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DECUS NO.	8-194
TITLE	NMR Simulator
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DATE	May 15, 1969
SOURCE LANGUAGE	PAL III

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NMR SIMULATOR

DECUS Program Library Write-up DECUS No. 8-194

ABSTRACT

NMR Simulation is designed to calculate the theoretical spectrum of compounds containing hydrogen, fluorine, carbon-13 and other nuclei of spin 1/2. The calculated theoretical spectrum is displayed on an oscilloscope.

Options for punched and typewritten output, change in x-axis offset (sweep offset) and spectrum resolution are available. Chemical shift and coupling constant parameters may be varied successively until the display spectrum matches that obtained experimentally. Redisplay of a "library" of theoretical spectra is possible by retaining punched output tapes.

REQUIREMENTS

Equipment

A PDP-8/I equipped with high-speed reader and punch, Teletype, 8K of memory, and AXØ8 are required. (Without AXØ8 and/or high-speed reader and punch see Appendix A.)

Memory

Field Ø-program uses Ø - 4577 and 54ØØ - 7577. Field 1-data is stored in location 2Ø - 7245.

Loading Procedure

Load the program into field Ø with the standard binary loader.

Operating Procedure

Set SR = ØØØØØØ press STOP, press LOAD ADDRESS, and press START.

The computer then begins to ask for information. The Teletype questions along with appropriate operator action are shown in Table I. (See Appendix B for typing error recovery.)

TABLE I

ORDER OF ENTERING DATA

Section	Teletype Output	Operator Action
A	"COMMENTS"	Type any amount of commentary such as the problem name etc. Exit to the rest of the program is achieved by pressing ALT MODE on the Teletype.
B	"THE NUMBER OF SPINS IS"	Enter the number of spins. Values from 2 - 6 will be accepted. With other values, "?" will be typed and the question asked again.
C	"PUNCHED OUTPUT?"	Type Y if punched output is desired, or N if it is not. If Y is typed, turn on the high-speed punch.
D	"SWEEP OFFSET:"	Enter the desired sweep offset (in cps). TYPE RETURN. This is the extent in cps to which the display is shifted to the right.
E	"SWEEP WIDTH:"	Type the number of cps to be displayed on the scope followed by a RETURN. Smaller width gives greater resolution. (Entering a Ø leads to division by Ø and one must return to SWEEP OFFSET (See below).)
F	"CHEMICAL SHIFTS (CPS)"	Enter the chemical shifts (in cps) in the order ν (1), ν (2),...., ν (n) following each with a RETURN. (See appendix C.)
G	"COUPLING CONSTANTS (CPS)"	Enter the coupling constants (in cps) in the order $J_{1,2}, J_{1,3}, \ldots, J_{1,n}, J_{2,3}, \ldots, J_{2,n}, J_{3,4}, \ldots, J_{n-1,n}$ following each with a RETURN. (See appendix C.)

The portion of the spectrum specified by the sweep width and sweep offset will now be displayed on the scope after the calculation is complete. (See appendix C.) It will be noted that, at regular intervals along the baseline, bright spots appear. These are calibration marks. The number of cps between two calibration marks is 1/25 of the sweep width. Thus, at a sweep width of 25Ø cps, there are 1Ø cps between calibration marks, but, at 5Ø cps sweep width, there are only 2 cps between calibration marks.

While the spectrum is being displayed, the operator can type any amount of commentary. When editing of the displayed spectrum is desired, typing one of the mnemonics in the table below followed by pressing ALT MODE on the Teletype will achieve exit to the portion of the program described in Table II.

TABLE II

COMMANDS AVAILABLE

OPTION #	MNEMONIC (to be typed by operator)	EXIT TO (The letters refered to program sections in Table I)
1	NEW DATA	Section F. Enter new chemical shifts and coupling constants.
2	START OVER	Section A. Begin a new problem.
3	NEW COUPLING CONSTANTS	Section G. Enter new coupling constants.
4	OFFSET	See below. Allows display of a different portion of the spectrum.
5	DO AGAIN	Section D. Enter new sweep offset, sweep width, chemical shifts, and coupling constants.
6	LISTING	See below. Allows a listing of transition energies and intensities on Teletype. (A punched tape is required for this option.)

Option 4: If this option is selected only parts D and E of Table I are repeated. After entering a new sweep offset and sweep width, the Teletype will print "TAPE?". If a punched tape has been prepared, type Y. If not, type N. If N is selected, the spectrum will be recalculated and displayed. If Y has been typed, the Teletype will write "LOAD AND CONT.". Place the tape in the high-speed reader and press CONTINUE. After the tape has been read, the offset spectrum will be displayed. If it is desired to display a previously punched tape, the program may be started at ØØØ2ØØ. This leads directly into the offset routine. When starting at this address, only options 2, 4, or 6 should be selected when the display spectrum appears.

Option 6: If this option is selected, "MINIMUM INTENSITY:" will be typed. Enter the minimum intensity to be listed. (Transitions with intensities lower than this will not be listed.) Type RETURN. The Teletype will then print "LOAD AND CONT.". Place the punched tape in the high-speed reader and press CONTINUE. "ENERGY INTENSITY" will then be typed, and the transition energies and intensities will be listed. When the listing is done, the spectrum will be redisplayed on the scope at half its original intensity. If a listing of a previously punched tape is desired, the program may be started at ØØ34ØØ. This leads directly to the listing routine. Again, when starting at this address only options 2, 4, or 6 should be selected when the spectrum appears. When the program is started at this address, there is no way of predicting what will be displayed on the scope.

Operating Suggestions

The punched output option (Section C Table I) is designed to provide a permanent record of a calculated spectrum, for display at any future time, and to provide listings of transition energies and intensities. Some time is saved in the five and six spin systems by having a tape punched and then using this for inspection with several offsets and different resolutions (i.e. Sweep Widths). However, the original spectrum calculation is rapid enough so that this is not saving for smaller systems. Thus it is probably best to select the N option here unless a large system (at least 5 spins) is being calculated or unless a permanent record is desired. If Y is selected, tapes will be punched until the N option is selected either by restarting the program or by using option 2 of Table II.

A useful starting point for many 60 megacycle nmr (hydrogen) spectra of organic molecules is a sweep offset of 0 cps and a sweep width of 500 cps. For best results, however, all peaks should eventually be examined at a considerably smaller sweep width, since rounding errors may give misleading scope displays with large sweep widths. It should be noted that increasing the sweep offset moves peaks to the right, and decreasing the sweep offset moves peaks to the left. Once the peaks are observed, the proper sweep width and sweep offset can be determined from the calibration marks.

As a starting point, 0.02 is a good intensity to select as the minimum intensity for option 6 Table II. Typing 0 will allow listing of all transitions, and for small systems this is wise. This is also the approximate minimum intensity that will be displayed on the scope.

Appendix D contains some typical input output from this program.

NMR Background

The discussion below assumes that the nuclei being studied are hydrogen, fluorine, carbon-13 or other nuclei of spin 1/2.

Each proton (or fluorine nucleus) in a molecule can be assigned a spin of either α or β. For a system containing n nuclei, there are 2^n spin states possible. Each of these states is called a basic product function. The energy of a basic product function can be calculated from equation (1); where $s_i = -1/2$ for β spin and $+ 1/2$ for α spin; ν_i is the frequency of absorption in cps; $T_{ij} = + 1/4$ if i and j have the same spin and $-1/4$ if i and j have opposite spin; and J_{ij} is the coupling constant between i and j in cps.

$$(1) \quad H_{uu} = \sum_{i=1}^{n} \left(s_i \nu_i + \sum_{j>i} T_{ij} J_{ij} \right)$$

The energy of interaction between two basic product functions is 0 unless both have the same number of α and β spins. When this condition is fulfilled, the interaction energy is calculated from equation (2) where U = 1 if the basic product functions differ only in the interchange of spins i and j. (J_{ij} as defined above.) Otherwise, U = 0.

$$(2) \quad H_{uv} = 1/2 U J_{ij}$$

Thus, to calculate an mnr spectrum, one contructs all of the possible basic product functions and sorts them into groups, each member of a group containing the same number of α and β spins. The energy of each of them is determined and used as the diagnal element in a square matrix. The off-diagonal

elements of this matrix (H matrix) are energies of interaction between the members of the group. This matrix is diagonalized and the trace of the matrix then contains the energies of the final spin functions. These final spin eigenfunctions are the columns of the matrix (U matrix) required to diagonalize the H matrix. Each element in a spin function represents the contribution of a basic product function to that spin function.

Before continuing, it is necessary to define the F_z value of a spin function as shown in equation (3) where the s_i is as previously defined.

$$(3) \qquad F_z = \sum_{i=1}^{n} s_i$$

Now the peaks on a recorder nmr spectrum are transitions from one spin function to another. These transition energies and their intensities can be calculated as outlined below. Transitions are allowed between spin functions whose F_z values differ only by 1. If this holds, the energy of the transition is the difference in energy of the final spin eigenfunctions, and the intensity of the transition is given by equation (4) where C_u is the uth element in one spin function, C'_v is the vth element in the other spin function, and $A = 1$ if the basic product functions represented by C_u and $\overline{C}'_v$ differ by one spin. Otherwise; $A = \emptyset$.

$$(4) \qquad I = \left(\sum_u \sum_v C_u C'_v A\right)^2$$

Program Description

The complete program listings are contained in Appendix E with extensive commentary. The following is a brief outline of the program; capital letters below refer to variables.

I. Begins with text mode for input of commentary.
II. Enter the number of spins and store in N.
III. Set "switch" for punched output.
IV. Set up basic product functions (BPF's).
  A. Calculate NARRY array which contains relative addresses of the BPF's of different F_z value.
  B. Calculate NUSE array. This array actually contains the BPF's. They are stored in groups. Each group having an F_z value one greater than the preceeding group.

V. Get sweep offset and sweep width.
VI. Get chemical shifts.
VII. Get coupling constants.
VIII. Initialize SPEC array.
  A. This array eventually contains the displayed spectrum.
  B. It is intialized to $\emptyset$ except for calibration points where it is set to $4\emptyset\emptyset\emptyset_8$.
IX. Calculate first H and U matrices.
  A. First H matrix is always a 1 X 1 which does not require diagonalization.
  B. First U matrix is always a 1 X 1 with its only element equal to 1.
X. Set FLAG which is the negative of the number of times the loop from XI to XVII must be executed.
XI. Set N2, calculate EN, and UOLD arrays.
  A. Copy the trace of the H matrix into the EN array.
  B. Copy the U matrix into the UOLD array.
  C. Set N2 equal to the size of the H matrix just copied.
XII. Calculate the size of the next H matrix and put it into N1.
XIII. Determine which transitions will be allowed between the BPF's represented by UOLD and those that will be represented by U. This is stored in the array called TABLE.

XIV. Initialize H and U matrices.
   A. Diagonal H elements are calculated by equation (1).
   B. Off-diagonal H elements are calculated by equation (2).
   C. The U matrix is initialized to all zeros except for ones on the diagonal.
XV. Diagonalize the H matrix and calculate the U matrix by the Jacobi method.
XVI. Calculate transitions.
   A. Calculate transition energies by forming the difference between the elements of the trace of the H matrix and the elements in the EN array.
   B. Calculate transition intensities from equation (4).
   C. Store appropriate values in SPEC array.
XVII. Test FLAG to see if the loop is done.
   A. If loop is not done, go to XI.
   B. If loop is done, display spectrum.
XVIII. If "ALT MODE" is typed, interpret mnemonic and execute option.

The listings include everything except Floating Point Package II (DEC-08-YQ2A-PB). Included, however, is an overlay of Floating Point Package II. These modifications force all indirect floating commands to operate on field 1. The field width for the output controller is now stored at location 3 in this version. All direct commands of the floating point package still operate on field Ø.

APPENDIX A

If the AXØ8 is not available, the table below shows the location of the scope control commands and their function. These then may be replaced with their counterpart instructions.

Location	Contents	Function
4511	63Ø2	clear and load X buffer
4516	6317	clear and load Y buffer, and display
4527	6317	clear and load Y buffer, and display
4541	6317	clear and load Y buffer, and display
4542	6317	clear and load Y buffer, and display
4543	6317	clear and load Y buffer, and display

If the high-speed reader and punch are not available the following changes should be made:

Location	Contents	Change To
Ø2Ø2	6Ø16	7ØØØ
Ø241	6Ø14	6Ø32
Ø244	6Ø11	6Ø31
Ø246	6Ø16	6Ø36
3135	6Ø26	6Ø46
3325	4336	4134
3334	4336	4134
34Ø2	6Ø16	7ØØØ
3447	6Ø14	6Ø32
3473	6Ø11	6Ø31
3475	6Ø16	6Ø36
4Ø17	6Ø14	7ØØØ
4Ø2Ø	6Ø26	7ØØØ
4272	6Ø21	6Ø41
4274	6Ø26	6Ø46
4323	6Ø11	6Ø31
4325	6Ø16	6Ø36
4337	6Ø11	6Ø31
4341	6Ø16	6Ø34
4353	6Ø26	6Ø46
4351	72ØØ	76Ø2
4322	73ØØ	6Ø32
4326	7ØØ6	71Ø6

When program is started punch should be off. Enter data as described in Table I. After the last coupling constant has been entered the computer will halt. Turn punch on, turn Teletype to local, press "HERE IS" on Teletype, turn Teletype to line, and press CONTINUE. Simply press CONTINUE if punched output is not desired.

APPENDIX B

Location of Typing Error	Recovery
Section B Table I	Any character typed will be interpreted. If an error is made, the Teletype will echo the character as it was interpreted (last ASCII code digit). Thus, if "D" is typed, "4" will be echoed and stored as the number of spins. Recovery can be made by restarting program.
Section C Table I	Restart program.
Section D, E, F, and G Table I, "MINIMUM INTENSITY:" of option 6 Table II	These use the standard floating point input. If an error is made, type rubout, and retype the entire number. An illegal character will terminate the input and recovery can be made by restarting the program or continuing until the display appears and selecting a suitable option from Table II.
"TAPE?" in option 4 Table II	Restart program at ØØØ2ØØ.
Mnemonic during display	Type RETURN, and retype mnemonic.

EXAMPLE I

COMMENTS

SAMPLE AB PATTERN, CHEMICAL SHIFTS 265 AND 28Ø CPS, COUPLING CONSTANT 5 CPS

THE NUMBER OF SPINS IS 2

PUNCHED OUTPUT? Y

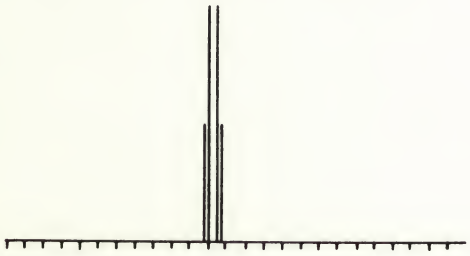
SWEEP OFFSET: Ø

SWEEP WIDTH: 5ØØ

CHEMICAL SHIFTS (CPS)
265
28Ø

COUPLING CONSTANTS (CPS)
5

THE DISPLAYED SPECTRUM IS SHOWN HERE:



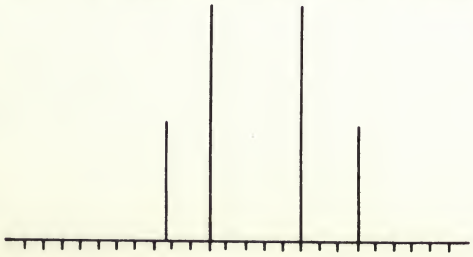
NOW USE THE OFFSET OPTION TO ENLARGE THE DISPLAY:
OFFSET

SWEEP OFFSET: 25Ø

SWEEP WIDTH: 5Ø

TAPE? Y LOAD AND CONT.

THE DISPLAYED SPECTRUM IS SHOWN BELOW:



APPENDIX C

# of Spins Selected	# of Chemical Shifts Required	# of Coupling Constants Required	Execution Time (SEC) if Tape is Not Punched
2	2	1	<1
3	3	3	2-3
4	4	6	8-1Ø
5	5	1Ø	3Ø-9Ø
6	6	15	3ØØ-6ØØ

THE LISTING OPTION WILL TYPE OUT THE ENERGIES AND INTENSITIES OF THE SPECTRUM WHICH WAS DISPLAYED:
LISTING

MINIMUM INTENSITY: Ø.Ø2

LOAD AND CONT.

ENERGY		INTENSITY
+ 277.9Ø5	+	1.316
+ 262.Ø94	+	.683
+ 267.Ø94	+	1.316
+ 282.9Ø5	+	.683

THE SCOPE DISPLAY IS NOW EXACTLY THE SAME AS BEFORE EXCEPT THAT THE INTENSITY HAS BEEN REDUCED BY HALF.

EXAMPLE 2

A COMPLETELY DIFFERENT SYSTEM WILL NOW BE CALCULATED:
START OVER

COMMENTS

ETHYL GROUP, CHEMICAL SHIFTS 9Ø AND 26Ø CPS, COUPLING CONSTANTS 8 CPS

THE NUMBER OF SPINS IS 5

PUNCHED OUTPUT? N

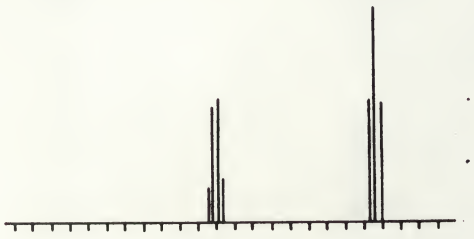
SWEEP OFFSET: Ø

SWEEP WIDTH: 5ØØ

CHEMICAL SHIFTS (CPS)
9Ø
9Ø
9Ø
26Ø
26Ø

COUPLING CONSTANTS (CPS)
Ø
Ø
8
8
Ø
8
8
8
8
Ø

THE DISPLAYED SPECTRUM IS SHOWN BELOW:



Program Listing

The listing is organized according to the table of contents shown below.