace a file with the same name if that file exists yet, so that parameters will be lost.*

Second, choose Calculations/Generate Hamiltonian. The program will generate the *Hamiltonian matrix* for the system, and will store the data in so many files as Fz values, using the same name as the parameters file, but with the extension 1,2... etc.

Third, choose Calculations/Diagonalize Hamiltonian. The program will diagonalize the Hamiltonian, and store the results. While diagonalizing, it displays the information in the messages bar.

Fourth, choose Calculations/Calculate frequencies and intensities. Finally, the program will calculate the frequencies and intensities of the spectral lines. This is the longest procedure, and the program will display the current Fz value in the messages bar. When the procedure finish, the message bar will display the lines calculated and the total of intensities. The calculated transitions, frequencies and intensities will be stored into a file with the Work's File Name and the extension LIN.

Now, you can see the results of the calculations. Choose Display, and one of the commands in that menu to display the spectrum (in a stick or lorentzian plot), the energy or Fz levels, the spectral lines, and the spin basis functions.

To simplify these operations, which can be very annoying, NMR Analyzer allows to execute all this steps automatically. Before choosing the Auto procedure, type the name of the file and the frequency of the spectrometer in the corresponding text boxes. Choose in the Menu bar File/Auto. In first place, the command allows user to delete current parameters. If you loaded an old set of parameters using the File/Open command, click No. If you click Yes, you will need to introduce the necessary parameters; the Auto procedure will open the four dialog boxes for you. The program will ask you for confirmation before initiate calculations. Click Ok or Cancel. If you choose Cancel, the parameters will not be saved. If you choose Ok, the program will automatically save the parameters and initiate the calculations. When finish, it will display the spectrum.

6. DISPLAYING RESULTS

After executing calculations on the parameters, you can display the results using the Display menu. You can also see the result of previously done calculations simply by typing the name of the parameters name into the Work Files Name Text Box, and selecting the appropriate Display command.

6.1 DISPLAYING THE SPECTRUM

Once the spectrum has been generated, user can display it choosing Display/Spectrum. The Spectrum parameters Dialog Box will appear. You can now select the

values with the spectrum will be displayed:

- By default, the range of chemical shifts is between 0 and 10 ppm. Click on the scroll bars or type the text into the boxes to adjust the scale. The maximum shift must be larger than the minimum shift. If not, a message error will appear.

- You can change the title for the spectrum by typing the new title in the text box.

- Click the check box to show or not the range of the spectrum.

- Click check boxes to select the type of plot. The stick plot is simplest, not very precise, but gives you an idea the spectrum is like. The Lorentzian plot is the normal representation of the spectrum, where the signals are represented by peaks. By default, the stick plot is selected. Take account that this representation is also faster than the Lorentzian plot. If you choose the Lorentzian plot, the Linewidth Scroll Bar will be enabled, allowing you to increase or decrease the width of the peaks (this means, the resolution).

- Finally, you can adjust the peaks height using the Scale factor Scroll Bar.

When you have finished, click Ok to display the spectrum. Click Cancel at any time to exit this dialog box.

6.2 DISPLAYING THE SPECTRAL LINES

Choose Display/Spectral lines to see the calculated spectral lines. The Spectral lines Dialog Box will appear. You can see the lines by intensities or by transitions.

- If you choose to see the lines by intensities, you must adjust the range using the scroll bars. The maximum intensity cannot be lesser or equal than the minimum intensity, except if both are equal to zero. Then, all lines will be displayed. To see all lines with intensity larger than zero, put the minimum intensity to 0.01, and the maximum intensity to 1. This option is recommended when displaying the calculated lines for a 6 or 7 spin system (792 and 3003 lines respectively).

- If you choose to see the lines by transition, you should type in the text boxes the initial and final energy levels for the transition. For example, if you want to see the transition between the levels 1 and 2, type in the Initial level Text Box the number 1, and in the Final level Text Box the number 2. If you change the numbers, the program will automatically change them again, displaying the transition between those two levels.

Click Ok when you finish. The lines will appear into the list box on the left. If you click one of the lines, the initial and final energy levels corresponding to that transition will appear in the text boxes on the right. Click Cancel at any time to exit this dialog box.

6.3 DISPLAYING THE LEVELS DIAGRAM

You can see the energy or Fz levels for the spin system by choosing Display/Levels diagram. The Diagram parameters Dialog Box will appear. You can display two types of diagrams: energy diagrams or Fz diagrams.

Once you have chosen one or another type, you can also choose see or not the transits between the levels. Click the check box to see them. This will enable the Intensities Scroll Bars, allowing you adjust the transitions which will be displayed by changing the range of intensities. If you make both intensities equal to zero, all transitions will appear. If not, only the transitions in that range will appear. If you want to see all transitions with intensities larger than zero, put the minimum intensity to 0.01 and the maximum intensity to 1. This option is recommended when displaying the calculated lines for a 6 or 7 spin system (792 and 3003 lines respectively).

Click Ok when finish to see the diagram. Click Cancel at any time to exit this dialog

box.

6.4 DISPLAYING THE SPIN BASIS FUNCTIONS

Finally, you can see the spin basis functions for the spin system. Choose Display/Basis functions to display the Spin basis functions Dialog Box. Initially, the function with the maximum Fz value will be displayed. Click Next to decrease the Fz value and see the spin basis functions with that Fz value, and Previous to see the basis functions with a larger Fz value. When you reach the maximum of minimum Fz value, a message will appear indicating there are no more spin basis functions, and the dialog box will disappear. Click Cancel to exit the Dialog Box.

7. ANALYSING COMPLEX SPIN SYSTEMS

One of the features of this program is the possibility of analyse complex spin system, in fact AB, AB₂, ABX and AA'XX' systems. The necessary data are obtained from an experimental spectrum, or even from a theoretical spectrum. The process is very simple, and there are only small differences between analyse one or another system.

Choose Analysis, and one of the four systems. In the screen will appear a dialog box for the chosen system. Type in the text boxes the frequencies of the observed peaks. When finish click Analyse to see the values of shifts and coupling constants. Clicking the Analysis button will also transfer the analysed data to the main calculation routines. This way, you can execute calculations on that parameters and see the theoretical spectrum, which should be almost identical to the experimental spectrum.

If you want to store the data into a file, click Save data. Data will be stored in a file with the current Work Files Name and with the extension DAT, using the title and comments introduced with the Parameters info command. Note you don't have to analyse data to save them. In fact, you can introduce the data, close the dialog box, change the name, frequency, title and comments, and then analyse and save the data.

7.1. ANALYSING AB SYSTEMS

For the AB system, there are four frequencies. Click Analyse to see the results and transfer them to the main calculation routines, and Save Data to store the analysis data. See *AB spin system* in the glossary for more information.

7.2. ANALYSING AB₂ SYSTEMS

For the AB₂ system, there are eight frequencies. Sometimes, nine frequencies are observed for a system like this, but the ninth (a combination line) can be ignored. Click Analyse to see the results and transfer them to the main calculation routines, and Save Data to store the analysis data. See *AB₂ spin system* in the glossary for more information.

7.3 ANALYSING ABX SYSTEMS

For the ABX system, there are fourteen frequencies, which can be separated in two groups of eight and six frequencies respectively. That are the AB and X subspectra. The AB zone is formed by two mixed pseudoquartets, called A and B. This spin system is sometimes resolved by the *method of the effective Larmor frequencies*, but the program uses other approach. The frequencies in the AB portion of the spectrum must be assigned to one or another pseudoquartet. Click Analyse to see the results and transfer them to the main calculation routines. Click Save Data to store the analysis data (including the pseudoquartets assignments). See *ABX spin system* in the glossary for more information.

7.4 ANALYSING AA'XX' SYSTEMS

For the AA'XX' system, there are twenty frequencies, which can be separated in two

groups of ten frequencies, corresponding to the A and X zones. Introduce the frequencies of each zone to analyse them separately. See *AA'XX' spin system* in the glossary for more information.

8. OPENING FILES

The program allows to save both the parameters and the analysis data to files, which can be loaded again. The parameters are stored into NMR files, and the analysis data into DAT files. To open a file, click File/Open. An Open Dialog Box will appear. This is a common window included into the COMM.DLG file, included with Windows 3.1, so its use is very known. You can click into the File type List Box to change the filter. Select the file and Click Ok to open it, or double-click the file directly. Click Ok to confirm the operation. *Loading a file will delete the current parameters.* The file will be loaded into the program. If some problem appears, an error message will be displayed.

9. DELETING CURRENT DATA

If you want to initiate a new series of calculations, use the New command in the File menu to delete the current parameters and analysis data. You will be prompted to confirm. If you do that, all current parameters, except the Work Files Name and the Spectrometer Frequency will be deleted.

10. SAVING CONFIGURATION

You can decide to save the current general parameters. Choose File/Save configuration. This will save the current Spectrometer Frequency, Work Files Name, directory and title into an INI file, called NMR.INI, and placed into the Windows directory. This is the only one program's file out of the program's directory. Remember to delete it when you uninstall the program. The configuration saved in this file is automatically read in when you start the program.

11. SAVING PICTURES

This feature is not yet implemented. It's intention is provide a way to save the picture on the Graphic Box into a graphic file (in BMP or WMF format), which can be imported into a Wordprocessor or Graphic editor. Actually, you can make almost the same using the PrtScr key. This will copy the contents of the screen to the Clipboard. You can paste the clipboard into the Paintbrush, and save the picture in BMP or PCX format.

12. GETTING HELP

You can get help at any moment by choosing Help command. You can get the help index, help about the commands or procedures (How to...), or see a brief glossary with the most common terms used in NMR spectroscopy. The About command in the File menu will show information about the program and copyright.

13. EXAMPLES

This section is a brief comment about the examples included with this package. I have included four files of each type. The contents of the files are the following:

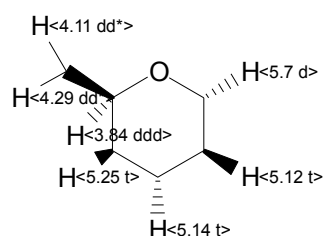
13.1 PARAMETERS FILES

EXAMPLE1.NMR: this file contains the parameters for the methyl acrylate. This

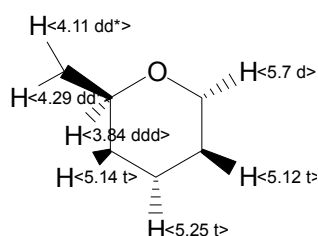
molecule presents a $^1\text{H-NMR}$ spectrum with three double doublets and a singlet. The singlet is very representative, at 3.6 ppm, and belongs to the ester methyl group. The three double doublets belong to the vinylic protons, which have three coupling constants, one geminal and two vicinal (cis and trans respectively). The experimental data for this spectrum were obtained in Cl_3D on a Brüker WM 250 spectrometer from a commercial sample of the compound.

EXAMPLE2.NMR: this file contains the parameters for the isopropyl bromide. This molecule presents in its $^1\text{H-NMR}$ spectrum a very clear 'heptuplet' which corresponds to the proton attached to the carbon two. The other only signal in the spectrum is the doublet, corresponding to the six methylic protons of the compound. This spectrum was not obtained experimentally. The data were obtained from the book *Organic Chemistry, Fifth Edition*, by Robert Thornton Morrison and Robert Neilson Boyd; Allyn and Bacon, Inc., Boston, Massachusetts, in the chapter concerning to spectroscopy and structure, and so on the data could be not totally correct.

EXAMPLE3.NMR: this file contains the parameters for the protons attached to the ring of the $\beta\text{-D-glucopyranose pentaacetate}$. The experimental spectrum shows a doublet at 5.7 ppm, a triplet (actually a false triplet) at 5.25 ppm, two mixed false triplets at 5.14, and another three clean signals, two double doublets (dd) and a double double doublet (ddd) at 4.29, 4.11 and 3.84 ppm respectively. A careful analysis of the signals allows to assign the doublet to the anomeric proton, the ddd to the proton of the carbon five, and the two dd to the protons on the carbon six. The other three signals must correspond to the protons attached to the carbons two, three and four.



Incorrect assignments



Correct assignments

To test the assignments, the parameters were introduced in the program. The first assignment proved to be incorrect through the theoretical spectrum. When the second assignment was introduced, where the shifts for the protons three and four were exchanged the calculated spectrum fitted perfectly with the experimental spectrum. All data were obtained in Cl_3D on a Brüker AMX 500 spectrometer.

EXAMPLE4.NMR: this file contains the parameters for a not yet published compound. This compound shows five signals in the spectrum; a double doublet at 3.99 ppm, two double double doublets at 1.68 and 2.10 ppm, and two double doublets at 2.29 and 2.58 ppm. A correct analysis of the signals was possible only for that at 3.99, 2.58 and 2.29 ppm. The other two exhibited certain symmetry, which allowed the analysis for the dddd signal at 1.68 ppm. The values of shifts and coupling constants so obtained were introduced in the program and proved to be correct. A small change in the coupling constant of the protons at 1.68 and 2.10 ppm resulted in a small but significant change of the spectrum. This spectrum was obtained in Cl_3D on a Brüker AMX 500 spectrometer.

13.2 ANALYSIS FILES

AB.DAT: the data included correspond to the AB system on the aromatic ring of the 4-(6,7-dihydro-5H-[1]pyridin-2-yl)-butyronitrile. The spectrum presents signals for the aliphatic chain, and the three-carbon bridge bonded to the pyridine ring. At low field the spectrum shows two signals for an AB system, corresponding to the only two aromatic protons.

ABX.DAT: the analysis data included are those for the (4S)-4-bromo-3-t-butylcyclopent-2-enone. This data were taken from E.W. Garbisch, Jr., *J. Chem. Educ.*, **45**, 410, (1968). A more extensive comment about this specific system and other related can be found in the reference 1. Two of the lines in the X zone of the spectrum are not included, probably because they are not observed experimentally. When this problem appears, introduce that two values as zero. Automatically, the program will suppose that those two value fit with the lines nine and fourteen.

AB₂.DAT: the analysis data included are those for the 2,6-dibromopyridine. The data were taken from a spectrum obtained in Cl₃D on a Brüker WM 250 spectrometer. Only the frequencies for the main eight lines of the system were observed. The ninth frequency, that corresponding to the combination line f₉, was not observed.

AA'XX'.DAT: the analysis data included are those for the 4-cyanopyridine. The data were taken from a spectrum obtained in Cl₃D on a Brüker WM 250 spectrometer.

14. TROUBLESHOOTING

Sometimes an error will occur when you are trying to display the results of the calculations you made. The common causes are these:

- You typed an incorrect name for the file. Try changing the name.
- The name is correct, but you don't have the file in that directory. Try changing the directory, using the File/Open command.
- You are in the correct directory, but the file doesn't exist. This error is very common, and it means you don't have the LIN file for that parameters file (calculations don't were done?) or, if you are trying to plot a levels diagram, the files where the Hamiltonian is stored don't exist. Sometimes you have deleted them to save space in the disk.

The parameters file is *always* necessary to display the results of the calculations. The LIN file is necessary to display the spectrum, the spectral lines, and the levels diagrams. The Hamiltonian files are only necessary to display the levels diagrams. This can be very annoying, but remember you can repeat the calculations if you have the parameters file.

Another known error occurs if the configuration in the [Intl] section of the Win.ini sets the sDecimal to ",". The program uses the "." to indicate the floating point. The program will truncate the values of shifts and coupling constants, so the parameters and analysis data will be incorrect.

This program has a serious known bug. If you try to see all lines of a seven spin systems, the program will crash. This error is caused by a limitation in the list box used in the Spectral Lines Dialog Box. I will try to correct this bug in later versions of the program. You can see the lines adjusting the intensities to values different than zero.

As I commented in the section 3, there can be problems loading the help file. This error should be caused by not selecting the appropriate work directory when installing the program.

15. ACKNOWLEDGMENTS

Many thanks go to the following people. Say that these people did great things for NMR Analyzer:

- Milton D. Johnston, Jr.; by his NMR Calc program. I used this program as source of inspiration. I used too the source code to see how to make things. Some routines are almost identical; at least the 90% percent of his code was changed.

- José Mejuto Porral; by his support, ideas and help about the code. He was also one

of the beta testers.

- José Antonio Zumalave; by his ideas and help about the code.
- Javier Gómez López; by his ideas about the program itself.
- Elena Martínez Sobrino; she obtained most of the spectra I used in this program.
- Eduardo Fernández-Megía, José Manuel Pintos, María Jesús Blanco Pillado and Javier Sardina; by some of the spectra and samples used in the program.
- Jesús Varela Carrete; by the sample of 2,6-dibromopyridine.

16. ABOUT THE PROGRAM

The program was written using Visual Basic 1.0. Why? Because it's very easy to program a new interface. The problem is the speed. Compiling the program of Johnston using PowerBASIC resulted in a great increasing of the speed, but remake all program in Visual Basic results in a decreasing of the speed, although the interface is more comfortable. Some of the routines written by Johnston were, more or less, conserved. The code was written again in more than 90%, including some of the crucial calculation routines. I have started the conversion of that routines into C language. The using of the CMDIALOG.VBX file can be avoided using the Windows API functions (some of that functions are already used for things like find out the type of processor or the free disk space).

The program was tested extensively on 386 and 486 based computers. The program was not tested on Pentium based computers, so I would appreciate any comments.

Some of the new features which I have thought about are:

- The possibility of display spectrum for more than seven nuclei by combining two or more LIN files. I have thought in other procedures.
- More speed. This can be achieved only by traslating the calculation routines into C language, and including them into a DLL file.
- Coupling diagrams. This option would display the coupling tree for a given nucleus, using the values in the coupling constants matrix.
- Printer support. Currently, there is no way to print results, unless user prints directly the files using a text editor.

17. BIBLIOGRAPHY

These books were used in the making of the program. For specific information about some of the topics mentioned in the glossary, see also references cited therein.

Ref. 1: NMR Spectroscopy. An introduction. Günther, Harald. John Wiley & Sons, Chichester, 1980.

Ref. 2: Nuclear Magnetic Resonance. Basic principles. Atta-ur-Rahman. Springer-Verlag, New York, 1986.

Ref. 3: The Visual Basic 3 for Windows Handbook. Gary Cornell. McGraw-Hill, New York, 1993.

Ref. 4: Tabellen zur strukturaufklärung organischer verbindungen mit spektroskopischen metoden. Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W.. editorial, ciudad,

año.

18. HISTORICAL REVISION

1.0 - The program worked. Nothing more. It had the imprescindible features to do calculations and display routines.

1.2 - Spin system analysis routines added. Spectral lines and spin basis functions displaying routines improved. The program could have been distributed in that stage.

2.0 - Help file added. INI file added. Auto command added. Using of the COMMDLG.DLL procedures implemented. Format of files changed. Comments added to files.

3.0 - Improved calculation routines. Improved auto command, allowing calculations on loaded parameters. Additional signals command.

Glossary

AA'XX' spin system

A system formed by four nuclei, characterized by only two resonance frequencies and four coupling constants. We encounter AA'XX systems in molecules such as *para*-disubstituted benzenes, furan, and 1,2-difluoroethylene. The spectrum for this system is composed of two subspectra, A and X, each one with ten lines. This kind of system can be considered a limit case of the AA'BB' system, where the $\Delta\nu$ is very large.

AB spin system

A system formed by two nuclei, characterized by two resonance frequencies and one coupling constant, as the AX system. Because of the small ratio $\Delta\delta/J$, the inner lines become bigger and the outer lines become smaller. Then, a distorted AX spectrum is observed. This is commonly known as *roof effect*.

AB₂ spin system

A system formed by three nuclei, observed in compounds that possess a two-fold axis of symmetry such as 2,6-dimethylpyridine and 1,2,3-trichlorobenzene. The spectrum can have up to nine lines, but the ninth line is normally not observed.

ABX spin system

A system formed by three nuclei, in which the A and B nuclei have similar chemical shifts, and the X nucleus has a very different shift. The X nucleus in such systems is said to be weakly coupled and the A and B nuclei are said to be strongly coupled. The spectrum is divided into two subspectra, AB and X. The AB subspectrum can be considered as two mixed pseudoquartets. The 1,2,4-trichlorobenzene is an example of the ABX system.

AX spin system

The more simple system of coupled nuclei; is characterized by two resonance frequencies and a coupling constant. Two doublets are observed, and the coupling constant can be measured directly. This is a very common spin system.

Chemical equivalence

The nuclei with the same resonance frequency are called *isochronous*. They are usually chemically equivalent, that is, they have identical chemical environments. Two nuclei

can be isochronous and have two very different chemical environments. The chemical equivalence is a necessary condition for the *magnetic equivalence*.

Chemical shifts

The resonance position of a given nucleus as a distance from a standard, commonly Tetramethylsilane (TMS). This value is reported in a δ scale, which is independent of the field of the magnet, and expressed in *parts per million* or ppm.

Coupling constants

This parameter expresses the magnitude of the splitting in a NMR signal, caused by the coupling of the spins of nonequivalent vicinal nuclei. It is known as J, and expressed in Hz. The value of J depends on the molecular stereochemistry and the number of bonds between the coupled protons, among other factors.

Doublet

A characteristic signal caused by the splitting of the single signal because a non-equivalent nucleus (a proton) attached to the same carbon or to adjacent carbon atom. The signal appears as two sharp singlets and the magnitude of the splitting is expressed as the coupling constant, J.

Eigenfunction

The spin system as a whole can exist only in certain states, the *stationary states* or *eigenstates*. Each eigenstate is characterized by a *wave function* or *eigenfunction*, which is normally constructed as a linear combination of *spin basis functions*.

Eigenvalue

The energy of an *eigenstate*. The *eigenvalues* are solutions of the Schrödinger equation, and they are determined by the interaction between the nuclei and the external magnetic field, as well as by the spin-spin interaction of the nuclei with one another.

Energy levels

The energy levels of a spin system are calculated by applying the Schrödinger equation to the considered nuclei. These energy values are therefore *eigenvalues* and give the energy for an eigenstate characterized by a *wave function* or *eigenfunction*.

Fz levels

The product functions for a spin system are characterized by the total spin, the sum of the magnetic quantum numbers of the individual nuclei. F_z is defined as an operator, which commutes with the Hamiltonian operator. This allows factorizing the Hamiltonian matrix into submatrices. The F_z levels are characterized by the same total spin. For the AX spin system, the values of the F_z operator are -1, 0 and 1.

Hamiltonian

The Hamiltonian operator gives the value of the energy (*eigenvalue*) of a wave function which is an *eigenfunction*. When applied to a spin system, a Hamiltonian matrix is obtained, which can be factorized into submatrices by results of the F_z operator.

Magnetic equivalence

Two nuclei are magnetically equivalent when they are chemically equivalent and have only one characteristic spin-spin interaction with the nuclei of a neighbouring group. The *chemical equivalence* is a necessary condition for magnetic equivalence.

Multiplet

A NMR signal is said to be a multiplet when its hyperfine structure (the couplings), cannot be easily resolved. This situation comes normally from the magnetic non-equivalence of the coupled nuclei and the so called *second order rules*. The analysis of some multiplets requires a theoretical treatment.

Multiplicity

For nuclei with spin quantum number $I = \frac{1}{2}$ the multiplicity of the splitting equals $n + 1$ where n is the number of nuclei in the neighbouring group. This is one of the *first order rules*.

Quartet

A signal with the relative intensities 1:3:3:1. This signal comes from the coupling of a proton with three other equivalent protons in the neighbouring group. A typical case is the splitting of the methylene protons signal in the ethyl radical.

Singlet

The NMR simplest signal. It consists on a sharp signal, and is therefore characterized only by a resonance frequency. Two or more protons chemically equivalent give a signal like this.

Spectral lines

These are the lines observed in a NMR spectrum. Spectral lines represent transits between energy levels of different F_z value. A theoretical spectrum can have many lines, but only the observed lines are spectral lines.

Spin basis functions

Basis functions are those which serve as basis for a linear combination. In this case, the linear combination gives an *eigenfunction* of the spin system. The spin basis functions for a two spin system, are $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$, where the second and third functions have the same value of F_z . Since the eigenfunction must have only one F_z value, only that two functions must be combined to give the eigenfunction with F_z zero.

Spin notation

The spin notation serves to abbreviate the description of complex spin systems. The notation uses shift letters to denote nuclei; AB means two nuclei, with their corresponding chemical shifts, which are very close; AX means two nuclei with very different chemical shifts. If two nuclei with the same chemical shift are magnetically non-equivalent, the spin notation denotes them as AA'... The AA'XX' spin system, is therefore a four nuclei system, with two very different chemical shifts, and all four nuclei are magnetically non-equivalent.

Triplet

A signal with the relative intensities 1:2:1. This signal comes from the coupling of a proton with two other equivalent protons in the neighbouring group. A typical case is the splitting of the methyl protons signal in the ethyl radical.

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