NMR-SIM Software Manual

Version 2.8

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Chapter 1

Introduction

NMR-SIM is a program for the simulation of a wide range of NMR experiments. The program runs on any IBM PC compatible computer under MS-WINDOWS NT operating system, and on SGI workstations.

The output of the simulation program is a FID or SER file in the format used on BRUKER spectrometers. NMR-SIM uses the standard BRUKER pulse sequences and experiment definition parameters used on AMX or Avance spectrometers series.

The program is designed to simulate the behavior of **general homo- and heteronuclear spin systems** [1]. Spin quantum numbers up to 2 are supported. NMR-SIM uses group theory to speed up the calculations when the spin system definition contains equivalent nuclei.

The simulation is based on the solution of the quantum mechanical Liouville equation. The spin system evolution during the radio-frequency pulse is taken into account, so you can simulate rotating frame magnetization transfer experiments (2D TOCSY or HOHAHA). The implementation of gradients allows to simulate gradient enhanced experiments.

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1. Only the simulation of 100% enriched molecules is directly possible at present. However, it is possible to simulate other concentration by defining the sample as a mixture (see page 80).

The ***NMR-Wizard*** simplifies the experiment setup and allows to calculate a lot of complicated NMR experiments without any user input.

The ***parameter optimizer*** calculates the dependency of an 1D-NMR experiment on any parameter used in the pulse program.

The ***Bloch module*** lets you visualize the time development of the nuclear magnetization during various experiments.

The ***pulse program display*** may be used for the visualization of BRUKER pulse programs.

To process the simulated data you can use the whole set of BRUKER processing software: from WIN-NMR to XWIN-NMR.

The ability to use BRUKER pulse programs offers the possibility of pulse sequence tuning or the analysis of complex NMR experiments under ideal conditions without instrumental imperfections.

This manual summarizes only the most important information needed for the simulation of NMR experiments. Please, read the section **Important changes** in Appendix (page 147). The most recent information can be found on the BRUKER WWW server, or in the on-line version of this manual.

Those manual parts, which are only meaningful for particular computer implementations are marked at the side of the text (as shown here for MS-WINDOWS). ***Windows***

1.1 Authors

From 1989 to 1991 program developments were done at the

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From October 1991 program development continued at Bruker Karlsruhe.

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1.2 New Features

1.2.1 NMR-SIM 2.8

for MS-WINDOWS NT and SGI workstations (Irix 5.2 or later).

- ***New tools for analysis of shaped pulses***
  The Bloch module contains new functions for the analysis of adiabatic pulses and several new display options. This tool may be also started directly from the XWIN-NMR shape tool to analyze the performance of generated pulses.
- ***4th rf channel available***
  up to 4 rf channels may be used in simulated experiments, the pulse program display supports 8 rf channels.
- ***New command line arguments***
  New set of command line arguments allows to define several experiment parameters from the command line.
- ***Changes in user environment***
  Release 2.8 unifies the storage of user data (spin systems,.....) for all platforms. All user data will be stored in the directory
  <home directory>/NMRSIM_SESSION.
  The old log-in box used on MS-Windows to emulate the multi-user feature disappeared.

1.2.2 NMR-SIM 2.7

for MS-WINDOWS NT and SGI workstations (Irix 5.2 or later).

- The MS-WINDOWS version requires now MS-WINDOWS NT. The MS-WINDOWS 95/98 will no longer be supported.
- ***XWIN-NMR mode for the Windows NT version.***
  The MS-Windows version is now able to write the calculated data in the XWIN-NMR format. To do it, start NMR-SIM from the command prompt using following command:

  nmrsim -x

  You may also modify the shortcut NMR-SIM created during the installation. The current version may be also started as usual from XWIN-NMR. The program behaves in the same way as the UNIX version: the user files are placed in the subdirectory NMRSIM_SESSION in your home directory, the pulse programs will be read from the standard XWIN-NMR directory

$(XWINNMRHOME)/exp/stan/nmr/lists/pp.

- ***Parameter optimizer***
  New command "***Go/Optimize parameter***" calculates a dependency of an 1DNMR spectrum on the value of one pulse or delay in the pulse program. It is the equivalent of the XWIN-NMR command ***paropt***.
  The result is available in three forms:
  - ***1D spectrum***
    all data are added to one FID
  - ***a series of 1D spectra***
    each value of optimized parameter produces one 1D spectrum
  - ***pseudo 2D spectrum***
    all data are stored as rows in one SER file.

- ***Reloading example files***
  The original version of example files may be now reloaded into your user directory using the command "***Options/Upgrade example files***".

- ***Stand-alone Bloch module***
  The Bloch module used for the calculation of excitation profiles may be now used in stand-alone mode. Command

  nmrsim -bloch

  opens the Bloch window without the NMR-SIM simulation functions.
- ***HASP licenses***
  The HASP support is now disabled. Start the program with parameter ***-hasp*** to enable the HASP support.

1.2.3 NMR-SIM 2.6

for MS-WINDOWS 95/98, MS-WINDOWS NT and SGI (Irix 5.2 or later).

This release comes with following new features:

- ***Gradient spectroscopy***
  The implementation of the gradients allows to simulate variety of new experiments. The gradients are implemented for the Avance series only.
  The sections ***Gradient spectroscopy*** on page 101 and ***Examples*** on page 141 bring more information about this topic.
- ***Pulse program display***
  The pulse program display is now more flexible. The pulse program display may be also started as a stand-alone application without the NMR-SIM simulation functions.
- ***Setup form XWIN-NMR***
  The NMR-SIM experiment setup may be now imported from an existing ***XWIN-NMR*** data set. This feature allows you to calculate spectra under the same conditions as you have used for the real experiment.

Windows

- ***User interface***
  The MS-WINDOWS version stores the position and sizes of all windows on the disk. All windows will preserve its sizes after program restart. A new method for the screen font size selection was implemented: The font size changes accordingly to the size of the graphic window.
- ***New example experiments***
  Several new example experiments are now available.

1.2.4 NMR-SIM 2.5

for MS-WINDOWS 95/98, MS-WINDOWS NT and UNIX workstations (SGI Irix 5.2 (or later) and BRUKER ASPECTstation). The 16-bit version for Windows 3.11 is no longer supported.

This release brings following new features:

- ***NMR-Wizard***
  The NMR-WIZARD calculates a NMR spectrum (i.e. the time domain signal) without any input. The user simply selects the spin system and the pulse program. NMR-SIM sets without any further interaction all necessary parameters. The parameters are read from the pulse program comments and from the spin system.
- ***Elapsed time display***
  The program shows the elapsed time of experiment. The time is updated every

second. The NMR Wizard also shows the approximate remaining experiment time.

- ***New limits for the spin systems***
  Up to 256 nuclei may be used in the spin system definition.
- ***New submenu "Edit/Create new"***
  This submenu is used to create a new pulse sequence, a new spin system description, one of the lists, or the job description. Just select the new name and edit the text using the built-in text editor.
- ***On-line manual***
  The on-line manual is now available. To use it you should install the PDF viewer (Acrobat reader or ***xpdf*** program) on your computer.
- ***Pulse program display***
  The pulse program display lets you configure the relative width of all pulses and delays in the pulse program scheme. Use the commands "Options/ Configure pulses" or "Options/Configure delays" in the pulse program display window to define the relative width and height of the pulses and delays.
- ***New pulse program organization***
  The PC version (for MS-WINDOWS 95/98 and MS-WINDOWS NT) implements a new pulse program selection strategy:

  a) Both AMX and Avance (DMX) pulse programs are installed. AMX in pp.exam, Avance in pp.dmx.

  b) The NMR-SIM program uses either AMX or Avance pulse programs. The selection may be done in the ***Options/NMR-Sim*** settings dialog box. The "Pulse compiler" switch selects between AMX and Avance pulse programs, i.e., it selects the default directory for pulse programs.
- ***More flexible graphics***
  The background color may be set in all graphic windows. The default background stays black.
- ***Windows 3.1 version***
  The version for MS-WINDOWS 3.1 will no longer be supported. The user of the 32 bit version (MS-WINDOWS 95/98 or MS-WINDOWS NT) will benefit from the new development. The 32 bit program is much faster on the same hardware, the pulse programs may use long file names.

1.3 Hardware requirements

1.3.1 MS-WINDOWS NT

The program runs on ***any*** IBM-compatible PC with Pentium (or equivalent) processor. The basic hardware configuration is set by the requirements of the MS-WINDOWS operating system, we recommend at least 64 MB.

The memory requirements differ substantially from experiment to experiment. For small spin systems they are negligible, but for larger spin systems (6 nuclei and more) and for complicated experiments (a lot of different pulses) much more than 1MB may be required.

The calculation of gradients requires more computational power as the usage of non-gradient pulse programs, the memory requirements may be also substantially higher.

The required disk capacity depends on the size of your simulated data, the program itself requires about 10 MB.

As an **optimum configuration** we recommend **at least**

- **MS-WINDOWS NT: 200 MHz Pentium CPU with at least 64 MB memory.**

1.3.2 UNIX

The UNIX version runs on SGI workstations (Indigo R4000, INDY, O2...), with Irix 5.2 or higher. To process the simulated data you need the XWIN-NMR package.

> **The NMR-SIM version 2.7 and later require the XWIN-NMR version 2.5 (or above). It may not be started from XWIN-NMR 2.1 or older! If you have the XWIN-NMR 2.1 and you would like to use the NMR-SIM 2.7, you should not start the NMR-SIM from XWIN-NMR!**
> **You will have to start NMR-SIM from a separate shell window.**

1.4 Differences between MS-WINDOWS NT and UNIX versions

The UNIX version was written for the Motif window manager, which has a different “look and feel” as the MS-WINDOWS, but the definition of control elements for the window manipulations (iconify, resize...) is the same.

The menu and dialog boxes in all versions of the NMR-SIM program are almost identical. The formats of all input files are the same.

The UNIX version writes the results of the simulation in the XWIN-NMR format, the MS-WINDOWS versions in the WIN-NMR or XWIN-NMR format.

1.5 Installation

The BRUKER programs are distributed on the BRUKER Software CD.

1.5.1 Installing the version for MS-WINDOWS

You must have MS-WINDOWS NT version 4.0, or later installed on you computer. To process the simulated data or to transfer them to other computers you should also install the WIN-NMR or XWIN-NMR package **before** installing NMR-SIM.

There are two different ways in which NMR-SIM can be installed: either as a ***single computer installation*** or as a ***network installation***. Both methods of installation can be selected independently of the licensing method you will use.

The program comes with a sophisticated installation program ***setup.exe***. You can start it from MS-WINDOWS or from the command prompt:

<CD-ROM drive>:\windows\nmrsim\setup

You will be asked for the destination directory. The default path is

c:\Bruker\NMR-Sim.

The installation program copies the simulation program and several utility files to this directory. The name of the executable is ***nmrsim.exe***[1], the *Help/About* command shows, which version is running. You may also use the command line parameters ***-i*** and ***-v*** to get more information about the installed version.

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[1] There are in fact two executables. ***nmrsim.exe*** with console (cmd) interface (i.e. you may use the command line parameters and the output is written on the console) and ***nmrsim_w.exe*** without console interface (the command parameters are read and interpreted but there is not output on the console).

In the case of the single computer installation all the files required for running NMR-SIM are installed on the local PC. In the case of the network installation some of the files (e.g. executables) are present only on the PC which acts as the server.

As for the single user installation, a ***network installation*** requires the presence of MS-WINDOWS on the PC's which will run NMR-SIM. In addition, these must be incorporated into a network. In contrast to the single user installation it is of no importance whether MS-WINDOWS is installed locally or loaded from the network server.

A network installation always requires two steps: ***the administrator installation*** on the server and the ***network user installation*** on the local PC.

The administrator installation should only be carried out by the network administrator, since only he/she normally has the necessary write permission on the network server. The administrator installation is carried out using the NMR-SIM installation media (CD) and is the necessary precondition for the network installation on the local PC's.

However, the administrator installation only prepares the installation of NMR-SIM within the network and does not create a directly executable program. When this step has been completed, the installation CD is no longer required.

During the installation, all required files are copied into the network setup directory (e.g. *c:\exports\Bruker\nmrsim*). This directory must be exported to all PCs that want to share this network installation.

The ***network user installation*** is done by executing the setup program which is stored in the exported setup directory.

The option ***network user installation*** is now available. A ***single user installation*** would generate a full installation of the program on the local PC. However, the recommended action is to carry out the network user installation.

1.5.2 Copy protection

NMR-SIM is copy protected. To start the program, a license is required. Following copy protection mechanism are supported:

- ***FLEXlm***
  The FLEXlm license manager is the most flexible option for the copy protection in a network.

The command
nmrsim -i
shows additional information necessary to get a FLEXLm license:

```
################################################
This is NMR-Sim version 2.6
installed in : /usr/people/pavel/xwinnmr/prog/nmrsim/
running on   : host name      = phobos
               host id        = 690c992e
FLEXlm license file = /usr/local/flexlm/Bruker/licenses/license.dat
################################################
```

- ***Wibukey***
  is a copy protection key in the printer port of your computer. Its setup program will install all necessary protection components.
- ***HASP***
  is a copy protection key used for the network installations. The HASP support is now disabled. Start the program with parameter ***-hasp*** to enable the HASP support.

All protection mechanism have their own installations. Please follow further instructions there.

1.5.3 How to install the UNIX version

The UNIX version is distributed on the BRUKER software CD. Login as superuser and start the installation:

/CDROM/startme

The installation program opens a new window. Select the programs you would like to install.

We recommend you to select both XWIN-NMR and NMR-SIM. In this case the installation program installs the NMR-SIM in the XWIN-NMR installation tree automatically:

<xwinnmrhome>/prog/nmrsim

The NMR-SIM installation script ***Install*** registers the basic information about BRUKER programs in the registration file ***/usr/Bruker/Software.ini***. The command

BrukerConfig extracts and prints the basic information about installed software.

NMR-SIM creates in your directory the subdirectory *NMRSIM_SESSION*. All private pulse programs and spin systems descriptions are placed here.

1.5.4 XWIN-NMR

XWIN-NMR must be configured **before** you start NMR-SIM. You should install the pulse programs using XWIN-NMR commands

cf
setup / expinstall /"Install High Resolution Pulse Programs"

Start NMR-SIM from the menu *Analysis/Simulation*, or type in the command *nmr-sim*.

Please note, that the if you start NMR-SIM from a UNIX shell, the **environment variable XWINNMRHOME must be defined**. You may set it by simply inquiring its value from the xwinnmr script:

XWINNMRHOME=‘xwinnmr -p‘
export XWINNMRHOME

1.5.5 Password protection

NMR-SIM is copy protected using a Flex-lm license manager.

If your password expires, or is missing, you will get simple message. When ordering the program, you must specify the target computer and the computer system information which you will get by using following command:

nmrsim -i

This is an example output:

```
##################################################
This is NMR-Sim version 2.6
installed in : /usr/people/pavel/xwinnmr/prog/nmrsim/
running on   : host name      = phobos
               host id        = 690c992e
FLEXlm license file = /usr/local/flexlm/Bruker/licenses/license.dat
##################################################
```

You may also use the Flex-lm utilities:

lmhostid

or

lmutil lmhostid

For more information about the network licenses and the installation of network-license manager, please refer to XWIN-NMR release letter.

Chapter 2

Theoretical background

The aim of this section is to give you some brief background information on the physical models and equations used for the simulation.

The simulation of a NMR experiment is based on the ***density matrix*** approach. Relaxation phenomena are implemented using a very simple model based on Bloch equations. ***Cross-correlation and cross-relaxation effects are neglected***.

2.1 Liouville equation

The basic equation describing the time development of the density matrix ρ is the ***Liouville equation***:

$$\begin{aligned} i\hbar\dot{\rho}(0) &= [H, \rho] \\ H &= H_0 + H_{rf}(t) \end{aligned} \qquad \textbf{\textit{(2.1)}}$$

where $\rho(0)$ is the density matrix and H is the spin system Hamiltonian.

The Hamiltonian may be divided in two parts. The time dependent part $H_{rf}(t)$ describes the interaction between nuclei and the radio frequency fields from spectrometer. The constant part H_0 describes the nuclear spin system, or in other words the sample.

$$\begin{aligned} H_0 &= \sum_i \omega_i I_z^i + \sum_{i<j} 2\pi J_{ij} I^i I^j \\ &= \sum_i \omega_i I_z^i + \sum_{i<j} 2\pi J_{ij}(I_z^i I_z^j + I_x^i I_x^j + I_z^i I_z^j) \end{aligned} \qquad \textit{(2.2)}$$

The program finds the solution of 2.1 in the form of the exponential propagator

$$U(t) = Te^{\left(-\frac{i}{h}\int_0 H(\tau)d\tau\right)}. \qquad \textit{(2.3)}$$

Only numerical approaches are used to calculate the propagator ***U***. So there are no approximations resulting from analytical formulas or simplifications (e.g. weak coupling approximation). The time evolution of the density matrix is calculated using

$$\rho(t) = U\rho(0)U^{\dagger}, \qquad \textit{(2.4)}$$

where $\rho(0)$ is the initial density matrix. These formulas are used for delays as well as for radio-frequency pulses. Thus, the exact evolution of the whole spin system during all pulses is taken into account. In this way, we are able to simulate the selective pulses and rotating-frame coherence-transfer experiments exactly. The propagators for radio-frequency pulses are phased using the appropriate phase specified by the pulse sequence, so you can use any general phase cycle. The propagator of the whole pulse sequence U_g is defined as a product of all interval propagators in the sequence

$$U_g = \prod_{i=1}^{N} U_i, \qquad \textit{(2.5)}$$

It is clear from this formula, that the most frequent numerical operation used by the simulator is **matrix multiplication**.

If you add one non-equivalent spin 1/2 nuclei to your spin system, you will double the dimension of the spin system density matrix, but the time necessary for matrix multiplication will increase by a factor of 8. Thus there is a significant loss of performance for larger spin systems. About $2*10^6$ floating point operations are needed to multiply two 64*64 complex matrices, which represent operators for six nonequivalent spin 1/2 nuclei.

It is a different situation, if you increase the multiplicity of some nuclei. In this case the program uses the **group theory** to split the spin system into several smaller ***fictitious***, independent ***systems***. Performance loss is far smaller than the factor 8 for nonequivalent nuclei. So, if you simulate the behavior of spin systems with equivalent nuclei, use the multiplicity parameter in the spin system definition file. If you specify the equivalent nuclei using different spin labels but the same resonance frequency and couplings, you will get the same result, but the calculation will be far slower and the probability that you will exceed the program limits will be larger.

The acquired FID is calculated using the formula

$$\mathrm{FID}(n) = \mathrm{Tr}\left\{ e^{-iH_0\tau n} U_g \rho(0) U_g^{\dagger} (e^{-iH_0\tau n})^{\dagger} J^{+} \right\} \qquad \textbf{\textit{(2.6)}}$$

where J^+ is the creation operator for the total angular momentum of the observed nuclei, Tr is the symbol for the trace operator.

2.2 Relaxation

Relaxation is implemented in NMR-SIM as follows:

During radio-frequency pulses the relaxation effects are neglected. During delays the program uses the Bloch equations for the relaxation of longitudinal magnetization

$$\dot{M}_z = -\gamma(\overline{B} \times \overline{M})_z + \frac{M_z - \overline{M}_0}{T_1}\ , \qquad \textbf{\textit{(2.1)}}$$

where $\overline{M}_0$ stands for the thermodynamic equilibrium value. The rest of the density matrix (i.e. off diagonal elements) is multiplied by the factor

$$e^{\frac{-t}{T^*}}\ , \qquad \textbf{\textit{(2.2)}}$$

where *t* is the interval length and T^* is the effective relaxation time

$$\frac{1}{T^*} = \sum_j \frac{1}{T_j}\ . \qquad \textbf{\textit{(2.3)}}$$

When the full relaxation simulation is switched on, the initial relaxation matrix $\rho(0)$ in the equation 2.3 is regularly updated to its relaxed value. This allows the simulation of relaxation artifacts in 2D spectroscopy.

2.3 Flow of the simulation

The flow of the simulation is the same as the flow of real NMR experiment:

All pulse program transients are calculated in the same order as they are carried out on a spectrometer.

The user can check the flow of an experiment by means of message lines in the NMR-SIM main window which display the current pulse program, transient (scan) and experiment numbers. When the program calculates the FID, this box displays the message *Acquisition*.

Generally it is not necessary to calculate the FID for every pulse sequence transient (scan). It is possible to accumulate the density matrix instead and to calculate the FID after the last scan. In this case the program displays the message *Acquisition* only at the end of the last transient. This approach substantially speeds up the simulation of multidimensional experiments with phase cycling.

All the NMR-SIM calculations are highly optimized for maximum performance, the pulse propagators ***U*** are stored in memory for later use in subsequent scans or the next time increment in multidimensional experiment.

There is also the possibility to save the propagator U_g (equation 2.5) of a pulse sequence fragment. Such a propagator is known as a ***compiled segment***.

Switching on the option ***Optimize sequence*** (See “NMR-Sim settings” on page 32), the program tries to find segments in the current pulse program which can be compiled. These segments are then compiled and saved in memory for later use. In the case of composite pulses, or magnetization transfer sequences (MLEV, WALTZ, DIPSI,....), this approach will substantially speed-up the simulation of an experiment, which uses this compiled fragment.

Chapter 3

Using the program

This chapter provides a short guide through the NMR-SIM menus and an introduction to the program user interface. Further detailed information about the experiment setup and several example experiments can be found in the section **Examples**.

3.1 Program start

Windows

It is possible to start the program in all the usual ways available under MS-WINDOWS, e.g. double-clicking its icon, but the best way is to use the *Simulation/NMR-SIM* command in WIN-NMR, or type ***nmrsim*** on the XWIN-NMR command line.

Unix

On UNIX workstation use the menu command *Analysis/Simulation* in XWIN-NMR or type ***nmrsim*** on the XWIN-NMR command line.

After start NMR-SIM seeks for further copies of itself (instances), that might already be running. If it finds an other instance, it opens its window and terminates itself. In other words, **every user may run only one instance of NMR-SIM at a time**.

3.2 Command line interface

It is also possible to start the program from a command-line shell. You may use the following start-up options.

3.2.1 Information options

The information options deliver status information and important information about your computer needed for the generation of licenses.

- ***-h***
  shows a list of all command line parameters
- ***-p***
  shows the directory where the program was installed
- ***-v***
  shows the program version
- ***-i***
  prints the information about your computer. The computer name and computer id shown here are important for the generation of the NMR-SIM license (if you use the FLEXlm license manager).

3.2.2 Parameter definitions

This set of options allows you to define several experiment parameters on the command line.

- ***-config <name>***
  this command loads the predefined experiment configuration.
  Example:
  nmrsim -config example1d.cfg
  starts NMR-SIM and loads the predefined configuration file example1d.cfg from the user directory $(HOME)/NMRSIM_SESSION/config.
- ***-xconfig <name>***
  load the experiment configuration from ***XWIN-NMR*** acquisition parameters
- ***-pulprog <name>***
  selects pulse program <name>.

nmrsim -pulprog cosydfsh

- ***-spnam<n> <name>***
  selects the waveform for shaped-pulse (acquisition parameter SPNAM0 .. SPNAM32).
  Example:
  nmrsim -spnam0 gauss
  nmrsim -config selcosy.cfg -spnam0 gauss

It is possible to combine several parameter definitions on one command line:

nmrsim -config cosy.cfg -pulprog cosydfsh

This example loads on the start the configuration file ***cosy.cfg*** and then selects new pulse program ***cosydfsh***. The **order of parameters is substantial**: the parameters are evaluated from left to right, so it ***does not make any sense to write***

nmrsim -pulprog cosydfsh -config cosy.cfg

The ***-config*** option will rewrite the pulse program selected in the ***-pulprog*** parameter!

3.2.3 Run time options

This set of parameters changes the default run-time behavior.

- ***-showp <pulse program>***
  This option opens the pulse program display window an shows the pulse program. Only the pulse program window is visible, the simulation functions are not available. You may start as many copies of this display as you will. Consult the chapter **Pulse program display** on page 61 for more details.
- ***-bloch***
  opens the Bloch simulator window as stand-alone application. You may start as many copies of the Bloch simulator as you need.

Windows

- ***-x***
  starts NMR-SIM in the XWIN-NMR compatibility mode. This means, that the

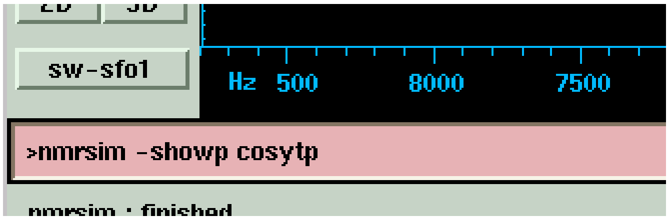
spectra are written in XWIN-NMR format and NMR-SIM uses pulseprograms and waveforms from XWIN-NMR tree (../exp/stan/nmrs/lists/..).

Windows

- ***-hasp***
  enables the HASP protection key. Without this option, only FlexLM and Wibukey passwords will be recognized.

The command line options are the same for all operating systems. The MS-WINDOWS version of NMR-SIM contains two program versions: one without the console interface (nmrsim_w.exe), the second with console interface (nmrsim.exe). The parameter definitions and run-time options are available for both versions, the information options are available only in the console version (the console is necessary to see the results).

All NMR-SIM options may be also used from the XWIN-NMR command line:



```
>nmrsim -showp cosytp
nmrsim : finished
```

3.3 Exiting NMR-SIM

You can exit the program in two ways: using menu the command *File/Exit*, or using the system menu (upper left corner of the NMR-SIM window). The first form saves the currents state (selected files, values of parameters) on disk, in the second form nothing is saved.

The saved state will be loaded at the next start from the file ***session.cfg*** in the user directory.

3.4 User data directory

All private data (pulse sequences, spin system definitions,...), created by the user are saved in the private user directories, but it is also possible to load files from any other directory. In this way possible interference between potential users is minimized, and a common database of sequences and spin system definitions can be created.

The program creates user private directory ***NMRSIM_SESSION*** in your home directory:

c:\users\otto\NMRSIM_SESSION
\usr\people\otto\NMRSIM_SESSION

All example files are copied here after the first start of NMR-SIM.

3.5 Main menu commands

The NMR-SIM main window displays basic information about current settings: the names of selected experiment definition files and the duration of the last experiment in seconds.

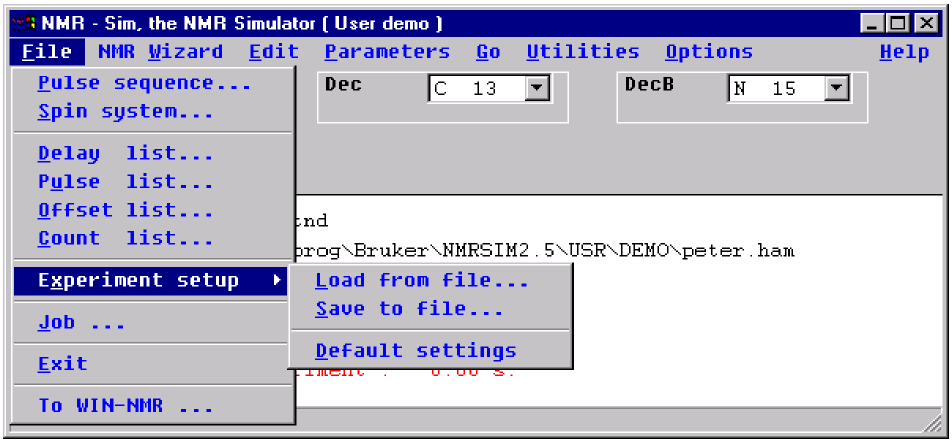
The combo-boxes on the top of the window show the nuclei assigned to each of four NMR channels. To change the assignment, click on the button and select new nucleus from the list.

The program commands are separated into several logical function groups.

3.5.1 File

The File menu (Figure 3.1) allows you to select current pulse sequence and spin system definition data files, as well as the current delay, pulse and offset lists.

- ***Experiment setup*** submenu contains following commands:
  - ***Load from file***
  - ***Save to file***
    All information about experiment set-up is saved on disk as well. The configuration is automatically loaded during the log-in procedure from the file ***session.cfg***, but the user has the possibility to create any number of private configuration files (any name with the extension ****.cfg***) and read them manually using the ***Load from file*** command.
    The configuration files reside in user private directories. Several pre-



```
nd
prog\Bruker\NMRSIM2.5\USR\DEMO\peter.ham
```

Figure 3.1 **File menu**

defined configuration files are installed in the demo user directory. You can use them to run several example experiments.

- ***Default settings***
  This command sets the default value for all NMR-SIM parameters. The default values allow you to execute a variety of NMR experiments without significant changes. Only spin system dependent parameters as evolution delays must be modified.
- ***Load from XWIN-NMR data set***
  This command reads the NMR-SIM experiment configuration from an existing XWIN-NMR data set. Only Avance spectra are supported.

- ***To Win NMR***
  This command starts WIN-NMR 1D or 2D and shows the processing window.

Windows

- ***Job***
  NMR-SIM allows execution of several experiments in one job. The job description is saved in a plain text file and contains only the names of configuration files which are loaded and executed. The progress of the job is recorded in a simple protocol file.
  The command ***Job*** only selects the job description file. The job may be started from ***Go*** menu.

- ***Exit*** This command closes all program windows, saves the current configuration on the disk and exits.

3.5.2 NMR-WIZARD

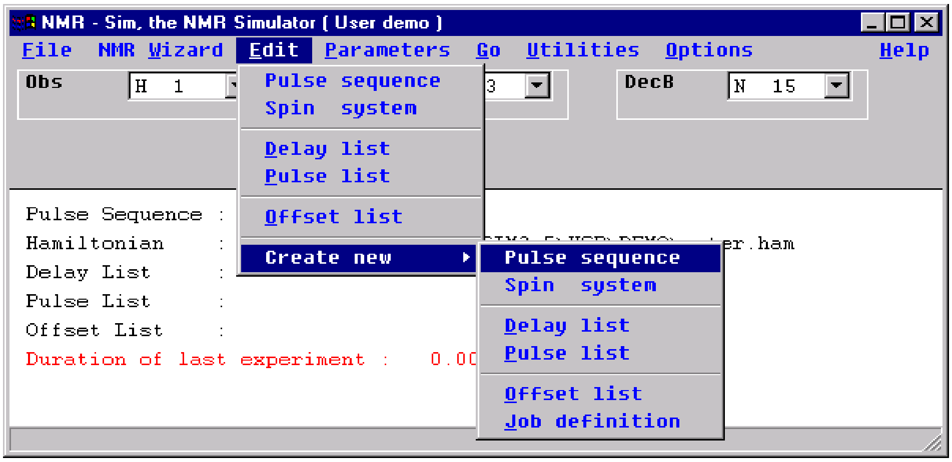
NMR-WIZARD is a tool which does its best to setup the NMR experiment without any user interaction.

The user merely selects the pulse program and the spin system. NMR Wizard interprets the parameters stored in the pulse program as comments and sets up the acquisition and processing parameters.

Refer to the section ***NMR Wizard*** for further details.

3.5.3 Edit

The experiment definition files which are saved as general text files in ASCII file



Obs H 1

DecB N 15

Pulse Sequence :
Hamiltonian :
Delay List :
Pulse List :
Offset List :
Duration of last experiment : 0.0

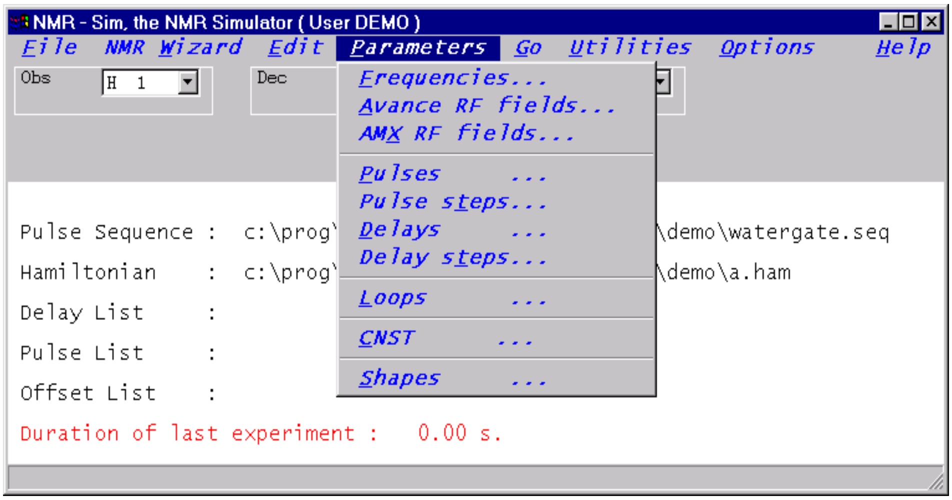
Figure 3.2 Edit menu

format (pulse programs, all lists, spin system definitions), are edited using a built-in text editor.
The pulse program editor may use the on line graphical display of pulse programs.
Refer to the ***Pulse program display*** section for further details

The ***Create new*** submenu may be used to create a new experiment description files. A new file is created and edited using the built in editor.

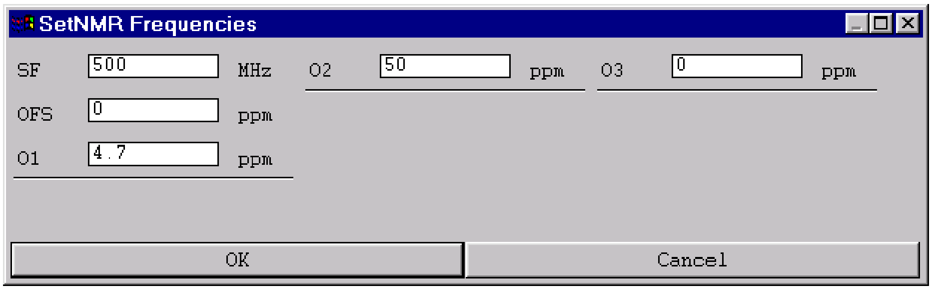
3.5.4 Parameters

From the Parameters menu editing of all of the experiment parameters is possible.



```
Pulse Sequence :  c:\prog\                    \demo\watergate.seq
Hamiltonian    :  c:\prog\                    \demo\a.ham
Delay List     :
Pulse List     :
Offset List    :
Duration of last experiment :   0.00 s.
```

Figure 3.3 Parameters menu



SF 500 MHz
O2 50 ppm
O3 0 ppm
OFS 0 ppm
O1 4.7 ppm

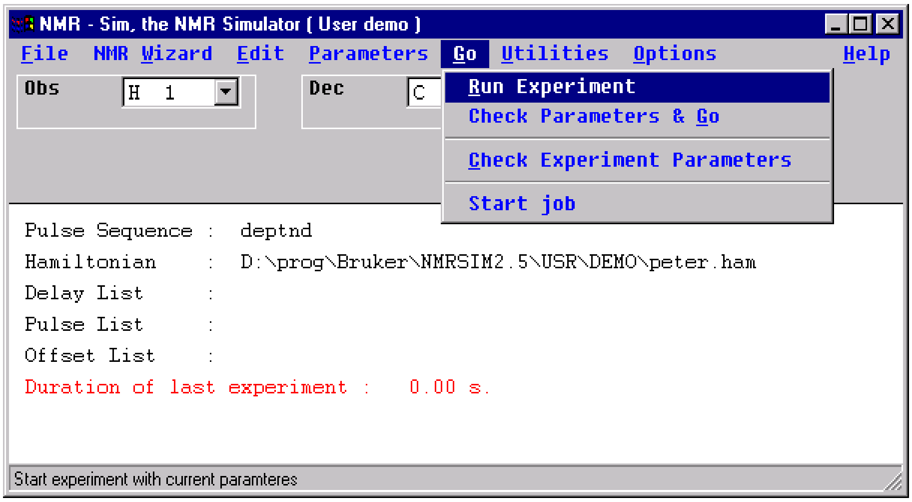
Figure 3.4 Set Frequencies dialog box

The command ***Frequencies*** opens a dialog box (Figure 3.4), where you set the basic spectrometer frequencies. The radio frequency field amplitudes may be edit using the commands ***Avance RF fields*** or ***AMX RF fields***.

Other experimental parameters are accessible using simple dialog boxes. The dialog boxes for pulses, pulse increments, delays, delay increments and loop counters all have the same layout. The format used for the input of all parameters is summarized in the chapter “NMR-Sim parameter definition” on page 87.

3.5.5 Go

The menu element ***Go*** starts the simulation.



```
Pulse Sequence  :  deptnd
Hamiltonian     :  D:\prog\Bruker\NMRSIM2.5\USR\DEMO\peter.ham
Delay List      :
Pulse List      :
Offset List     :
Duration of last experiment :   0.00 s.
```

Start experiment with current paramteres

Figure 3.5 NMR-SIM Go menu

It is possible to start the simulation immediately - ***Run experiment***, or check and edit the value of all parameters before the start - ***Check Parameters & Go***[1].

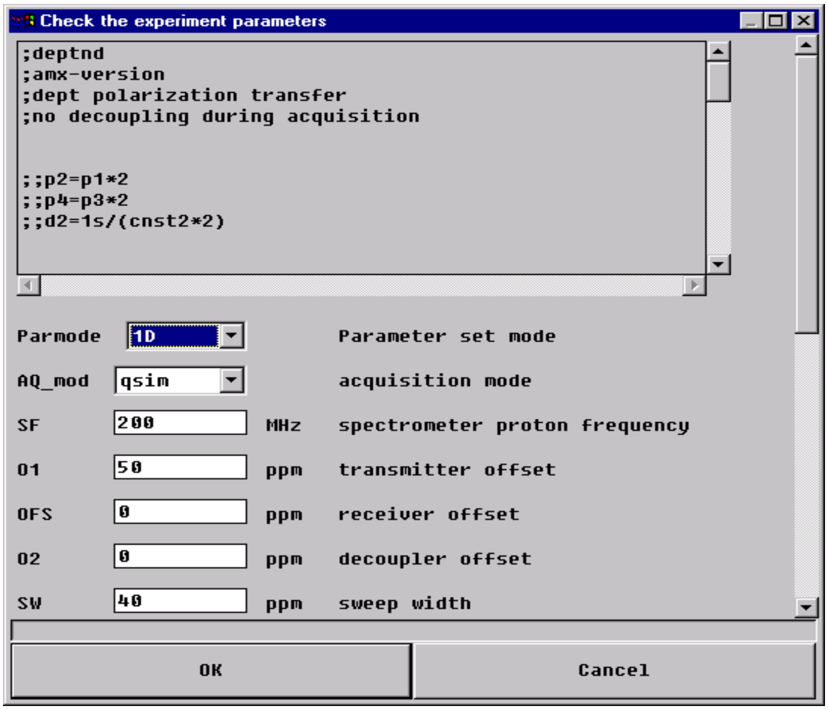
The dialog box for the editing of current experiment parameters (Figure 3.6) displays only those parameters, which are really used during the simulation.

The command ***Check experiment parameters*** shows the parameter dialog box. You may change any parameter. Parameters are stored, but the experiment is not started.

Command ***Start job*** starts the NMR job.

---

[1] This is the equivalent of XWIN-NMR command *ased*



```
;deptnd
;amx-version
;dept polarization transfer
;no decoupling during acquisition


;;p2=p1*2
;;p4=p3*2
;;d2=1s/(cnst2*2)
```

Parmode	1D		Parameter set mode
AQ_mod	qsim		acquisition mode
SF	200	MHz	spectrometer proton frequency
O1	50	ppm	transmitter offset
OFS	0	ppm	receiver offset
O2	0	ppm	decoupler offset
SW	40	ppm	sweep width

Figure 3.6
Check parameters dialog box. The text of the pulse program may be switched off in the dialog ***Options/NMR-Sim options.***

3.5.6 Utilities

This menu contains several useful tools

- ***List energy levels***
- ***Show energy levels***

These two commands show the spin system energy levels in a simple graphical, respective text forms.The numerical representation of the spin system *hamiltonian* and its *eigen vectors* (ev) as well as the *observing operator* are also shown in the energy levels listing.

Example: the protons in ethanol (ethanol.ham)

```
;
;Protons in ethanol
;Bruegel, Handbook of NMR Spectral parameters,
;vol 2, p 316
;
proton 3*a 1.19
proton 2*b 3.66
proton   c 5.27
;
couple a b 6.9
couple b c 4.76
```

The energy levels listing for this spin system is generated by using following commands:

Experiment setup/Load from file -> *demo1d.cfg*, ***Utilities/List levels***.

The output contains the basic information about the fictitious spin systems used for the calculation:

- Matrix dimension of each group
- Nuclei labels with their fictitious spin numbers

All matrices are printed in block-form, the elements equal to 0 are printed as dots. Small, non zero elements are printed as 0. Symbol NULL is printed, when all the elements in one block are equal to 0. The matrix names use the following notation:

- ***ham*** - Hamiltonian
- ***obs*** - observing operator
- ***ev*** - matrix of hamiltonian eigenvectors

The example output has been truncated:

```
     List of spin system energy levels
ethanol.ham
Tue Jul 25 19:34:41 1995
SF 500 MHz
```

```
The spin system contains
1 Molecules
3 Nuclei
4 Groups
-----------------------------------------------
Nuclei -  [12x12]  a(1/2)  b(1)  c(1/2)
Energy Levels  [Hz]
     0 :       450.83
     1 :      1348.95
     2 :       114.99
.
.
Lines
                Frequency        Intensity
   1 ->   0  :      -342.8        0.9171
   2 ->   0  :      -241.6          1.29
   3 ->   0  :       898.2        0.9066
.
.

List of matrix ham

-----------  [8x8]  a(3/2)  c(1/2)   ------------
size 8 x 8
real :

 -790.0      .       .       .       .       .       .
     .    115.0      .       .       .       .       .
     .       .   1020.0      .       .       .       .
     .       .       .   1925.0      .       .       .
     .       .       .       .  -1925.0      .       .
     .       .       .       .       .  -1020.0      .
     .       .       .       .       .       .   -115.0
     .       .       .       .       .       .       .
imag :
```

The ***Show pulse program*** command opens a new window and presents the current pulse program in a simple graphical form. More details may be found in the chapter ***Pulse program display*** on page 61.

The command ***Bloch module*** opens the Bloch simulator window described on page 39.

3.5.7 Options

Several parameters can be controlled from this submenu.

1. NMR-Sim settings

- ***Modify RF fields***

  when switched on, the program multiplies all radio frequency field intensities with the γ factor of corresponding nuclei. The default value is on.
  The length of the 90 degree pulse with 10000 Hz radio frequency intensity is calculated using the formula

$$\tau = \frac{90/360}{10000 \times \gamma}$$

  The section “Radio frequency field intensities” on page 88 contains more information.

- ***Filter Signals***

  when on, a rectangular filter is applied on the acquired signal. Signals with frequency outside of the selected bandwidth are filtered out and no signal foldback occurs.

- ***Optimize sequence***

  controls the automatic optimization of pulse programs (See “Theoretical background” on page 15.). The default value is on.
  Set this parameter to off only if you suspect that the pulse program compiler does not work properly.
  This switch will have no effect on the simulated spectra. The optimization of the pulse program only speeds up the calculation and will not affect the results.

- ***Start Win NMR***

  this option controls whether the simulator starts the WIN-NMR program after the end of simulation.

- ***Change Object***

  this option is used to control the XWIN-NMR context switching (See “Communication with other ***Bruker software products” on page 38.***).

- ***Show sequence***
  controls the display of the pulse program text preview in the Check parameters dialog box.
- ***One column edit***
  When on, uses the NMR-SIM one column format in the Check parameters dialog box. The second column is used to display a short description for each parameter.
- ***Pulse compiler***
  This switch selects the default pulse sequence compiler version. The NMR-SIM contains a pulse sequence interpreter, which supports all dialects of Bruker pulse program languages (AMX/ARX, Avance).

  The following algorithm is used to detect the compiler, which will be used.

  a)The 2nd line of pulse program contains the keyword *"amx-version"*, *"arx-version"* or *"avance-version"*:

```
;sample sequence for AMX spectrometer
;amx-version
.

;sample sequence for DMX/DRX/DPX spectrometers
;avance-version
.
.
```

  b)the pulse programs without this keyword are compiled using the ***default*** compiler set in this dialog box field.
- ***Define***
  This field lets you define symbols for the pulse sequence preprocessor. Multiple symbols are separated by semicolons. The symbol may by tested on their existence in pulse programs and definitions of spin system. Example:

  WEAK_ONLY;

  the definition of the symbol WEAK_ONLY allows one to switch between full coupling and the X-approximation in the following spin system example

```
#ifdef WEAK_ONLY
#define  couple weak
#endif
proton a 5.6
proton b 3.4
couple a b 10
```

This example defines the spin system as normally coupled. If you define the symbol WEAK_ONLY, the program takes the interaction as explicit weak, i.e. the 2nd order effects in your spectrum will vanish.

- ***Output file***

  a)Default redirects the output of simulation to the default file. The default file may be set using the command ***Options/Output file.***

  b)User Selected means, that the program asks before every start of experiment for the name of an output file. If the file exists, the program asks for the overwrite permission.

- ***Relaxation*** - here you can select the relaxation mode
  - ***None***

    Relaxation effects are ignored.
  - ***Acquisition***

    Relaxation is used only to simulate the natural line widths (signal decay during FID).
  - ***Full***

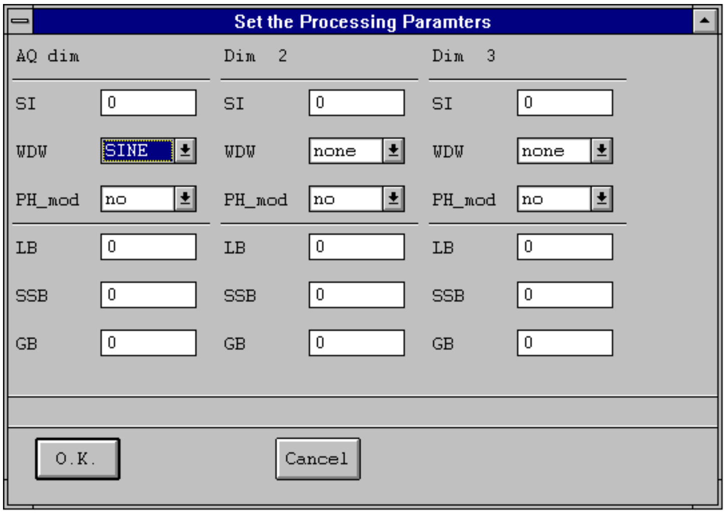
    Full relaxation as described in the section ***Theoretical background*** (page 15). This option significantly reduces the speed of calculations.
- ***P.S. Editor***

  Use this command to switch the behavior of the pulse program editor.
  - ***Text only***

    The pulse program is edited in the editor without any graphics.
  - ***Interactive display***

    The pulse program is edited in the text editor and the changes are shown on-line in the pulse program display window. Please, refer to chapter ***Pulse program display,*** page 68 for more details.

2. Processing parameters
   This command opens a dialog box (Figure 3.7) which lets you define the processing parameters. These parameters are saved on disk, i.e. you only need to execute the processing command (e.g. ***xfb***) when processing the simulated spectrum.



AQ dim		Dim 2		Dim 3	
SI	0	SI	0	SI	0
WDW	SINE	WDW	none	WDW	none
PH_mod	no	PH_mod	no	PH_mod	no
LB	0	LB	0	LB	0
SSB	0	SSB	0	SSB	0
GB	0	GB	0	GB	0

Figure 3.7 Processing parameters dialog

3. Output file
   This command defines the default output file.

Windows

4. Dialog font
   This command selects the font used in the dialogs.

Windows

5. Graphic font
   This command selects the font family for the graphic font in all NMR-SIM graphics windows. The font resize policy may be also selected. More details are available in the section ***Font selection*** in Appendix.

3.5.8 Help

The ***What's new*** command shows a short summary of new features and changes in the NMR-SIM version you are running.

The command ***On line Manual*** shows this manual. The commands ***Avance pulse programs*** and ***AMX pulse programs*** show the summary of pulse programming language syntax.

All the manuals are stored in the *"pdf"* format. The ***Adobe Acrobat Reader*** is used as a viewer for all manuals. The reader is on the Bruker Software CD, or you can get it directly from Adobe (www.adobe.com).

The ***About*** dialog box displays the copy-right message and you can check there the version and release date of your program. The installation directory and information about available licenses are also shown.

3.6 Spin system definition

A simple language is used to define the spin system. The spin system definitions are saved in text files with the extension ***.ham**. The program constructs, from the spin system definition file, the Hamiltonian operator H_0. So, we refer in some cases to this file as the **Hamiltonian definition**.

The user specifies the chemical shifts of all nuclei in the spin system and nuclei multiplicities. If the nuclei multiplicity is 1, it is possible to define its spin quantum number larger than 1/2. The nuclei chemical shifts are defined in ppm units, which are converted to absolute units using the spectrometer frequency parameter SF, which defines the **proton resonance frequency of the spectrometer**. The basic frequency of each radio frequency channel is calculated as

$SFO_i = SF*\gamma_{Chan}/\gamma_{proton}$,

where γ_{Chan} is the gyromagnetic factor of the isotope selected for the channel.

If necessary, the user can specify the start value of the density matrix ρ(0) different from the thermodynamic equilibrium ρ_0.

Nuclear chemical shift parameters in the spin system description can be specified as a variable. There are 32 such variables ***var1-32***, their values can be changed from the same dialog box as the general set of experimental parameters. Each

Hamiltonian variable is defined by two values:

- the start value ***HV1-32***
- the step ***HS1-32***. The user can change their values from the pulse sequence: it is possible to increment only one parameter (***ihv1-32***)or increment all parameters by one command (***ihc***).

The full description of spin system definition commands may be found in the chapter “Spin system definition summary” on page 75.

3.7 Pulse sequence definition

The program uses standard BRUKER pulse sequences (the AMX,ARX or Avance family of spectrometers) for the definition of the experiment. However, there are some restrictions and enhancements.

The pulse sequence is syntactically checked before the start of an experiment. In the case of errors in the sequence, the user has the possibility to edit the file with a simple editor.

The editor can be invoked from the ***Edit*** menu, or directly from the error message box. After opening the editor from error message box is the cursor placed on the line with the syntax error and the whole line is highlighted.

If the user starts the simulation using the command ***Go*** or ***Check Parameters & Go***, he is asked for the value of all parameters (Pulse and delay lengths, Rf intensities...), which are used in the sequence.

3.8 Running the simulation

After the start of simulation the menu in NMR-SIM main window changes.

The menu element ***Calculation/Stop*** aborts the simulation immediately after finishing the current command in the pulse sequence, no data are saved on the disk. Pressing ***Calculation/Halt*** interrupts the simulation, the program finishes the phase cycle and the data will be saved on the disk.

The information about the current state of running experiment is displayed in two lines below the menu bar. The first line, the **Experiment counter** is incremented when the acquisition command finishes the last transient (scan). The limit being displayed is identical with the TD1 variable. The 2nd line **Scan counter** shows the number of current transient (scan), the negative numbers are used to display the dummy scans (the dummy scan parameter DS is active only in the case, where the relaxation switch has the value Relax Full).

The bottom line of the NMR-SIM main window shows the elapsed time for the current calculation. The program also tries to predict the duration of the current experiment. In this case, both elapsed time as the predicted total time are shown. The prediction is improved during the calculation, so the value may vary.

Windows

When is the calculation finished and the button Start WIN-NMR in ***Options*** dialog box is checked, changes the program the size of the simulator window and opens the WIN-NMR processing window which displays the calculated FID.

3.9 Communication with other BRUKER software products

The output of NMR-SIM is compatible with other BRUKER software products, the data are written on the disk in WIN-NMR or XWIN-NMR format. The automatic connection between the simulation program and processing software combines 2 in one to create a **software-only** based BRUKER **spectrometer**.

3.9.1 WIN-NMR

When NMR-SIM program finishes its calculation, it automatically opens the 1D or 2D WIN-NMR processing window and displays the calculated FID.

3.9.2 XWIN-NMR

Starting the NMR-SIM from XWIN-NMR, the program switches the context to the simulated data set, when the simulation finishes. You can disable this option in ***Options/Change Object.***

Chapter 4

Bloch simulator

The command ***Utilities/Bloch module*** in the main NMR-SIM menu opens a new window (Figure 4.1) with its own menu bar. You may also start the bloch simulator as stand-alone application using following option:

nmrsim -bloch

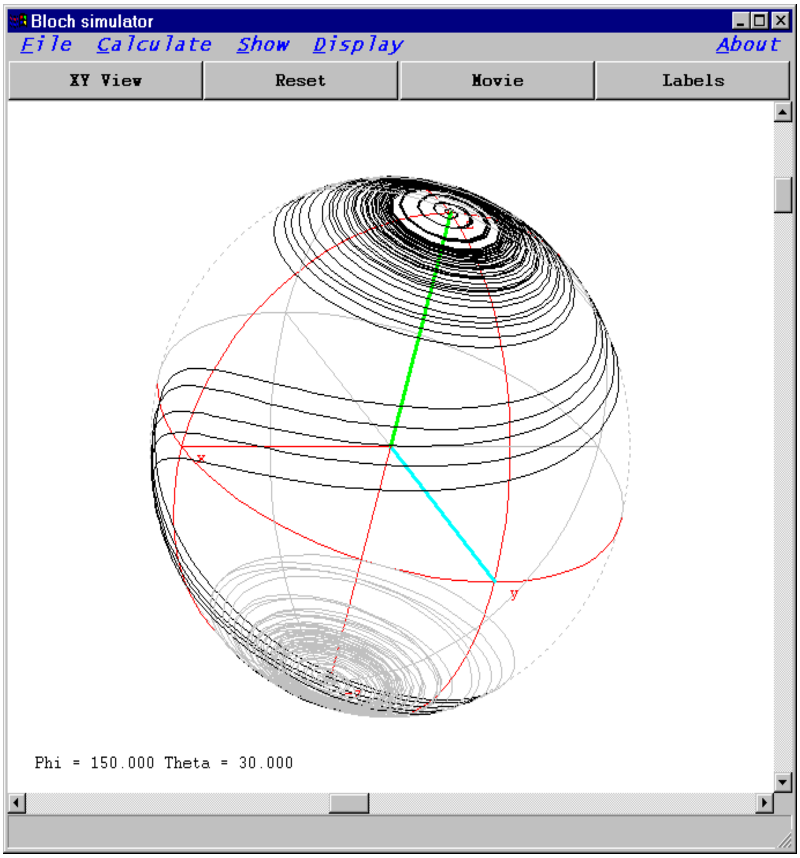
The stand-alone module contains only the functionality described in this chapter.

The Bloch simulator module is designed to calculate and visualize the motion of the nuclear magnetization vector during a NMR experiment. The calculation of ***excitation profiles*** and ***waveform analysis*** brings important information about the behavior of pulses or pulse sequences in a real experiment.

The motion of the magnetization vector is described by the Bloch equation

$$\dot{\overline{\mathrm{M}}} = -\gamma(\overline{\mathrm{B}} \times \overline{\mathrm{M}}) \quad , \qquad \textbf{\textit{(4.1)}}$$

This is a classical equivalent of the Liouville equation (Equation 2.1) for spin 1/2.



```
Phi = 150.000 Theta = 30.000
```

Figure 4.1
The time evolution of a nuclear magnetization vector during an adiabatic pulse, calculated for several offsets, is shown as a projection on the sphere

4.1 File

- ***Select***
  selects the waveform for the calculation. The waveform is immediately shown on the screen. The buttons on the top of window may be used to switch between cartesian and polar coordinates.

- ***Save***
  Saves the calculated information to disk. Always the displayed profile or waveform analysis will be written. This could be imported into other programs (it is a plain text file).
- ***Print***
  Prints the current picture. The UNIX version supports only output to disk file in PostScript format. The MS-WINDOWS versions support all MS-WINDOWS printers, including color ones.
- ***Copy to Clipboard***
  Copies the picture into MS-WINDOWS clipboard.

Windows

- ***Close***
  Closes the Bloch module window and pops up the NMR-SIM main window.

4.2 Calculate

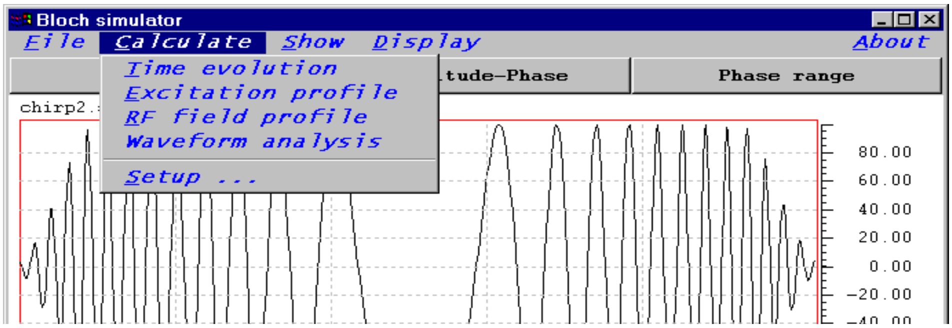
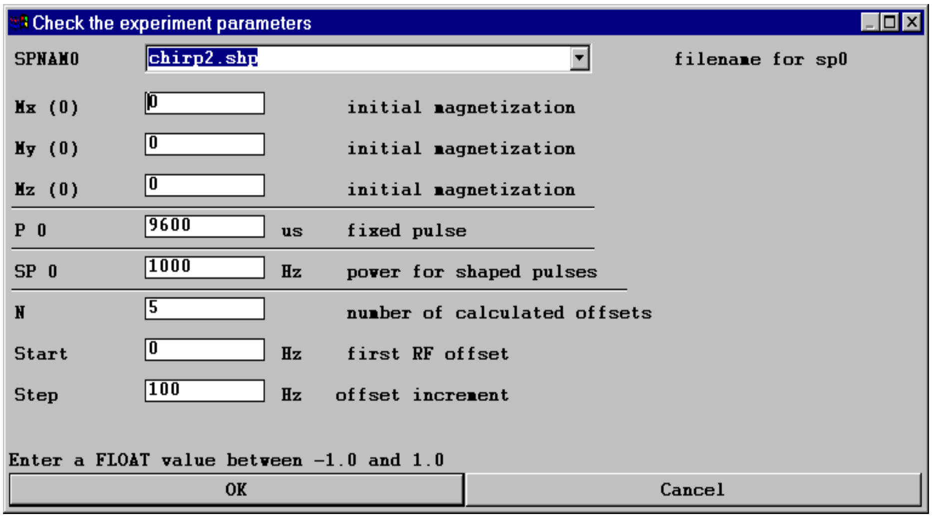


Figure 4.2 *Calculate* pull-down menu

4.2.1 Time evolution

Command ***Time evolution*** calculates the motion of the magnetization vector during the pulse for several radio frequency offsets and shows it on the sphere (Figure 4.1).

The command opens dialog box (Figure 4.3), which defines following experiment parameters:



SPNAM0	chirp2.shp		filename for sp0
Mx (0)	0		initial magnetization
My (0)	0		initial magnetization
Mz (0)	0		initial magnetization
P 0	9600	us	fixed pulse
SP 0	1000	Hz	power for shaped pulses
N	5		number of calculated offsets
Start	0	Hz	first RF offset
Step	100	Hz	offset increment

Enter a FLOAT value between -1.0 and 1.0

Figure 4.3 Parameters for the calculation of the time evolution of the magnetization

- ***MX(0),MY(0),MZ(0)***
  The initial value of the magnetization vector. The values are later so normalized, that the ***vector length is 1***.

  Example:
  (0,10,0) is equivalent to ***(0,1,0)***,
  (1,1,1) is equivalent to $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3})$

  The value ***(0,0,0)*** is identical to the equilibrium value ***(0,0,1)***.
- ***SPNAM0***
  Waveform name.

A list of all pulses, delays and variables that occur in the pulse program:

- ***SP 0***
  The radio frequency field intensity for the shaped pulse.
- ***TSlice***
  This parameter defines the maximal time step between two samples. It is necessary to set it only to sample the evolution during rectangular pulses.
  The value 0 means, that this parameter is ignored and the magnetization is sampled only at the end of each interval in the shaped pulse.
- ***N***
  Number of slices (offset values) which will be calculated. One slice represents the simulated experiment for one radio frequency offset.
- ***Start***
  The first value of radio frequency offset used for the calculation.
- ***Step***
  The radio frequency offset increment between two slices.

The result of the calculation may be shown either using spherical coordinates (Figure 4.4) or in cartesian coordinate system (Figure 4.5). Use the buttons on the top of the Bloch simulator window to select the type of coordinates and the visible magnetization component. The scroll-bars on the bottom and on the side of the window may be used to adjust the angle of view. The button ***Reset*** will restore default angle of view. The button ***Labels*** toggles the display of time labels. Each labels shows the time elapsed form the start of the pulse.

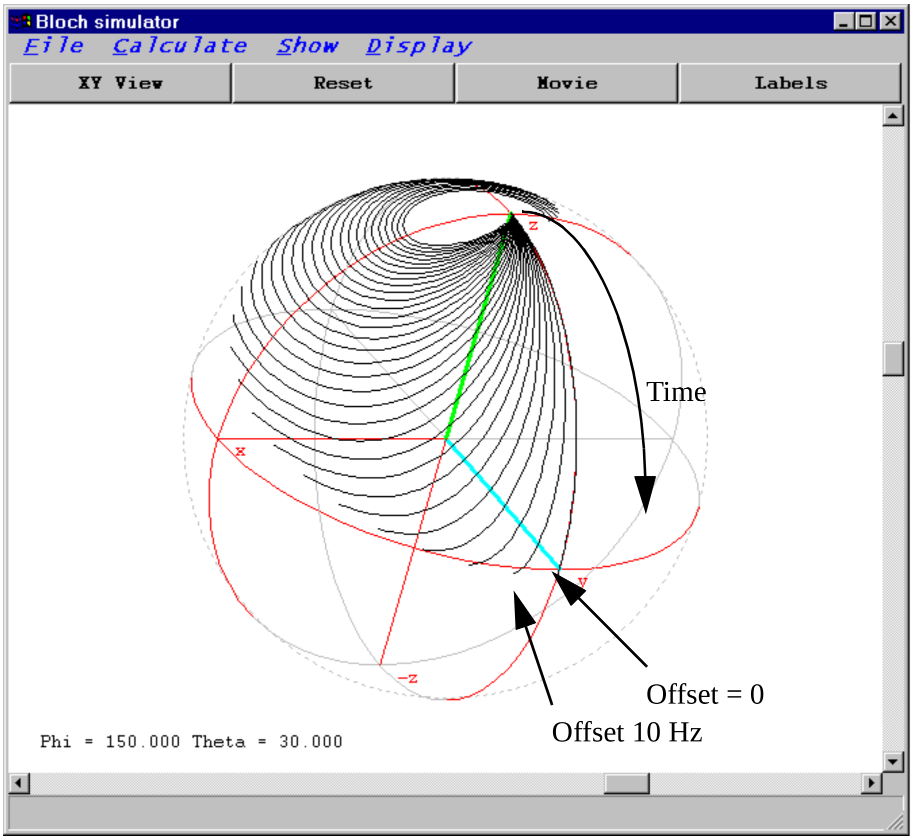


Figure 4.4 The time evolution of the magnetization vector shown as a projection on the sphere.

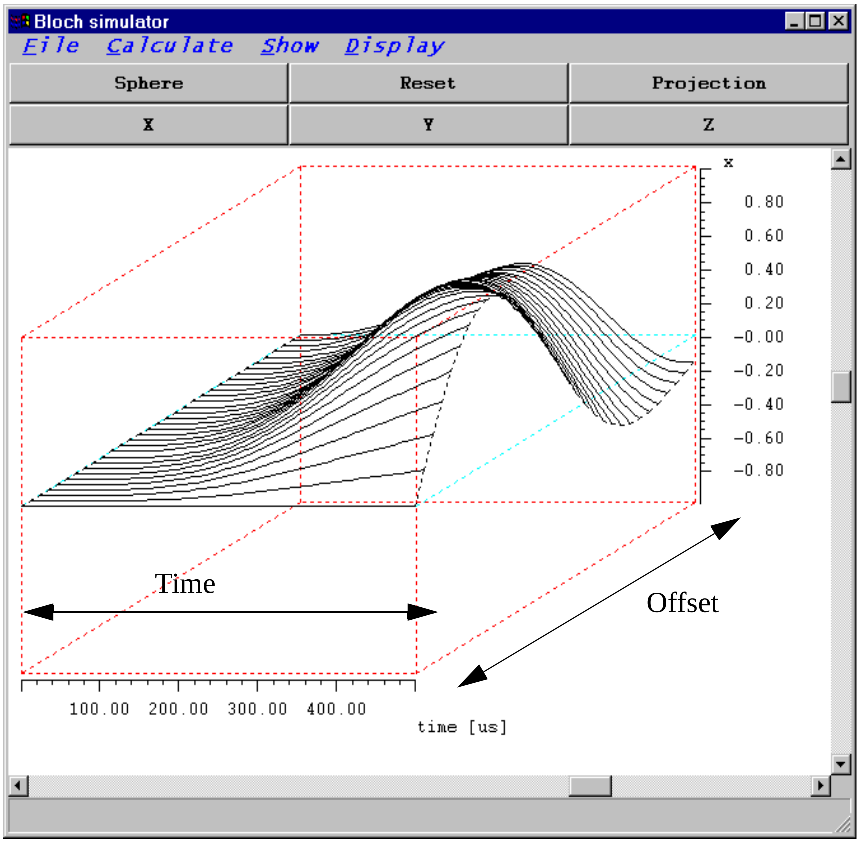
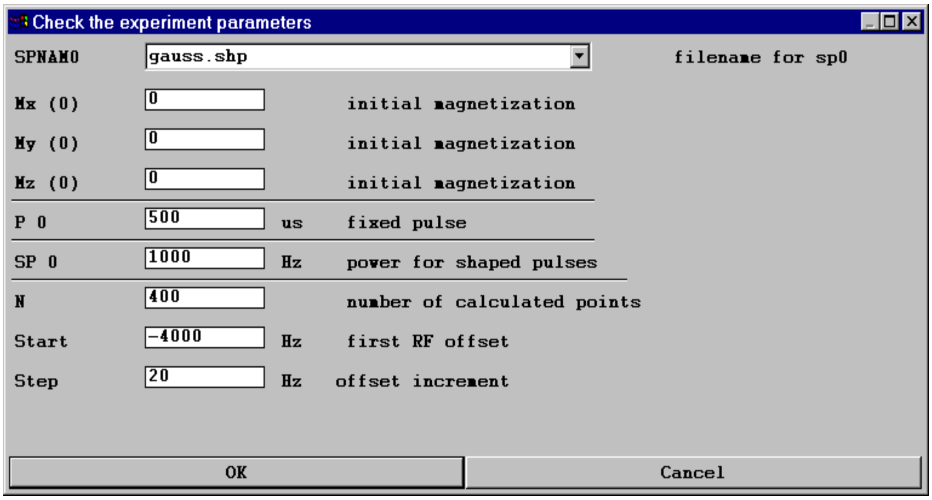


Figure 4.5 The time evolution of the Mx magnetization component shown as a surface.

4.2.2 Excitation profile

The command ***Excitation profile*** calculates the excitation profile of a shaped pulse.



SPNAM0	gauss.shp		filename for sp0
Mx (0)	0		initial magnetization
My (0)	0		initial magnetization
Mz (0)	0		initial magnetization
P 0	500	us	fixed pulse
SP 0	1000	Hz	power for shaped pulses
N	400		number of calculated points
Start	-4000	Hz	first RF offset
Step	20	Hz	offset increment

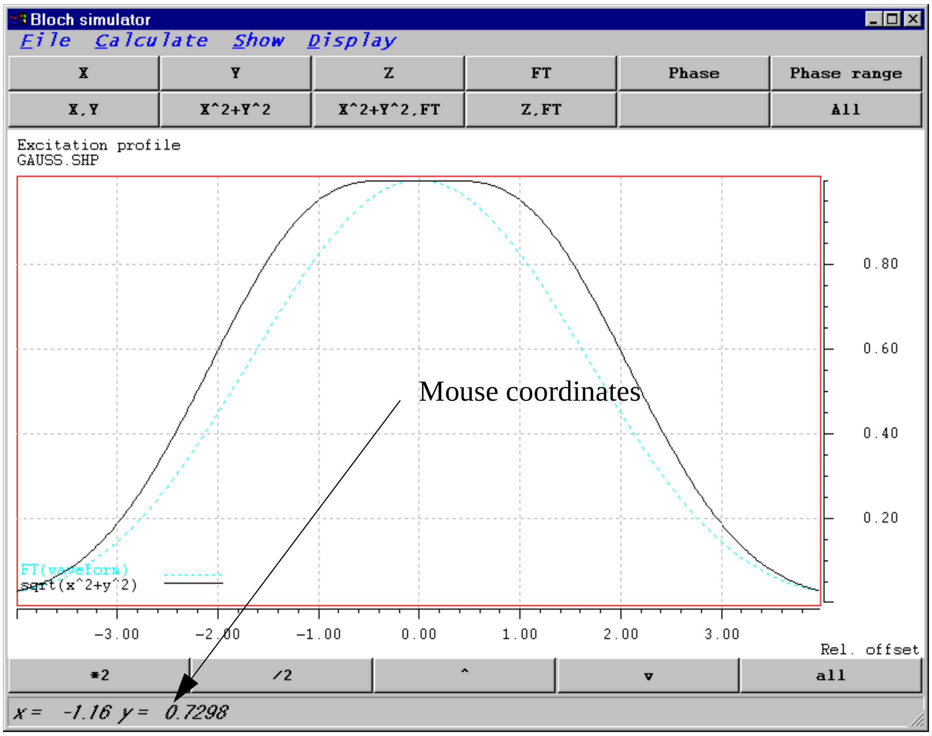
Figure 4.6 Parameters for the excitation profile calculation

The parameters are the same as for the time sequence. The window layout changes and the calculated excitation profile is shown (Figure 4.7). The buttons on the top of the window allow you to select the visible component. You may select either one magnetization component, the fourier transformation of the waveform[1], or combination of them. The button ***Phase range*** toggles the phase display between <0..360> and full phase range.

The buttons on the bottom may be used to scale the graph. On the bottom of the window is shown the position of the mouse cursor in the coordinates used for the axis.

---

[1] The fourier transformation of the waveform is in the first approximation (small flip angles) very near to the excitation profile of the pulse.



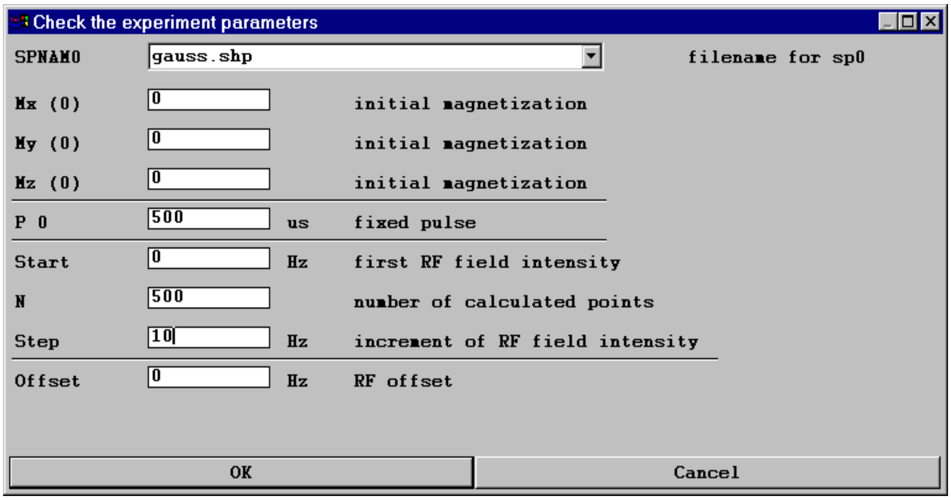
Mouse coordinates

x = -1.16 y = 0.7298

Figure 4.7
The excitation profile of the gaussian 90 degree pulse. The x axis uses as a unit the relative offset - the ratio of the radio frequency field and offset. Such a presentation is independent on the absolute value of radio frequency fields. The bottom status line shows the coordinate of the mouse cursor in this graph.

4.2.3 RF field profile

The RF filed profile command calculates the dependency of the magnetization on the RF filed intensity. You define the pulse length, the RF offset, the starting value of used radio frequency filed, number of calculated points and the step (Figure 4.8)



SPNAM0	gauss.shp		filename for sp0
Mx (0)	0		initial magnetization
My (0)	0		initial magnetization
Mz (0)	0		initial magnetization
P 0	500	us	fixed pulse
Start	0	Hz	first RF field intensity
N	500		number of calculated points
Step	10	Hz	increment of RF field intensity
Offset	0	Hz	RF offset

Figure 4.8
Parameters used for the calculation of radio frequency profiles

Calculated profile (Figure 4.9) is shown as a dependency of magnetization components on the RF field intensity. The displayed component may be selected using the bottoms on the top of the window. The cursor position is shown on the bottom status line.

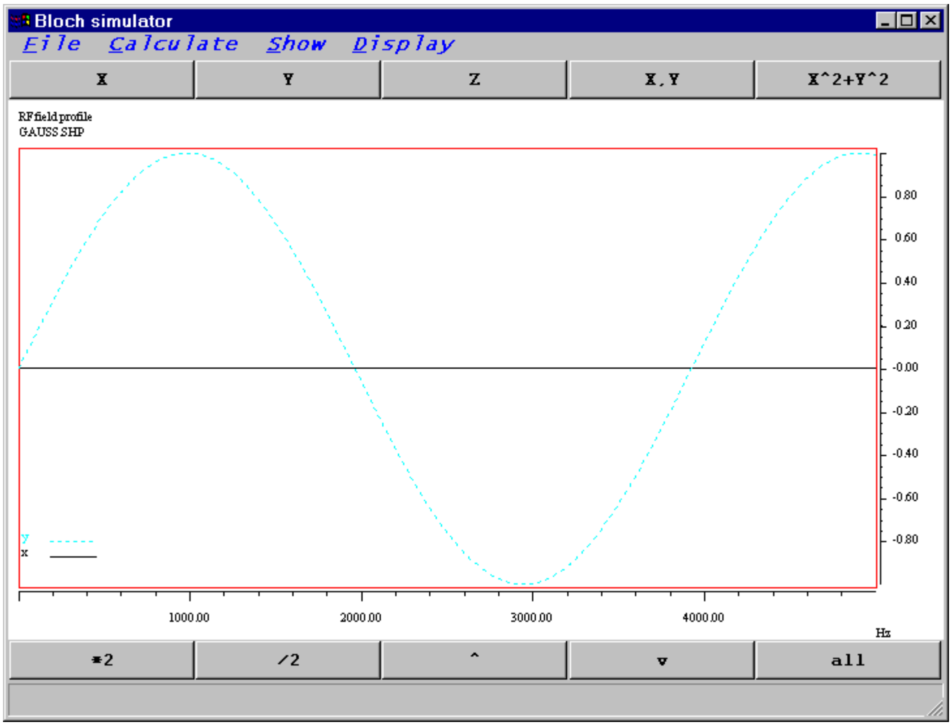
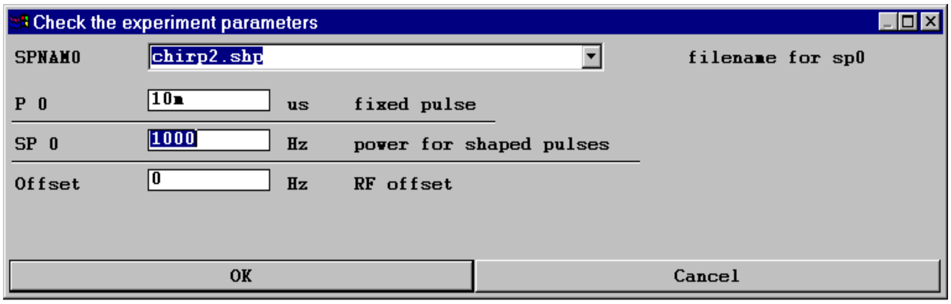


Figure 4.9
Calculated radio frequency profile. The length of the 90 degree pulse is 1000 ms.

4.2.4 Waveform analysis

The command "Calculate/Waveform analysis" is used to analyse features of adiabatic pulses. The program requires the pulse length, the rf intensity and the offset of the examined pulse and calculates following output:


Check the experiment parameters

SPNAM0	chirp2.shp		filename for sp0
P 0	10m	us	fixed pulse
SP 0	1000	Hz	power for shaped pulses
Offset	0	Hz	RF offset

Figure 4.10 Parameters used for the waveform analysis

- Θ_M and Θ_{B1eff} are the angles between the magnetization or B1eff vectors and the xy plane .

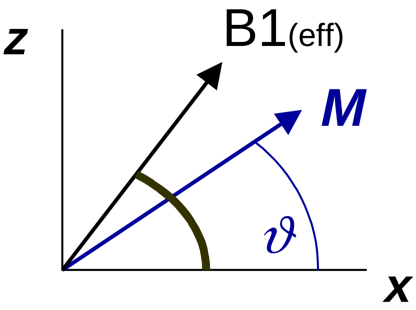


Figure 4.11

The definition of adiabatic condition requires, that the magnetization vector M follows the trajectory of the effective radio frequency field vector B1eff.

- Quality factor
- Frequency sweep.

Following pictures show the same pulse analyzed under two experimental conditions - on resonance and off resonance. The on resonance picture shows very good adiabatic condition, the off resonance case shows rising misalignment between the magnetization and rf field vectors - the adiabatic condition is not valid anymore.

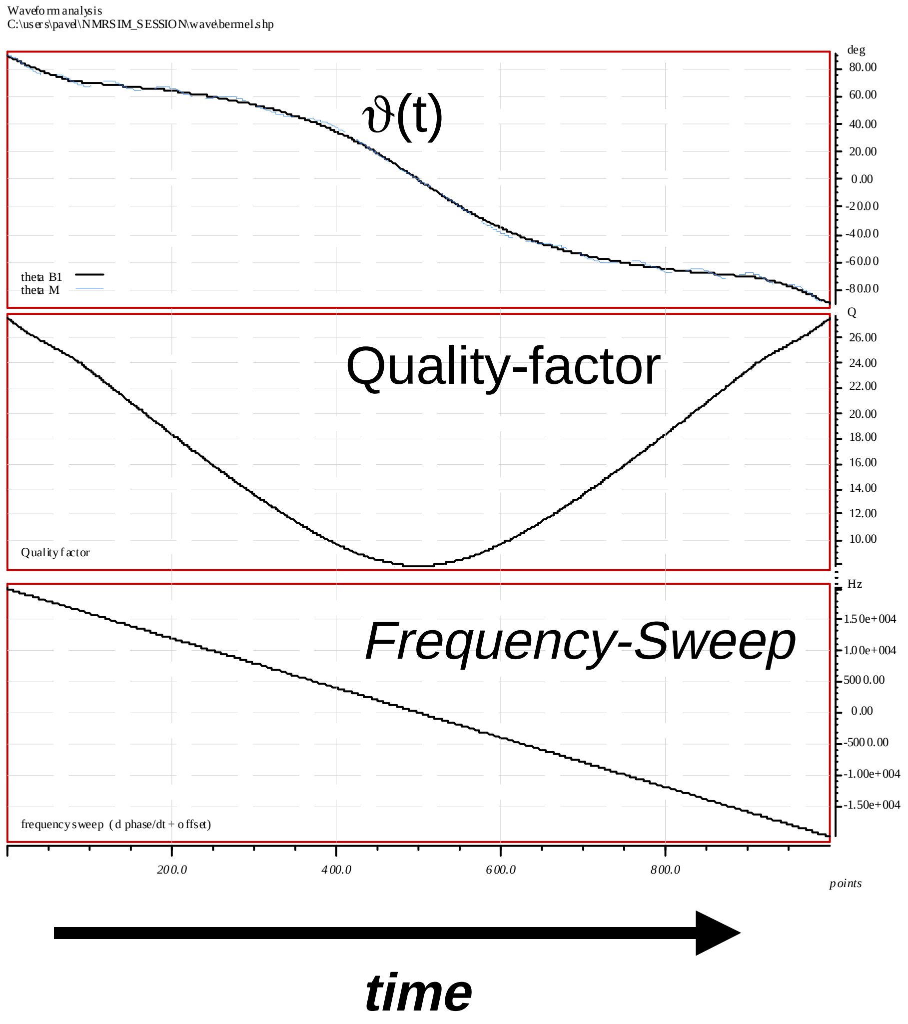


Figure 4.12 On resonance

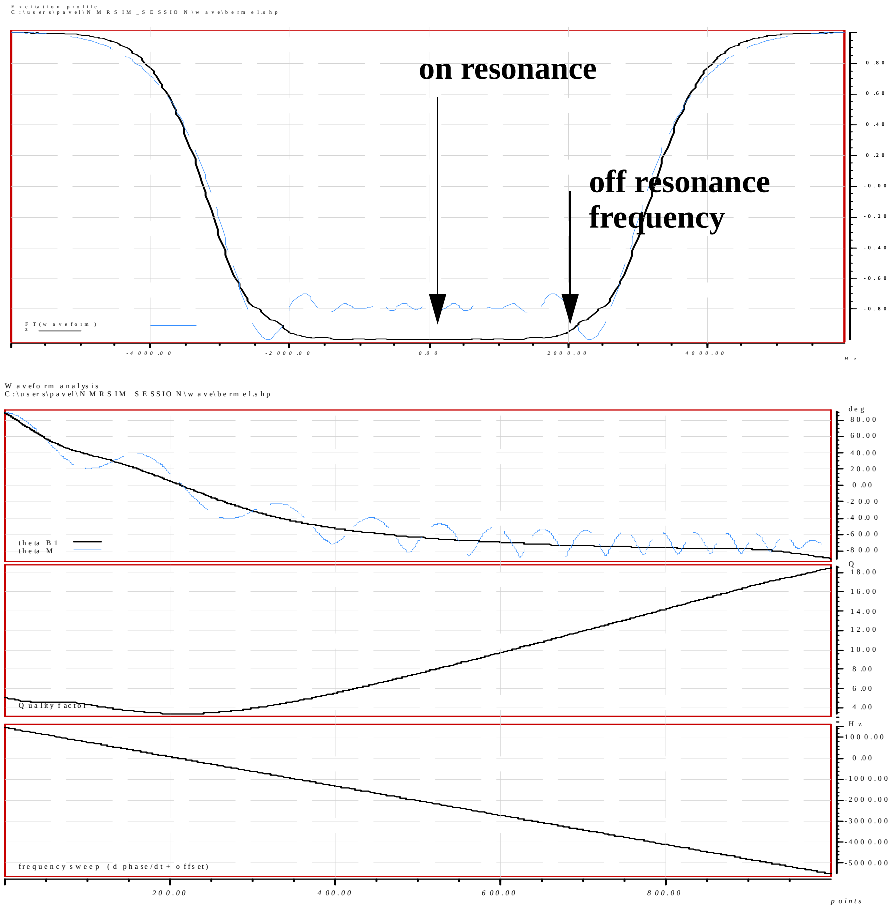

Excitation profile
C:\users\pavel\NMRSIM_SESSION\wave\bermel.shp
on resonance
off resonance frequency
FT(waveform)
0.80
0.60
0.40
0.20
-0.00
-0.20
-0.40
-0.60
-0.80
-4000.00
-2000.00
0.00
2000.00
4000.00
Hz
Waveform analysis
C:\users\pavel\NMRSIM_SESSION\wave\bermel.shp
deg
80.00
60.00
40.00
20.00
0.00
-20.00
-40.00
-60.00
-80.00
theta B1
theta M
Q
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
Quality factor
Hz
1000.00
0.00
-1000.00
-2000.00
-3000.00
-4000.00
-5000.00
frequency sweep (d phase/dt + offset)
200.00
400.00
600.00
800.00
points

Figure 4.13

4.2.5 Calculation setup

Command ***Setup*** opens a dialog box which allows you to select the calculation mode and the names of input files.

NMR-SIM supports two calculation modes:

1. ***Shaped Pulse***
   The shaped pulses are used for the calculation in this mode.
2. ***Pulse sequence fragment***
   You can calculate the excitation profile or time evolution of the magnetization through any pulse sequence. You must write your own pulse program to do this.

Follow this scheme:

```
ze
1  sample  ; starts sampling
; the pulse sequence fragment begins here
; you can use any pulse,loop or delay command
   p1  ph1
...............
.............
;  finish the sampling
   sample
;
;  increment the hamiltonian variables
;  and start the next run
   ihc
   lo to 1 times l2
exit
;
;  specify phases
;
```

```
ph1 = 0
ph2 = 2
```

The command ***sample*** is used to record the magnetization value. It replaces the command ***go=*** used in normal pulse programs.

4.3 Show

This command selects the information shown on the display.

- ***Time evolution***
  Shows the calculated time evolution projected on the sphere. The position of the viewpoint can be changed using the slider on the sides of the drawing area. You can also set the position directly from the ***Options*** dialog box. The position is defined using the two *Euler angles* ψ and θ. The button ***Reset*** brings the sphere back to the standard position.
- ***Excitation profile***
- ***RF profile***
- ***Analysis***
- ***Waveform***
  Show the selected waveform (*TPNAM0*). You may toggle the display between polar and Cartesian (x,y) coordinates (Figure 4.14)..

4.4 Options

This command opens a dialog box, which defines the current position of the viewpoint on the sphere, the step for the sphere rotation and controls the display of hidden lines for the sphere (by default are the hidden lines dashed and dark).

The switch ***Background*** selects the background color for all graphics in the bloch module. Other windows (pulse program display,...) are not affected.

The units for the frequency axis may also be set here. There are two possibilities:

- ***Hz***
  The x axis of the excitation profile shows the rf offset in *absolute* units - Hz.

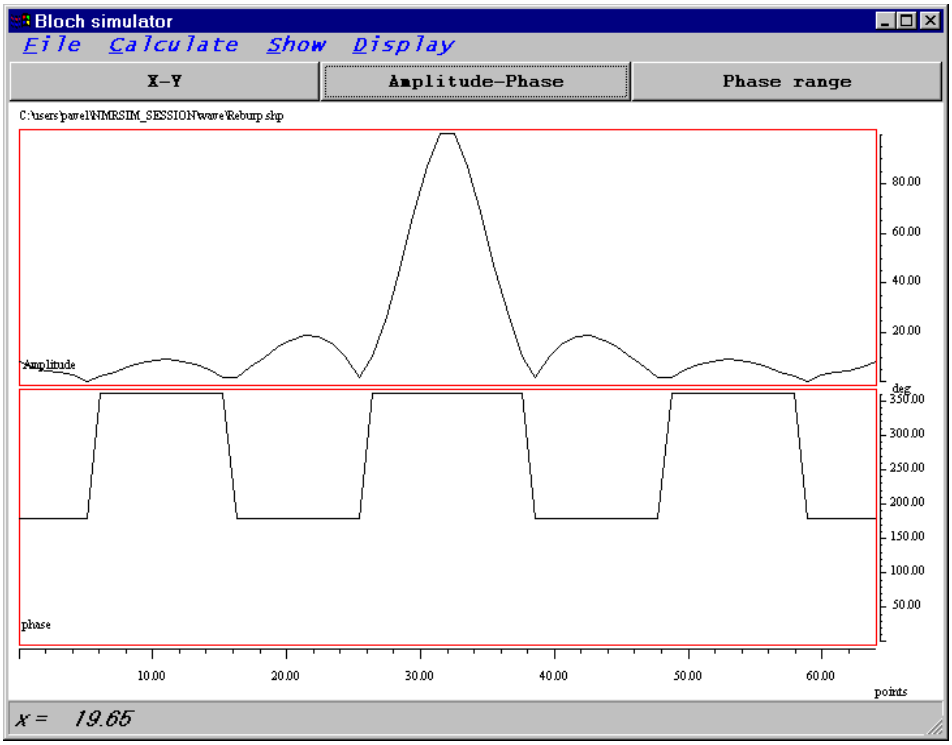


Figure 4.14 Shaped pulse display in NMR-SIM

- ***Offset/H1***
  The x axis shows the rf offset *relative* to the radio frequency field strength used during the shaped pulse.

4.5 Examples

There are two predefined configuration files which may be used to start your own work with this part of program: ***bloch.cfg*** and ***chirp.cfg***.

Load the configuration saved in the ***bloch.cfg*** (use the main menu command ***File/***

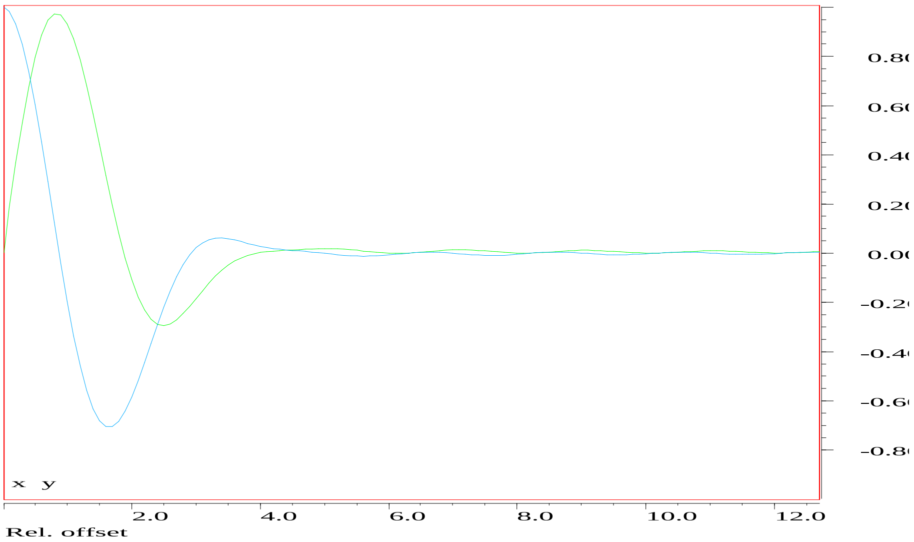


Figure 4.15 **The excitation profile of shaped gauss pulse. The M and M_y components are shown. The x axis is in relative offset units δ/B_1**

Experiment setup/Load from file).

Command ***Calculate/Time evolution*** shows the trajectories of the magnetization for a gaussian 90 degree pulse. It is not necessary to change any parameters.

The result of command ***Calculate/Excitation profile*** is on the Figure 4.15. The picture was copied into the MS-WINDOWS clipboard (***File/Copy to clipboard***) and pasted in this document.

The next example shows the behavior of the magnetization vector during composite inverse pulse.

Load the configuration file ***bloch.cfg*** and change the calculation mode (in ***Calculate/Setup***) to ***Sequence fragment.***

The command ***Calculate/Time evolution*** opens a dialog box. The meaning of all parameters is the same as in the previous case. Change the value of the ***TSlice*** parameter to 10 µs. The preview of the analyzed pulse program ***inverse.seq*** is

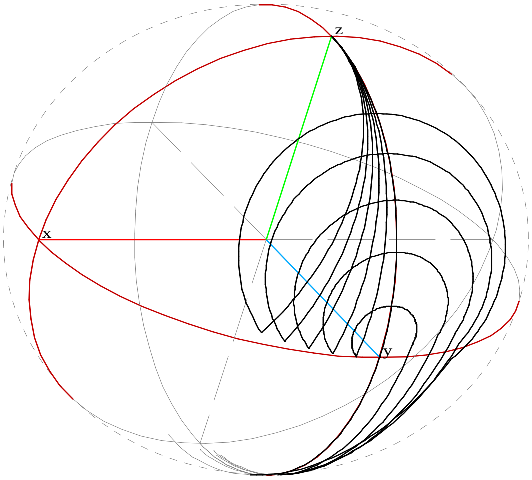


Figure 4.16 **The time evolution of magnetization during composite $90_x\ 240_y\ 90_x$ pulse.**

shown additionally:

```
;NMR-SIM example sequence - 1 3 1 inversion pulse
;avance-version
;
  ze
1  sample
   p1
   p2 ph2
   p1
   sample
   ihc
   lo to 1 times l1
   exit
```

ph2 = 1

You may use this pulse program fragment as an example for your further development. It is possible to use the command ***Edit/Pulse program*** in the main window to modify it.

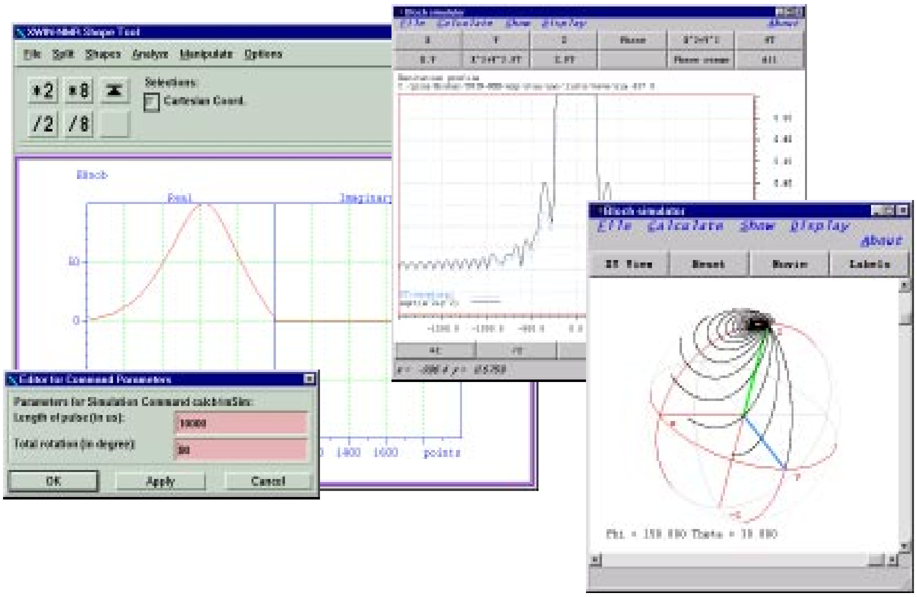
The Figure 4.16 shows the result, the self refocusing feature of this pulse is apparent.

The file ***chirp.cfg*** contains the setup for the phase modulated inverse chirp pulse. The result of the time evolution calculation is on the Figure 4.1.

4.6 Waveform analysis using the XWIN-NMR shape tool

Standard tool for the definition of waveforms is the XWIN-NMR Shapetool. Start it using ***stdip*** command on the XWIN-NMR command line. You may generate a lot of different waveforms. The Shapetool command ***Analyze/Simulate*** opens the Bloch simulator window and shows the excitation profile of your pulse (Figure 4.17). Each ***Analyze/Simulate*** command opens a new Bloch simulator window.

You may now use all Bloch module functionality to investigate the features of your pulse.



Parameters for Simulation Command calcbinoSim:

Length of pulse (in us): 10000

Total rotation (in degree): 90

Figure 4.17 Shape toll and Bloch simulator windows

Chapter 5

Pulse program display

This command opens a new window, which shows the selected pulse program in a

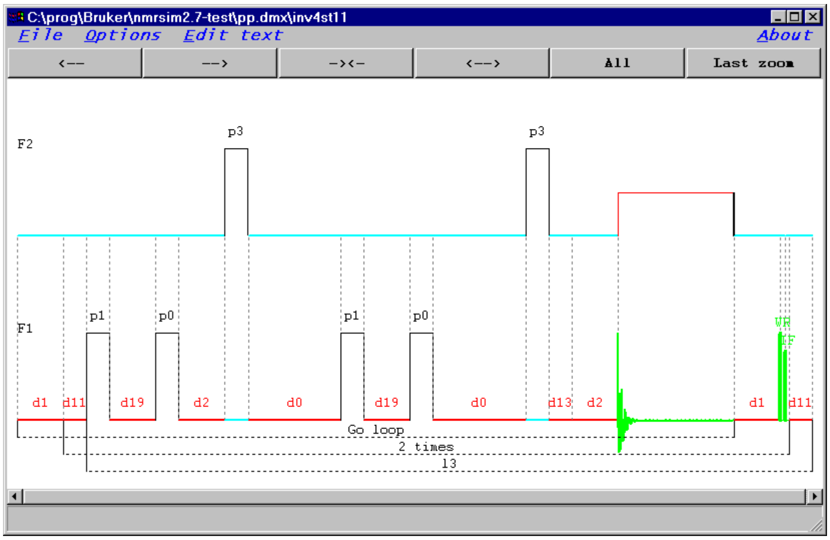


Figure 5.1 Window with the pulse program scheme

graphical form.

All pulse program schemes in this manual were created using this tool. Use the local menu ***File*** in this window to print the picture, or copy it to clipboard.

The labels of radio frequency channels depend on the pulse program version. The AMX/ARX pulse programs use the labels *Obs*, *Dec* and *DecB*. The Avance pulse programs use Avance conform labels *F1*, *F2* and *F3*.

The simple tool bar on the top of the pulse program window can be used to zoom and scroll the pulse program display. The command ***All*** shows the whole pulse program again.

5.1 File menu

- ***Select***
  Select a new pulse program to be displayed. This will not affect the pulse program selection in the main NMR-SIM window.
- ***Print***
  Print the pulse program scheme on the current printer.
  The Unix version of NMR-SIM does not print the picture, but writes the picture to disk in postscript format.
- ***Copy to clipboard***
  Copy the picture in the MS-WINDOWS metafile format to the clipboard. This allows easy transfer of pulse program schemes to other programs.

Windows

- ***Start windows explorer***
  This command starts the MS-WINDOWS explorer and shows the list of all pulse programs.
- ***Movie***
  This command shows all available pulse programs from one directory in a series.
- ***Close***
  Close the pulse program display window and pop-up the main NMR-SIM window.

5.1.1 Using "Drag and Drop" for the file selection

Drag and drop provides a very efficient mechanism for the enhancement of the user interface. The pulse program display uses the ***drag and drop*** mechanism for the selection of the pulse program being displayed.

- ***Unix***
  Open the file selection dialog, select one pulse program name in the right window of the file selection dialog and use the ***middle*** mouse button to move the drag symbol into the pulse program display. Drop the file name by releasing the middle mouse button. The drag symbol disappears and the pulse program display shows the new pulse program.
- ***Windows***
  Start the MS-WINDOWS ***file manger***, or the MS-WINDOWS ***explorer***. Drag the name of the pulse program of your choice into the pulse program display and release it.

5.2 Options menu

The ***Options*** menu controls the features of the pulse program display.

5.2.1 Display

The ***Display*** command opens a dialog box used for setting the following parameters:

- ***Channels*** - select the arrangement of the spectrometer channels on the display. You may place the acquisition channel either on the top, or on the bottom of the pulse program display:

- ***Show disk commands***
  Toggle the display of disk commands (wr,if) . The disk commands are marked as vertical marks in the pulse program diagram.
- ***Show loops***
  Toggle the display of loops in the pulse program. The loops are marked as dashed lines below the acquisition channel.

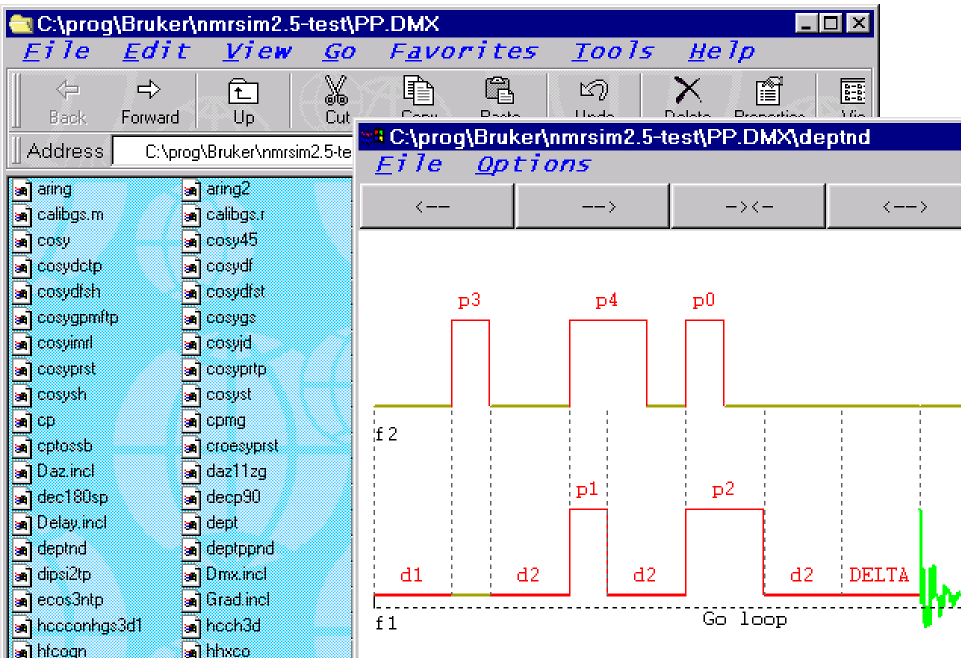


Figure 5.2 Pulse program display window with the MS-WINDOWS explorer window in background. The explorer window shows all available pulse programs. Use drag and drop to visualize the pulse programs.

- ***Grid***
  Switch the grid lines in the pulse program display. The grid lines between different channels connect synchronous points in the pulse program. This is an important feature for the visualization of “pulse trains”. A pulse train is a parallel asynchronous execution of pulses and delays in two or more channels.
- ***Labels***
  Toggle the display of pulse and delay labels.
- ***Background***
  Here you can select the background color. The colors used for the pulse program display are changed automatically to get a optimal contrast for all elements.

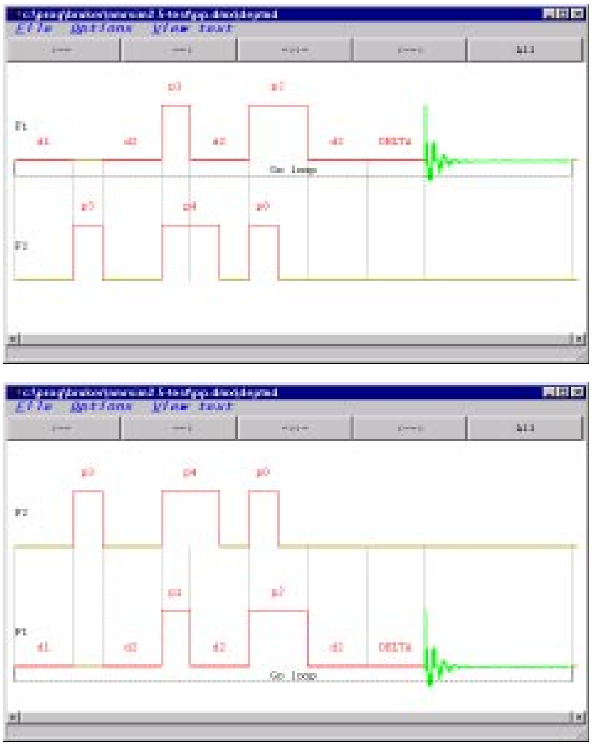


Figure 5.3 Different channel arrangement in the pulse program display

5.2.2 Configuration

The commands ***Configure pulses*** and ***Configure delays*** allow you to set the relative width and height of the pulse box, or the length of the delay on the display. The Figure 5.4 presents two possible layouts of the dept pulse program.

The configuration may be stored to disk (commands ***Load configuration*** and ***Save configuration***).

Windows

5.2.3 Fonts

The fonts menu allows to set the font family and the font resizing policy for the pulse program display window. More details are available in the section ***Font selection*** on the page 148 in Appendix.

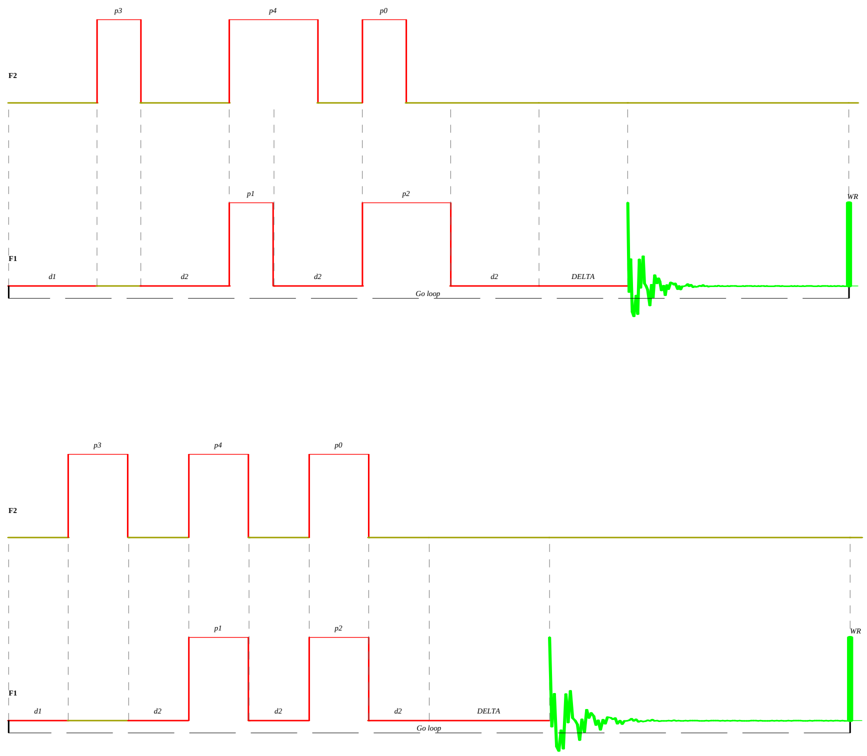


Figure 5.4 Dept pulse program with two different pulse and delay configurations.

5.3 Pulse trains

Pulse train is a part of pulse program, executing several pulses or delays simultaneously on one or more channels.

The pulse program ***coloc*** contains following line:

(d6):f1 (d0 p4 ph2):f2 (d0 p2 ph4):f1

There are two independent fragments which are executed on the same channel ***F1***. NMR-SIM creates in such a case one additional "virtual" channel which allows to split visually the overlapping pulses and delays.

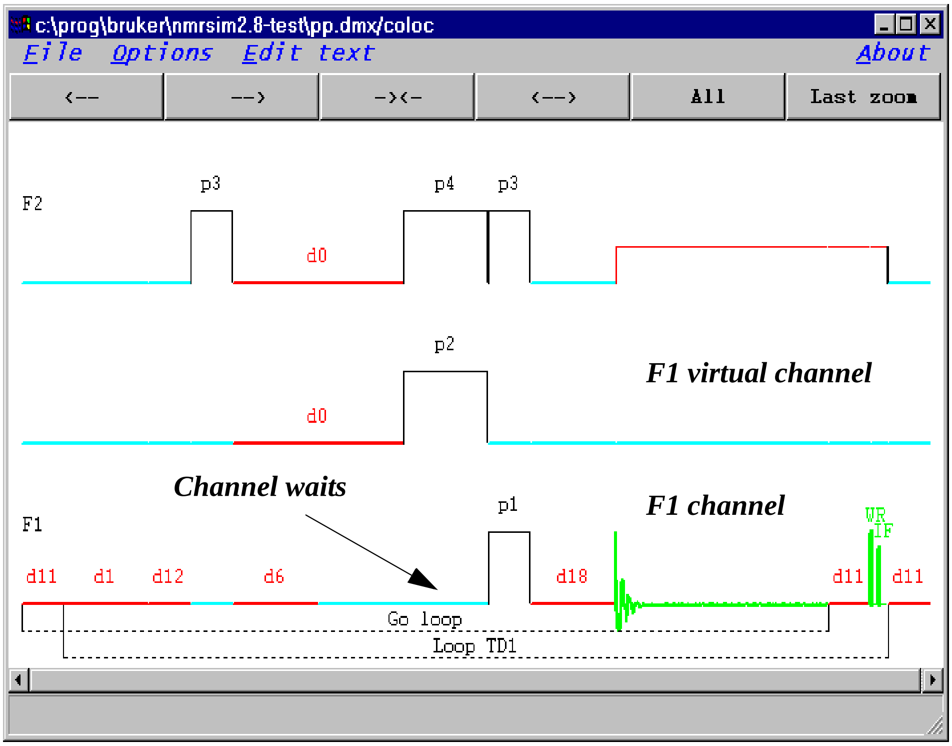
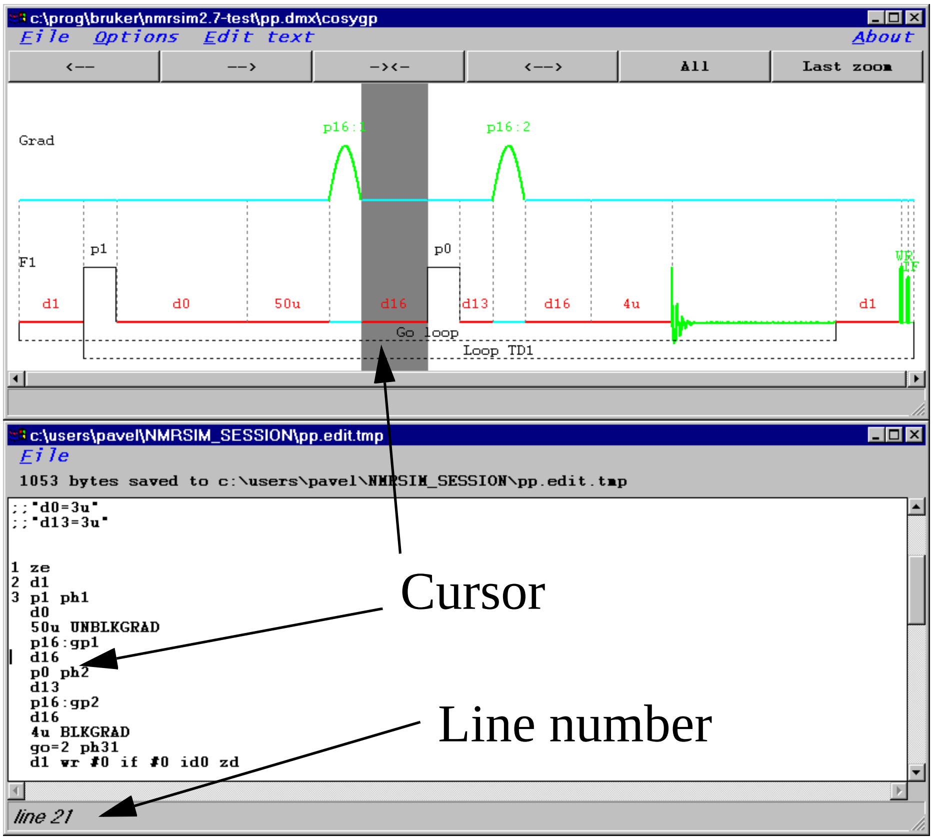


Figure 5.5 Virtual channel

5.4 Pulse program editor

The NMR-SIM program offers the possibility to couple the pulse program text editor to the pulse program display. This feature may be switched on or off in the ***NMR-SIM Options*** dialog. See “Options” on page 32.

The pulse program display is updated after each change of the pulse program. It is



```
1053 bytes saved to c:\users\pavel\NMRSIM_SESSION\pp.edit.tmp
```

```
;;"d0=3u"
;;"d13=3u"


1 ze
2 d1
3 p1 ph1
  d0
  50u UNBLKGRAD
  p16:gp1
  d16
  p0 ph2
  d13
  p16:gp2
  d16
  4u BLKGRAD
  go=2 ph31
  d1 wr #0 if #0 id0 zd
```

```
line 21
```

Figure 5.6 Pulse program editor. The cursor position in the text window is highlighted on the pulse program display possible, that the actual version contains a syntax error. In such a case the pulse program display shows the last syntactically correct version and the message line of the display window displays the error message.

The cursor position in the pulse program text is highlighted in the pulse program diagram as a region with a different background color. This feature simplifies the orientation in complex pulse programs.

5.5 Stand-alone pulse program display

The pulse program display may be also started as a stand-alone application:

nmrsim -showp *<pulse program name>*

or

showpp *<pulse program name>*

The script ***showpp*** may be found in the NMR-SIM installation directory.

This command opens a pulse program display window without any simulation functions. There is possible to start any number of copies of the stand-alone display (The NMR-SIM program may be started for each user only once).

The menu bar in this stand-alone version contains one additional command ***Edit text***. This command opens a new editor window with the text of the current pulse program.

Chapter 6

Pulse programs

This section contains the information about pulse program language implementation in the NMR-SIM program.

The description of BRUKER pulse program syntax is available in two forms. The NMR-SIM program contains the description of AMX-ARX and Avance pulse programs in electronic form (see Help, page 36). The help files may be viewed using the Adobe Acrobat viewer. It is also possible to consult the printed manuals, which are included in the XWIN-NMR documentation.

Windows

The MS-WINDOWS version of NMR-SIM installs both Avance and AMX-ARX pulse programs on the disk. The pulse programs are installed in the directories

<NMR-SIM install>\pp.amx
and
<NMR-SIM install>\pp.dmx.

By default, the program uses the pulse programs in the Avance directory (pp.dmx). This may be changed in the ***Options*** dialog box (page 32).

6.1 Pulse program commands implemented in *NMR-SIM*

NMR-SIM implements all substantial commands necessary for pulse program execution. All trigger commands and commands used to set spectrometer control words are ignored. The pulse program display and the pulse program interpreter support only three radio frequency channels. The pulse program display is able to show most available pulse programs.

6.2 Pulse program versions

The NMR-SIM program supports both AMX/ARX and Avance pulse programs. Following algorithm is used to detect the compiler, which will be used.

1. The 2nd line of pulse program contains the keyword *“am-version”* or *"avance-version"*:

```
;sample sequence for AMX spectrometer
;amx-version
.

;sample sequence for DMX/DRX/DPX spectrometers
;avance-version
.
.
```

2. the pulse programs without this keyword are compiled using the ***default*** compiler set in the NMR-SIM options dialog.

All standard BRUKER pulse programs use the keywords described here.

6.3 Decoupling

The pulses in the decoupler are implemented in the same way as the pulses in the Obs (F1) channel, just as the pulse trains are executed in the same way as on the spectrometer.

Only simple, ideal decoupling has been implemented. Any decoupler command (e.g. cpd, cw, ...) switches on the **total decoupling of all heteronuclear interactions**, the heteronuclear coupling are set to zero. The interactions are restored to the original state, when the decoupler is switched off (e.g. command do).

Example: a H-C-O group. Setting the decoupler to the O nucleus will decouple the oxygen, but the C-H coupling still stays intact.

6.4 New Commands

- ***ihc, dhc, rhc***
  Increment, decrement or reset **all** spin system variables ***var1-32.*** The increment or decrement step is defined by ***HS1-32***.
- ***ihv1-32, dhv1-32,rhv1-32***
  Increment, decrement or reset **one** spin system variable ***var1-32*** by ***HS1-32***.
  Example:

```
1      ze
2      p1
       ....
;  this is not allowed !
      ihc
       ....
       go= 2
;  the end of acquisition loop
       ihv1    ; increment var1 by HS1
       lo to 1 times l1
```

Please note, that **commands manipulating the spin system variables may not be used in the acquisition loop** (e.g. ihc in the example above).

The change of a spin system variable forces the recalculation of the spin system hamiltonian and its eigen values. This means that the resonance frequencies in the spectrum may change! Such an operation does not make any sense in the acquisition loop. It will not crash the calculation, but you will get false results!

The change of a spin system variable after the ***go=*** command allows you to simulate efficiently the experiment dependency on the spin system parameters.

- ***sample***
  This command is used in the bloch simulator for the sampling of magnetization values.

Chapter 7

Spin system definition summary

In this chapter all the commands used for the definition of spin systems will be summarized. The spin system description has the same role in the simulation as the sample does for the real experiment.

The nuclear spin system is defined using a simple language. The definition is based on a plain text file and it can be edited using any ASCII text editor such as ***notepad*** or ***emacs***. However, NMR-SIM implements a simple editor to do this. We recommend you to use the built-in editor.

7.1 Syntax

Each line contains at most one command. The lines starting with a semi-colon (;) are comments, the language does not discriminate between upper and lower case. The following predefined commands are available:

- ***Nucleus*** or isotope name
- ***Couple***
- ***Weak***
- ***Dipolar***
- ***Qpolar***
- ***Add***

- ***Molecule***
- ***Endmol***

It is also possible to use the C language preprocessor macro definitions and conditional expressions.

7.1.1 Nucleus

The ***nucleus*** command has the following syntax with each parameter separated by one or more blanks (the fields in square brackets are optional):

nucleus [*multiplicity* *] *label* [*spin number*] [*isotope*] *chemical shift* [*relax. time*]

label

one-letter label denoting a particular nucleus

isotope

label denoting the isotope. The defined isotopes are listed in table on page 77.

chemical shift

chemical shift in ppm units. The acquisition parameter SF is used to define the spectrometer frequency, which is used to convert the values in ppm to absolute frequency:

$$\omega = (offset+1)*SF*\gamma \qquad (7.1)$$

Instead of writing the number, you could use the spin system variable symbol ***var1..32***.
The nuclear chemical shift can be also defined in absolute units - Hz. To do that, you must specify the unit Hz after the value of chemical shift.

Example:

```
nucleus a 350.5 Hz
nucleus b 6 ; 6 ppm
nucleus c var1
```

multiplicity

an integer number denoting the multiplicity of nucleus (spin equivalence). The maximum allowed value is 4, the default value is 1. This parameter is not allowed for nuclei with spin quantum number greater than 1/2.

Symbol	Isotope	Name	Spin	γ
h1	proton	`proton`	1/2	1
d2	deuterium	`deuterium`	1	0.15351
li6	lithium 6	`lithium6`	1	0.14717
li7	lithium 7	`lithium7`	3/2	0.38866
b11	bor 11	`bor11`	3/2	0.32809
c13	carbon 13	`carbon`	1/2	0.25144
n14	nitrogen 14	`nitrogen14`		
n15	nitrogen 15	`nitrogen`	1	0.10133
f19	fluorine 19	`fluorine`	1/2	0.94077
si29	silicon 29	`silicon`	1/2	0.19867
p31	phosphor 31	`phosphor`	1/2	0.40481
y89	yttrium 89	`yttrium`		
rh103	rhodium 103	`rhodium`		
sn115	tin 115	`sn115`		
sn117	tin 117	`sn117`		
sn119	tin 119	`sn119`		
yb171	ytterbium 171	`yb171` `ytterbium`		
hg199	mercury 199	`hg199` `mercury`		

Table 7.1 Nuclear isotopes defined in the NMR-SIM program.

spin number

defines the spin quantum number of the nuclei. The following values are available:

j1/2, j1, j3/2, j2,

the default value is j1/2. For spin quantum numbers greater than 1/2 the multiplicity parameter is not allowed.

relaxation time

defines the relaxation times for the nucleus. The relaxation times T1 and T2 are defined in seconds with following formats and values:

t= *value*	T1 = T2 = *value*
t1=*value*	T1 = T2 = *value*
t2=*value*	T1 = *infinity*, T2 = *value*
t1=*value_1* t2=*value_2*	T1 = *value_1*, T2 = *value_2*

The default value is infinity (no relaxation). The relaxation time is used for the simulation of line widths (T2*) and for the relaxation of z magnetization (T1) when the option **full relaxation** is chosen (see page 32).

Example:

```
;3 equivalent spin - 1/2 nuclei labeled "a"
;with a chemical shift of 3.6 ppm
nucleus  3*a3.6
;
; nucleus b has spin 3/2, shift 8.3 ppm and t1 = t2 = 0.32 s
;
nucleus  b j3/2  8.3  t=  0.32
; nucleus c  is C13 , we define t1 and t2
nucleus  c c13 83 t1=  0.32  t2=0.1
```

7.1.2 Isotope labels

To simplify the work with different isotopes, you may omit the command *nucleus* and use the isotope name directly. The isotope names used for the spin system definition are listed in the isotope table on page 78.

The following nuclei definitions are equivalent

```
;   3 equivalent protons  labeled "a"
;   with a chemical shift of 3.6 ppm
nucleus  3*a    3.6   ; default isotope is h1
nucleus  3*a h1 3.6
proton   3*a 3.6
;
;   nucleus b is carbon, shift 83 ppm
;
nucleus  b c13 83
carbon   b 83
```

```
;
; phosphor  10 ppm
;
nucleus  c phosphor 10
phosphor 10
```

We prefer to use the isotope names described here, because the spin system definition is more readable and simpler. All examples in this manual will use the isotope names and not the command *nucleus*.

7.1.3 Couple

This is the command for the full scalar coupling between two nuclei using the operator $I_xS_x + I_yS_y + I_zS_z$. This should be used to define all homonuclear couplings (no X approximation)

couple *nucleus*$_1$ *nucleus*$_2$ *coupling*

The parameters *nucleus*$_1$ and *nucleus*$_2$ are the spin labels, the parameter *coupling* is the scalar coupling constant in Hz, or spin system variable

Example:

```
couple   a   b  10.32
; spins a and b are coupled with J = 10.32 Hz
couple  a    b var1
```

7.1.4 Weak

This command is used to define a weak scalar coupling (X approximation) between two nuclei I_zS_z. It is normally used for heteronuclear J couplings or to simplify the AX type homonuclear spin systems.

weak *nucleus*$_1$ *nucleus*$_2$ *coupling*

The parameters *nucleus*$_1$ and *nucleus*$_2$ are the spin labels, the parameter *coupling* is the scalar coupling constant in Hz, or spin system variable.

Example:

```
; nuclei a and x are coupled with J = 56.2 Hz
weak   a   x  56.2
```

7.1.5 Dipolar

This command defines a dipolar coupling between two nuclei.

$$H_{DD} = J_D (I_z * S_z - (I_x * S_x + I_y * S_y)/4) \qquad (7.1)$$

(only energy conserving parts of the dipolar Hamiltonian are implemented). The dipolar coupling J_D includes the geometrical factor (3cos(*theta*)^2 -1)/r^3 too.

dipolar *nucleus*$_1$ *nucleus*$_2$ *coupling*

The parameters *nucleus*$_1$ and *nucleus*$_2$ are the spin labels, the parameter *coupling* is the coupling constant J_D in Hz.

Example:

```
dipolar a b 100
```

The dipolar coupling may be used to simulate the spectra of solid state **monocrystals**.

7.1.6 Qpolar

This command is used to define a quadrupolar coupling of one nucleus. The quadrupolar coupling is allowed only for nuclei with spin > 1/2.

qpolar *nucleus* *coupling*

Example:

```
; the nucleus a has the quadrupolar coupling constant 100 Hz
qpolar a 100
qpolar  b var11
```

The quadrupolar coupling may be used to simulate the spectra of solid state **monocrystals**.

7.1.7 Molecule

This command starts the definition of a molecule. You can define several molecules in one spin system description file.

Every molecule must have a unique name, the labels of atoms in one molecule need to be unique. The label of atoms in different molecules may be the same (see

Example below). The molecules are completely independent, NMR-SIM calculates the resulting signal as a weighted mixture of signals from single molecules. It is not possible to define an interaction between nuclei in different molecules.

molecule *molecule_name weight*

molecule_name is any string with no more than 31 characters.

weight is a float number defining the **relative concentration** of this molecule in the mixture. It is also possible to use the spin system variable here. It is good practice to keep the weights of molecules close to 1!

Instead of

```
molecule  alpha 0.00001108
...
endmol
molecule  alpha 0.00099
...
endmol
```

use

```
molecule  alpha 1.108
...
endmol
molecule  alpha 99
...
endmol
```

Example: mixture of two CH_3 groups, one with C^{13},2nd wit C^{12}. The weights are identical with the natural abundance of C^{13} isotope:

```
molecule  alpha 1.108
proton   3*a  10
carbon      x  130
weak        a  x   80
endmol

molecule  beta  98.882
;
; the proton labeled a has nothing to do with the proton a from
; the molecule alpha
;
```

```
proton   3*a  10
endmol
```

The nuclei from different molecule definitions with the same label are different.

Omitting the *molecule* command in your spin system definition means, that all nuclei in the spin system are part of one molecule. The following two definitions are equivalent:

```
;
molecule  any_name 1.108
proton   3*a  10
carbon     x  130
weak       a  x   80
endmol
```

and

```
;  the same spin system definition without the molecule command
proton   3*a  10
carbon     x  130
weak       a  x   80
```

The weight factor 1.108 does not play in this case any role.

7.1.8 Endmol

The command *endmol* finishes the definition of a molecule. Every *molecule* command must be followed by endmol.

7.1.9 Add

The spin system definition commands described above are used to define general nuclear spin systems in liquid. For special purposes you can use the command ***add***. This command lets you create user-defined types of interaction between nuclei which you can use to create virtually any spin system Hamiltonian. The command multiplies a spin operator by a real constant and adds it to the specified inner matrix of the simulator:

add *matrix_name* *real_constant* *operator* ,

where *matrix_name* is the internal name of a spin-system matrix. At present one can only use the symbol *ham to* specify the Hamiltonian matrix and *ro0* - to specify the initial density matrix.

operator is any operator expressed in product operator formalism, e.g.

operator		notation
Ax	=	ax_
Ax*By	=	ax_by = by_ax
Ax*By*Cz	=	ax_by_cz = by_ax_cz = ...(any permutation is allowed)

Example: define a scalar coupling interaction between the nuclei *I* and *S* with coupling constant 3.5 Hz, i.e. $I_xS_x + I_yS_y + I_zS_z$.

```
proton i 10.3
proton s 9.2
add  ham  3.5  ix_sx
add  ham  3.5  iy_sy
add  ham  3.5  iz_sz
```

7.2 Initial spin system state

The system sets the value of the initial density matrix ρ(0) to be proportional to the thermodynamic equilibrium value $\rho(0) = \sum_i I_{iz}$

If you use the command ***add ro0*** in your spin system definition file, the program assumes, that you have set the value of ρ(0) yourself and will not modify it!

This feature allows you to start the experiment from any state which may be far from equilibrium. A particular interesting feature is that you can use initial states that are very hard to create by a simple pulse (e.g. pure double quantum coherence I^+S^+ in a coupled system).

Example: the initial state of the spin system is $I_z + S_z + C_x$

```
add  ro0  1  iz
add  ro0  1  sz
add  ro0  1  cx
```

7.3 Spin system variables

To simplify the calculation of an experiment dependence on various spin-system parameters, the program offers a set of variables which can be used in the spin system definition. These variables are controlled from the pulse sequence.

Example:

```
;       here the three chemical shifts and coupling constant are written
;       as variables which can be altered from one FID to the next
nucleus   3*a  var1
nucleus   b     var2
nucleus   c     var3
couple     a  b  var11
```

At the beginning of the pulse sequence the variables have their initial values set by the parameters ***HV1..32***. When the pulse program encounters a command to increment a variable, the variable is incremented by the value ***HS1..32***.

All spin system variables use Hz as unit!

The command to increment the spin system variable recompiles the spin system Hamiltonian, and the program continues the experiment with the new settings. To use these commands it is necessary to observe the following rule:

- **The pulse program commands manipulating the spin system variables (*dhc, rhc, ihc , ihv,..*, see page 71) should not be used inside the acquisition loop. The program will not detect such programming violations!**
  Such command in the acquisition loop will probably not crash the calculation, but will lead to nonsensical results.

Example:

```
;
1  ze
2  d1

;
;  spin system modified in the acquisition loop !!
;  this is forbidden
   ihv1
   go = 2
;
;  this is allowed , the modification is done outside the acquisition loop
   ihv2
   loto 1 times td1
```

The spin system variables are also used in the calculation of shaped pulse excitation profiles.

7.4 Preprocessor commands

Following C preprocessor commands may be used in the spin system definition:

#define
#ifdef
#if
#else
#endif
#include

Example:

```
; include your private definitions
#include <my_definitions.ham>
;
; define some constants
;
#define SHIFT_1  10
#define SHIFT_2   15

#define COUPLE_1 10.3
#define noSOLUTION

molecule alpha 1
proton  2*a SHIFT_1
proton  3*b SHIFT_2
couple  a   b COUPLE_1
endmol
; the include file water.ham contains the definition of water
; it is placed in a subdirectory my_library
#ifdef SOLUTION
#include <my_library/water.ham>
#endif
```

The include files must be in the same directory as the spin system description files.

7.5 Spin system limitations

The current NMR-SIM release supports up to 255 nuclei in the spin system definition. The nuclear labels are characters from the English alphabet, so you may use up to 26 different nuclei in one molecule. The nuclei from different molecule definitions with the same label are different.

But the limit of 26 interacting nuclei is not realistic. A group of 10 interacting nuclei with spin 1/2 without any symmetry is described by a 1024*1024 density matrix (about 8 MB). The NMR-SIM program needs at least 10 matrices for the simplest experiment. This means that the memory requirements for a simple experiment with 10 interacting nuclei exceeds 80 MB!

So, the limits of the spin system you may use are determined by your computer and not by the NMR-SIM program.

Let us compare this to a 10 nuclei spin system consisting of two interacting clusters with 5 nuclei. One matrix representing the operators in this case requires about 16 kB, this means that the whole experiment needs less than 200 kB!

The limit of 255 nuclei is sensible one when defining large, complex mixtures of many simple molecules.

Chapter 8

NMR-Sim parameter definition

Parameter definition is based on the standard BRUKER parameter set. For the sake of simplicity and flexibility, some new features and new parameters, have been added.

8.1 Durations

All the parameters specifying pulse durations use microseconds as default units, delay parameters use seconds as default. You can override this default by specifying the time units directly as a terminator for each entry:

- 10u = 10 microseconds
- 13.5m = 13.5 milliseconds
- 5s = 5 seconds

Pulse length can be specified in two ways: as a time, or as a tilt angle. In the second case the actual pulse length is calculated from this angle and using the current radio frequency field strength parameter (***HLi or PLi***)

- 90d = 90 degree pulse
- 10u = 10 microsecond pulse

8.2 Radio frequency field intensities

The radio frequency field strengths are defined in Hz. The dB units used on the spectrometer are not available here. The dB is a ***relative*** unit and we need a absolute value.

All values define the ***corresponding frequency for a proton*** ^{1}H.

For other nuclei the value multiplied is by the γ factor:

$$B_1^{nucl} = B_1^{proton} * \gamma_{nucl} / \gamma_{proton} ,$$

Example:

You specify the power level PL2 for the f2 channel 100 kHz and the channel is set to proton frequency. This gives you a **90 degree pulse length of 2.5 µs**. Assigning the same channel to carbon, you will give you a **90 degree pulse of about 10 µs** (the $\gamma_{carbon}/\gamma_{proton}$ is about 0.25).

It is possible to define your pulse as 90 degree - use 90d for the pulse length (see above). In this case you will get **2.5us for protons** or **10us for carbons** automatically.

This feature is controlled by the switch ***Modify RF fields*** in the NMR-SIM settings dialog (page 32). By switching this option off, you will suppress the multiplication of the radio frequency field with the factor $\gamma_{nucl}/\gamma_{proton}$.

Example:

You now specify the power level PL2 for the f2 channel 100 kHz and the channel is assigned to proton frequency. Then you will get (approximately) a **2.5 us long 90 degree pulse**. Assigning the same channel to carbon, you will have **90 degree pulse which is also 2.5 us long**.

8.3 Size parameters

The parameters which specify the number of points or increments (TD, TD1,...) may be specified in multiples of 1024 , you simply append the letter k: 1k, 8k,... .

8.4 Error checking

Most of the parameters are syntactically checked before closing the dialog box. When the program finds an error (e.g. a negative value, where a positive is expected), the bad parameter is highlighted and short error message is shown on the bottom of dialog box.

8.5 Parameter description

- ***Parmod***
  This parameter defines the **dimension** of the experiment. Possible values are 1 .. 2 (NMRSim for Unix 1..4). The value of this parameter defines the dimension of the experiment and the output file name type (**fid** or **ser**). The function of the file increment command differs in 1D an nD modes. The experiment number is incremented and **new file** is created in 1D mode, in nD mode program only shifts the position in the file for the next write command.
- ***OBS***
  This parameter defines the nucleus assigned to the acquisition channel (OBS or f1) of the spectrometer. The basic frequency of the channel is calculated as $SFO = SF*\gamma_{OBS}/\gamma_{proton}$, where γ_{OBS} is the gyromagnetic factor of the selected isotope.[1]
- ***DEC***
  This parameter defines the nucleus assigned to the decoupler channel (Dec or f2) of the spectrometer. The basic frequency of the channel is calculated as $SFO = SF*\gamma_{DEC}/\gamma_{proton}$, where γ_{DEC} is the gyromagnetic factor of the selected isotope.[2]
- ***DECB***
  This parameter defines the nucleus assigned to the 2nd decoupler channel (DecB or f3) of the spectrometer. The basic frequency of the channel is calculated as $SFO = SF*\gamma_{DECB}/\gamma_{proton}$, where γ_{DECB} is the gyromagnetic factor of the selected isotope.[3]
- ***SF***
  This variable defines the **proton resonance frequency** of your spectrometer.
- ***OFS***
  This variable defines the offset between the receiver and transmitter frequencies in ppm.

- ***O1***
  Difference (in **ppm**) between the basic frequency of Obs (or f1) channel and the transmitter irradiation frequency.
- ***O2***
  Difference (in **ppm**) between the basic frequency of Dec (or f2) channel and the decoupler irradiation frequency.
- ***O3***
  Difference (in **ppm**) between the basic frequency of DecB (or f3) channel and the 2nd decoupler irradiation frequency.
- ***AQ_mod***
  Acquisition mode. Possible values are *qf*,*qsim* or *qseq*. For more details see the pulse program manuals.
- ***TD***
  Total number of time domain data points to be acquired.
- ***TD****n*
  Total number of time domain data points in higher dimensions for multidimensional experiments.
- ***NS***
  Number of pulse program transients ("Number of scans")
- ***DS***
  Number of pulse program transients without acquiring data ("Number of dummy scans"). This parameter has meaning for experiments with ***full*** relaxation only. In other cases dummy scans are not executed and you are not prompted for this parameter.
- ***HL****1..4*
  Radio frequency field intensities in Hz for the first channel on an AMX spectrometer.
- ***DL****0..7*
  Radio frequency field intensities in Hz for the decoupler channel on an AMX spectrometer. The value DL1 is identical to the "high power level", DL0 is "low power level".
- ***DBL****0..7*
  Radio frequency field intensities in Hz for the 2nd decoupler channel. The value DBL1 is identical to the "high power level", DBL0 is "low power level".

- ***P****0..31*
  Length of pulse p0-31 in pulse sequence
- ***PL****0..31*
  Radio frequency field intensities in Hz on an Avance spectrometer.
- ***D****0..31*
  Length of free precession delay d0-31 in pulse sequence
- ***IN****0..31*
  Increment of delay D0-31 in pulse sequence used by id0-31 commands. You may use the symbol ***sw***. In this case the time increment is calculated from the formula $1/SW$. This feature automatically guarantees the same spectrum width and calibration in both dimensions for **homonuclear** 2D experiments.
- ***L****0..31*
  Loop limits used in pulse program loops.
- ***HV****1..32*
  Start value of spin system variable ***var1..32***
- ***HS****1..32*
  Step value for the spin system variables ***var1..32***
- ***TP0..7***
  The radio frequency intensity used for the shaped pulse, the unit is Hz.
- ***TPNAM****0..7*
  The name of file which contains the shape pulse definition.
- ***SP0..16***
  The radio frequency intensity used for the shaped pulse, the unit is Hz.
- ***SPNAM****0..16*
  The name of file which contains the shape pulse definition.
- *AW0..7*
  On resonance, the flip angle of shaped pulse ***tp0-tp7*** in deg. The radio frequency field strength for the shaped pulse is calculated from this angle and the pulse length. These two parameters fully describe the shaped pulse. The length of pulses ***P0-31***, which are combined with shaping factor ***tp0-tp7***, cannot be specified using the flip angle, but you must enter the length in units of time!
- ***GPZ****0..31*
  Gradient intenzity modifier. The shape gradient intenzity is multiplied by this factor. The possible values are -100 .. 100 %.

8.6 Expressions in pulse programs

The Avance spectrometer series allow one to define own pulses and delays. For example

```
define delay MY_DELAY
define pulse MY_PULSE

"MY_PULSE=p1*0.3333+3/4*p2+10u"
"MY_DELAY=d2+d3/2"

   ze
.
.
   MY_DELAY
   MY_PULSE
.
.
.
```

defines one pulse and one delay. Every such declared pulse must be initialized in the pulse program. The ***Checkall parameters*** dialog box shows all the actual values of all user defined delays and pulses.

The pulses used in any expression in the pulse program cannot be defined using the tilt-angle value, exact time values must be used instead. The value of the actual radio frequency field is not known at setup time and so is not possible to convert the tilt angle to the time unit.

Chapter 9

NMR-Wizard

9.1 What is NMR-WIZARD

The NMR-WIZARD is a new tool which calculates the NMR spectrum (i.e. the time domain signal) without any user input. The user simply selects the spin system description and the pulse program. NMR-SIM sets all necessary parameters, without any further interaction.

The parameters are read from the pulse program comments and from the spin system. The current version supports cosy...... and j-resolved experiments. If the NMR-WIZARD is not able to recognize the experiment type, or the pulse program uses a feature, which is currently not supported, an error message is shown. In such cases, the experiment will be not run. You should set up the additional parameters manually.

It is essential that you use the standard BRUKER rules in your own pulse programs (the most up to date description is always stored in the file ***Param.info*** in the pulse program directory):

;p0 : no default value
;p1 : f1 channel - 90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;p3 : f2 channel - 90 degree high power pulse

```
;p4 : f2 channel - 180 degree high power pulse
;p5 : f1 channel -  60 degree low power pulse
;p6 : f1 channel -  90 degree low power pulse
;p7 : f1 channel - 180 degree low power pulse
;p8 : f2 channel -  60 degree low power pulse
;p9 : f2 channel -  90 degree low power pulse
;p10: f2 channel - 180 degree low power pulse
;p11: f1 channel -  90 degree shaped pulse
;p12: f1 channel - 180 degree shaped pulse
;p13: f2 channel -  90 degree shaped pulse
;p14: f2 channel - 180 degree shaped pulse
;p17: f1 channel - trim pulse                      [2.5 msec]
;p18: f1 channel - shaped pulse for off resonance presaturation
;p19: 2nd homospoil/gradient pulse
;p20: f2 channel - trim pulse                      [2.5 msec]
;p21: f3 channel -  90 degree high power pulse
;p22: f3 channel - 180 degree high power pulse
;cnst1 : J (HH)
;cnst2 : J (XH)
;cnst3 : J (XX)
;cnst4 : J (YH)
;cnst5 : J (XY)
```

All the standard BRUKER pulse programs use these rules.

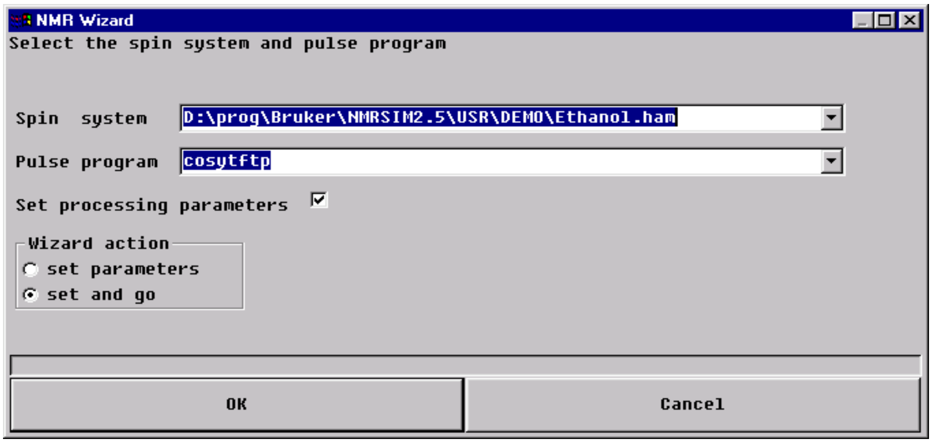
9.2 Using NMR-WIZARD

The ***NMR-Wizard*** command in the main NMR-SIM menu opens a simple dialog box (Figure 9.1).

You may select the spin system and pulse program here. The toggle ***Set processing parameters*** allows you to suppress the definition of processing parameters by NMR-WIZARD.

The ***Wizard action*** selects the further action:

- ***Set parameters***
  NMR-WIZARD will set all the experiment parameters and stop. You may proceed with the experiment using one of the command from the ***Go*** menu (page 28).
- ***Set and go***



Select the spin system and pulse program

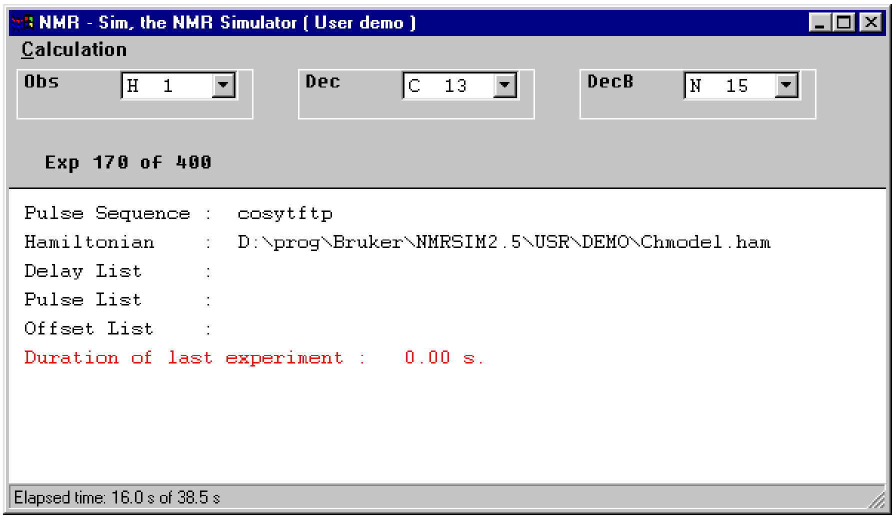
Spin system D:\prog\Bruker\NMRSIM2.5\USR\DEMO\Ethanol.ham

Pulse program cosytftp

Set processing parameters ☑

Wizard action
- ○ set parameters
- ● set and go

Figure 9.1 NMR Wizard input dialog



Obs H 1

Dec C 13

DecB N 15

Exp 170 of 400

```
Pulse Sequence :  cosytftp
Hamiltonian    :  D:\prog\Bruker\NMRSIM2.5\USR\DEMO\Chmodel.ham
Delay List     :
Pulse List     :
Offset List    :
Duration of last experiment :   0.00 s.
```

Elapsed time: 16.0 s of 38.5 s

Figure 9.2 NMR-SIM main window. The elapsed time and the guess of the total time are shown.

NMR-WIZARD sets all parameters and starts the experiment.

NMR-WIZARD also tries to predict the duration of the calculation. The total elapsed time and the estimation of the experiment total time are shown on the status line in the main NMR-SIM window (Figure 9.2).

Chapter 10

Parameter Optimizer

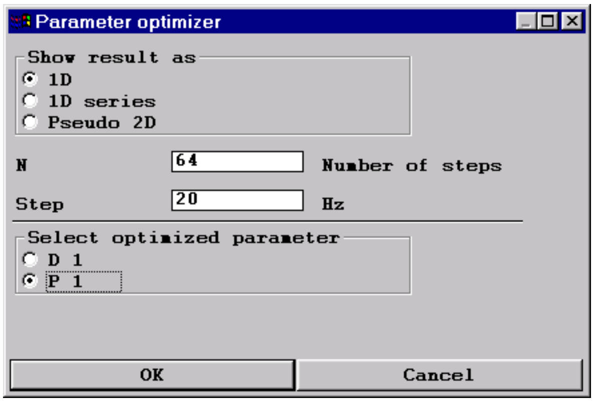
The parameter optimizer is a tool used to investigate the dependency of the spectra on pulse program parameters. Its functionality is equivalent to the XWIN-NMR command ***paropt***: the program changes selected parameter in the pulse program and writes the result either as 1D spectrum or as a pseudo 2D data set. Two example experiments are available.

10.1 90 degree pulse length optimization

paropt_90.cfg may be used to find out the length of 90 deg pulse. Load the example using the command ***File/Experiment setup/Load from file.*** Start the parameters optimizer ***Go/Optimize parameter.***

The optimizer dialog box (Figure 10.1) allows to select the output format and the parameter being optimized. Choose ***1D spectrum*** and ***P1***.

The parameter ***N*** defines the number of calculated spectra and the relative shift of them. Next dialog (Figure 10.2) shows the initial value of the optimized parameter (in this case pulse P1) and the parameter increment. The result is shown on Figure 10.3.



Parameter optimizer

Show result as

● 1D

○ 1D series

○ Pseudo 2D

N 64 Number of steps

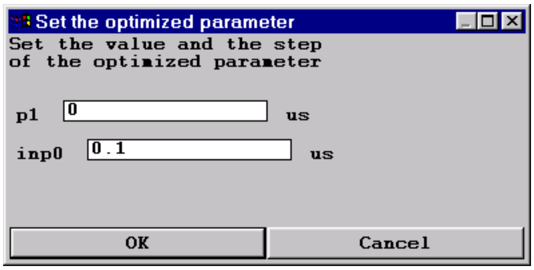
Step 20 Hz

Select optimized parameter

○ D 1

● P 1

Figure 10.1



Set the optimized parameter

Set the value and the step of the optimized parameter

p1 0 us

inp0 0.1 us

Figure 10.2

10.2 Dependency of the DEPT experiment on the evolution delay

Load the configuration file ***paropt_dept.cfg*** and select the delay D2 to be varied. The Figure 10.4 shows the result. The optimal value of the D2 delay is 1/(2J(XH)). The picture Figure 10.4 shows the changes in the spectrum caused by the mismatch between the value of D2 and the actual XH coupling in the spin system.

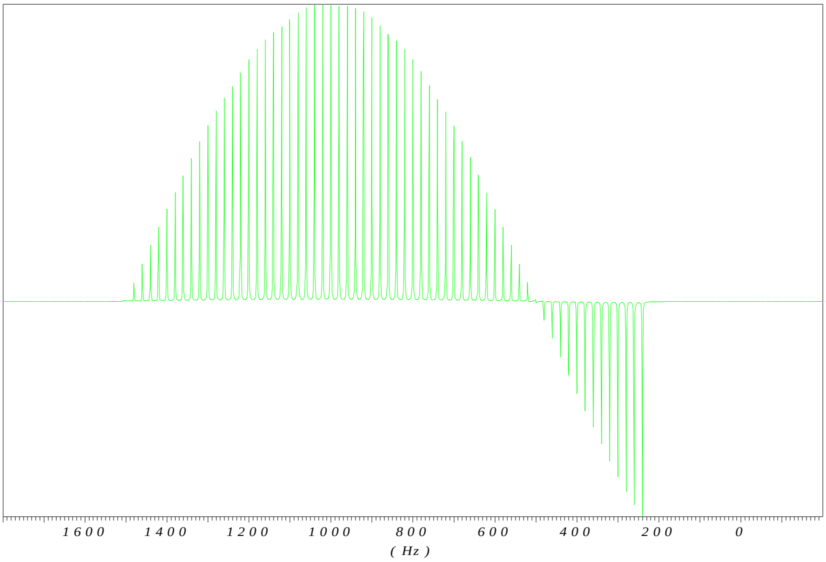


Figure 10.3 90 degree pulse length search. The pulse length increment is 0.1 us.

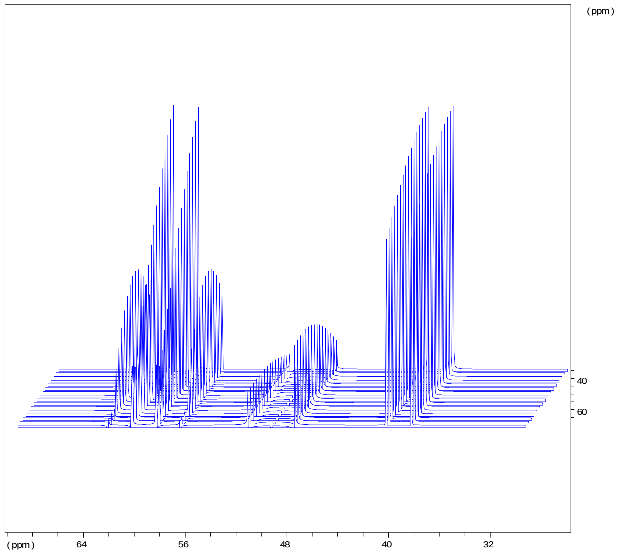


Figure 10.4 Pseudo 2D spectrum shows the dependency of a DEPT experiment on the size of the evolution delay D2 = 1/2J(C,H)

Chapter 11

Gradient spectroscopy

This chapter describes the basics of the gradient spectroscopy implementation in NMR-SIM. The chapter ***Examples*** contains several examples of gradient experiments (page 141).

11.1 Gradients in pulse programs

The BRUKER pulse program language has several different gradient control methods. The NMR-SIM implementation uses the ***Avance shaped gradient syntax***.

p16:gp2

This command invokes a gradient pulse with the length P16 and the gradient shape 2. The parameter ***GPZ2*** defines the relative amplitude (in %) of gradient number 2. It is possible to use values between -100 and 100.

Gradients for the AMX pulse program language are not implemented.

11.2 Gradients in NMR-SIM

NMR-SIM does not use gradient shapes. Shaped gradients in NMR spectroscopy are used to suppress the experimental artifacts induced by the rapid static field change.

The theoretical calculations in NMR-SIM do not require this. For spectroscopy, there is no difference between x, y or z gradients. So, NMR-SIM only implements the gradients along the z axis.

11.2.1 Numerical simulation of gradients

The gradient pulse applied to the sample introduces a rapid dephasing of the coherent magnetization. The global magnetization is not destroyed, but it is dephased. The measured NMR signal is a sum of all magnetization vectors. Using a second gradient pulse with inverted magnetic field reconstructs the original magnetization (neglecting the spin system evolution due to J-coupling).

It is not possible to use one density matrix to describe such systems. NMR-SIM divides the sample into a number of layers. Each layer is taken to be a system with homogenous fields, so it is possible to use the density matrix formalism. The evolution of the spin system in this layer is described by the Liouville equation. The NMR signal is then calculated as a sum over all layers. This approach allows for the simulation of gradient experiments the main goal of NMR-SIM program: Flexibility.

This approach is a challenge for the program performance. The Liouville equation must be solved separately for each layer in the sample. This means, that the simulation will be much, much slower compared to the simulation of “classical” experiments without gradients. A trade-off between program speed and the output quality should be found. NMR-SIM implements a lot of optimizations to achieve acceptable performance. The number of layers used for the simulation is defined on fly using an ***adaptive ageratum*** which guarantees good quality of results and acceptable speed. In fact, the calculation of sample gradient experiments presented in this manual takes only several seconds on modern hardware.

The current implementation of gradient experiments neglects any ***diffusion effects*** and the ***full relaxation*** mode is ***not available*** for gradient experiments.

11.3 Examples of gradient experiments

This part presents some principles of gradient spectroscopy.

11.3.1 Decay of magnetization under the influence of gradients

The dephasing (decay) of the magnetization under the influence of a homogeneous static field gradient may be described using following formula:

Figure 11.1 shows a simulated decay. The vertical axis is proportional to the pulse length, the full vertical scale is about 4ms. The absolute value of the resulting display is shown. The projection on the side of the spectrum shows, that the calculated decay is in a form very near to the theoretical formula above.

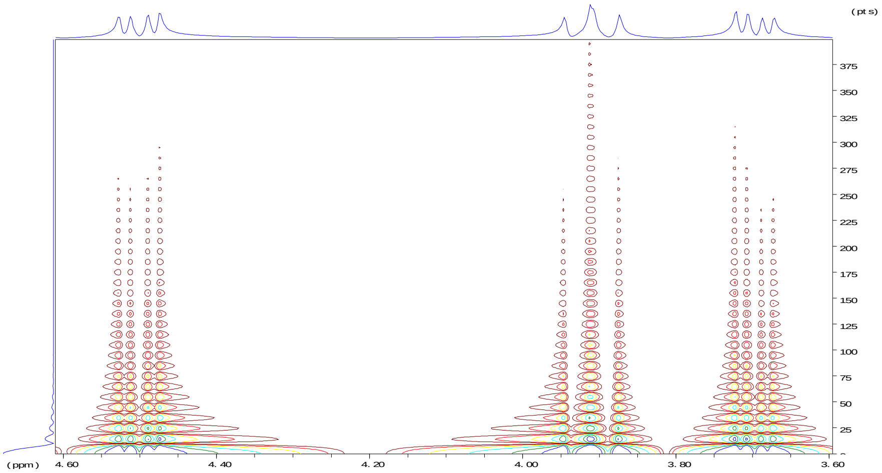


Figure 11.1 The magnetization decay during a gradient pulse

11.3.2 COSY experiment

The gradient COSY demonstrates the ability to select the coherence to be observed using gradients.

The classical COSY pulse program uses phase cycling to achieve the coherence selection. So at lest two transients (scans) are necessary to get a two dimensional

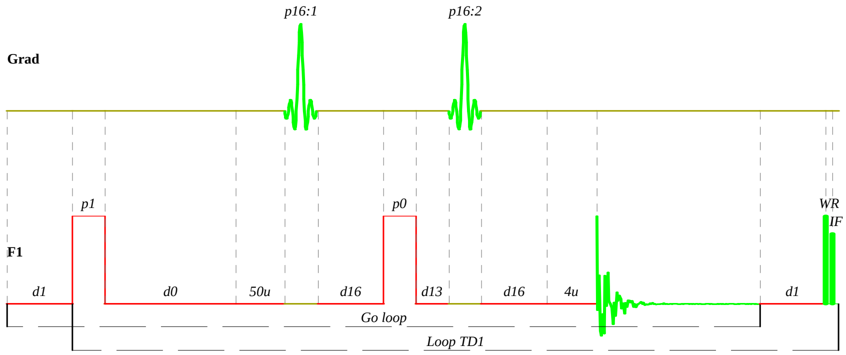


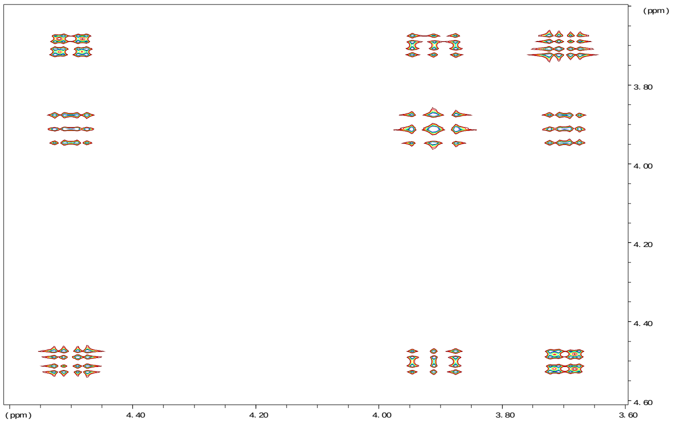
Figure 11.2 The cosygp pulse program

spectrum.

The gradient pulse program selects the coherence using a static field gradient. Only one transient is required. Figure 11.3 demonstrates the coherence selection. The gradient ratio 10:10 selects the “normal” +1 coherence. Inverting the sign of the second gradient selects the -1 coherence and the sign of the indirect detection axis changes.

The suppression of the unwanted coherence achieved in this case is better then 1:1000. The configuration of this experiment is stored in the file ***gradient_cosy.cfg***.

a) p-type spectrum



b) n-type spectrum

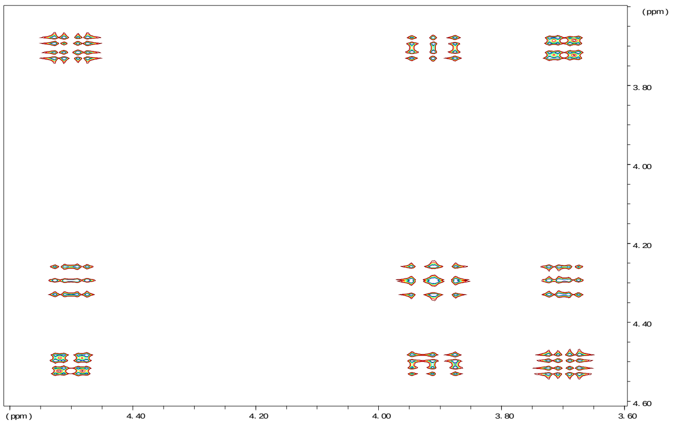


Figure 11.3 Gradient COSY spectrum, gradient ratio 10:10 and 10:-10

Chapter 12

Examples

This chapter describes several example experiments.

Start the NMR-SIM program either typing nmrsim on the XWIN-NMR command line, or using the simulation menu in Win-NMR.

Select the user name DEMO after starting the MS-WINDOWS version of NMR-SIM.

The UNIX version and the MS-WINDOWS in the XWIN-NMR compatibility mode copies (after the first start) all example files to the user directory *$HOME/NMRSIM_SESSION*.

The command ***Options/Update example files*** in the NMR-SIM main menu bar may be used to reload a full set of the original example files. This should be invoked after each installation of new NMR-SIM version.

In your user directory you will find the configuration files, which will assist you to start these examples. Read the specified settings into the simulator using menu command ***File/Experiment setup/Load from file***. This step defines all parameters for your experiment properly. Only the experiment parameters are defined, this step does not create the spectra.

To start the experiment, execute the main menu command ***Go/Run*** or ***Go/Check parameters & Go***. This will start the simulation and the time domain signal will be generated. Use the XWIN-NMR or WIN-NMR to process the calculated spectra.

The NMR-SIM installation contains the following example configuration files:

demo1d.cfg	1d spectrum of ethanol
selco.cfg	selective COSY of di-brom propionic acid
select.cfg	a selective excitation experiment in a strongly coupled system (di-brom propionic acid)
dept.cfg	dept experiment on a sample CH-CH2-CH3 spin system
hohaha.cfg	selective excitation and magnetization transfer using the MLEV mixing sequence
invreco.cfg	simple inversion recovery experiment
profile.cfg	excitation profile
jres.cfg	j-resolved experiment on di-brom propionic acid spin system.
cosytp.cfg **cosydtp.cfg** **cosytftp.cfg**	COSY experiments on dbpa
hetcor.cfg	heteronuclear correlation experiment on a sample C-H spin system
invitp.cfg	inverse heteronuclear experiment
inv_1d.cfg	1D H-X correlation via heteronuclear zero and double quantum coherence
Gradient spectroscopy	
inv_1d.cfg	1D H-X correlation via heteronuclear zero and double quantum coherence using gradients
gradient_cosy.cfg	gradient COSY experiment
gardient_calibrate.cfg	simulates the magnetization decay in the gradient pulse as a function of time.
watergate.cfg	water signal suppression using binomial pulse sequence and gradients
Bloch Module	
bloch.cfg	investigation of a gaussian pulse

chirp.cfg	investigation of a phase modulated chirp inverse pulse
Parameter optimizer	
paropt_90.cfg	90 degree pulse length optimization
paropt_dept.cfg	dependency of the DEPT experiment on the evolution delay length

These example files may also be used as a templates for the definition of your private experiments. Just change necessary parameters and save the configuration on the disk under a new name.

The spin system used in all examples are small, so you will get the results in very short time on any computer. It takes just a matter of seconds to calculate most of the 2D experiments described here.

The following section describes details of selected example experiments. Every part contains a listing of the experiment configuration file. To reduce the storage requirements the files contain only parameters which are non-zero or different from the BRUKER default settings.

The negative values of pulse lengths in configuration files are in fact the tilt angles. The program uses this coding for the sake of simplicity.

12.1 How to setup a new experiment

You have two possibilities of setting up a new experiment:

a) **Load the existing experiment configuration** which is similar to the new experiment you want to calculate. Select a new spin system or pulse program and modify the existing parameters.

b) **Use the NMR-WIZARD**.
The NMR-WIZARD only uses two input sources: the spin system definition and the pulse program. It sets all necessary parameters in the pulse program. Use this automatic setup for your further development. See "NMR-Wizard" on page 93.

12.2 The first 1D experiment

The configuration file ***demo1d.cfg*** contains the description of a simple one dimensional experiment. The spin system description files ***ethanol.ham***

```
; Protons in ethanol
;
; Bruegel, Handbook of NMR Spectral parameters,
; vol 2, p 316
;
proton 3*a 1.19 t=1
proton 2*b 3.66 t=1
proton   c 5.27 t=1
couple a b 6.9
couple b c 4.76
```

and ***ethanol2.ham*** contain the protons and the protons and carbons from ethanol molecule respectively.

The file ethanol2.ham uses the molecule definition to create the natural **mixture** of molecules with c13 and c12 isotopes. The c12 atoms are omitted, because the c12 nucleus does not have any magnetic moment.

```
;
; Carbons and protons in ethanol
; Bruegel, Handbook of NMR Spectral parameters,
; vol 2, p 316
;
molecule alpha 0.98
proton 3*a 1.19
proton 2*b 3.66
proton   c 5.27
;
couple a b 6.9
couple b c 4.76
endmol
;
; follow two molecules with carbons
molecule beta 0.01
proton 3*a 1.19
proton 2*b 3.66
proton   c 5.27
```

```
carbon e 56.30
couple a b 6.9
couple b c 4.76
;
; H/C spin coupling in Hz
;
weak a e 100
endmol

molecule gamma 0.01
proton 3*a 1.19
proton 2*b 3.66
proton   c 5.27
carbon   f 16.95
;
couple a b 6.9
couple b c 4.76
;
; H/C spin coupling in Hz
;
weak b f 100
endmol
```

The resulting 1D spectrum is on the Figure 12.1.

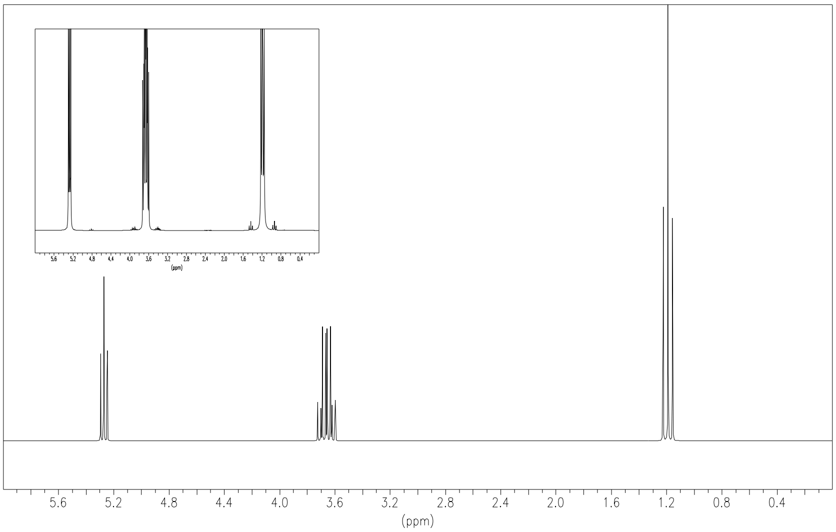


Figure 12.1 The proton spectrum of ethanol at 200 MHz. Experiment definition file demo1d.cfg. The inset shows the C13 satellites (vertical scale with 8 times magnification).

12.3 Excitation profiles of shaped pulses

The usage of ***ihc*** command allows for the simulation of rather complicated experiments, you can study the dependence of NMR experiments on various spin system parameters.

The results of such an experiment is shown in Figure 12.2c): excitation profile of a gaussian pulse on a two spin system. Chemical shift of one nucleus varied in the range ± 700 *Hz*, the chemical shift of the second nucleus was fixed on 1000 Hz. Comparison to the excitation profile of isolated nucleus Figure 12.2b) shows, that the excitation profile is not affected by the spin-spin interaction.

The configuration file is **profile.cfg**

```
[NMR-Sim-Experiment]
sequence= $root$\usr\demo\shape.seq
hamiltonian=a.ham
SF=200
p5=5000
l1=81
sh1=gauss.shp
Relaxation=1
TD=8192
NS=4
HL1=100000
HL2=200
SW=8.192
hv1=-800
hs1=200
```

Please note, that the values of spin system variables used for chemical shift definition are interpreted as frequency in Hz!

Every pulse may be described using **three dependent parameters -** the pulse

length, the intensity of the radio frequency field and the tilt angle.
The shaped pulse used here is defined by two parameters: its ***length***, specified in this case by ***P5*** parameter an its ***on-resonance flip angle*** defined here by the ***AW1*** parameter.
It is also possible to use the ***pulse length*** and the ***rf field intensity*** **-** using exactly the same approach as is used on the spectrometer. The use of the flip angle (e.g. 90d) instead the pulse duration is available only for pulses without phase modulation!

Use the switch ***Shape pulse*** in the ***NMR-SIM options*** dialog to select the method you prefer.

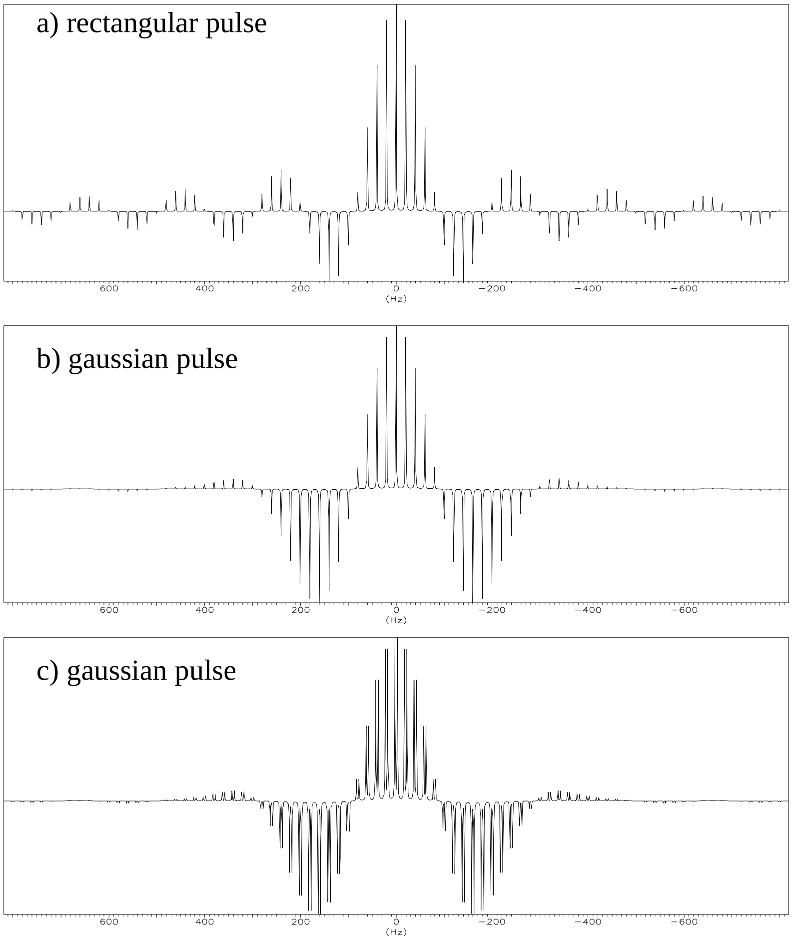


Figure 12.2 The comparison of excitation profiles of three different selective pulses. The length of all pulses is 5 ms, tilt angle 90 deg (effective field amplitude 50 Hz). The configuration file name is ***profile.cfg***

12.4 Selective COSY

This example demonstrates the practical use of a shaped pulse for the selective excitation.

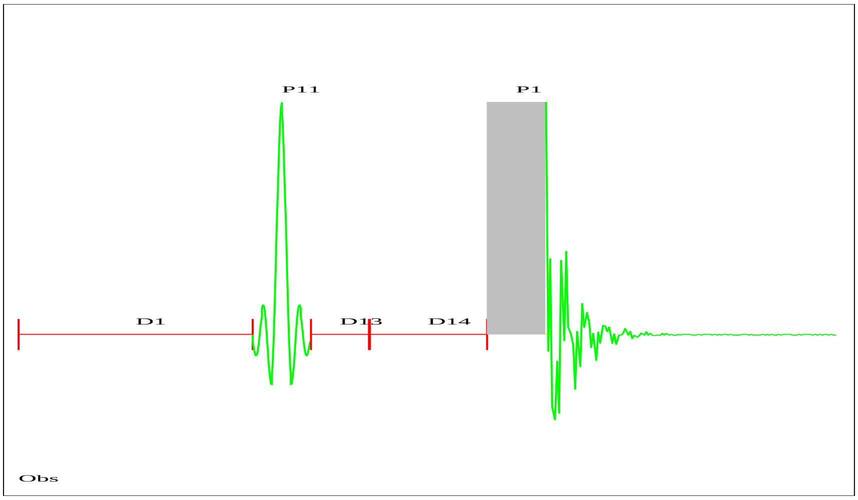


Figure 12.3 Schema of 1D selective COSY experiment

The comparison of the experimental and simulated spectra shows a very good agreement between the theoretical and experimental results. The pulse program being used is the standard Bruker pulse program **selco**.

```
;selco
;1D COSY using selective excitation with a shaped pulse
;C.J. Bauer, R. Freeman, T. Frenkiel, J. Keeler & A.J.
Shaka,
;   J. Magn. Reson. 58, 442 (1984)
;H. Kessler, H. Oschkinat, C. Griesinger & W. Bermel,
;   J. Magn. Reson. 70, 106 (1986)
1 ze
2 d1 tlo
  p11:tp1 ph1
```

```
  d13
  d14 thi
  p1 ph2
  go=2 ph31
  wr #0
exit
ph1=(360)  90 270 270 90 180 0 0 180
ph2=0 2 0 2 1 3 1 3
ph31=0 2 2 0 1 3 3 1
;hl1: ecoupler high power level
;tp1: power level for shaped pulse tp1 in tlo mode
;p1 :  90 degree transmitter high power pulse
;p11:  90 degree transmitter shaped pulse
;d1 : relaxation delay; 1-5 * T1
;d13: short delay (e.g. to compensate delay line)    [3
usec]
;d14: delay for evolution after shaped pulse: (p11)/2 +
d14 ~ 1/(2J)
;NS: 8 * n
;DS: 4
;x : phase difference between thi and tlo output
;choose p11 according to desired selectivity
;the flip-angle is determined by the amplitude
;the use of an external attenuator might be necessary
;O1  has  to  be  on  resonance  on  the  multiplet  to  be
excited
```

`Experiment definition selco.cfg:`

```
[NMR-Sim-Experiment]
sequence=selco
hamiltonian=$root$\usr\demo\dbpa.ham
p11=80000
d1=0.003691
sh1=gauss.shp
Relaxation=1
TD=4096
NS=8
HL1=100000
SF=300.13
SFO1=4.1
SW=1.2
```

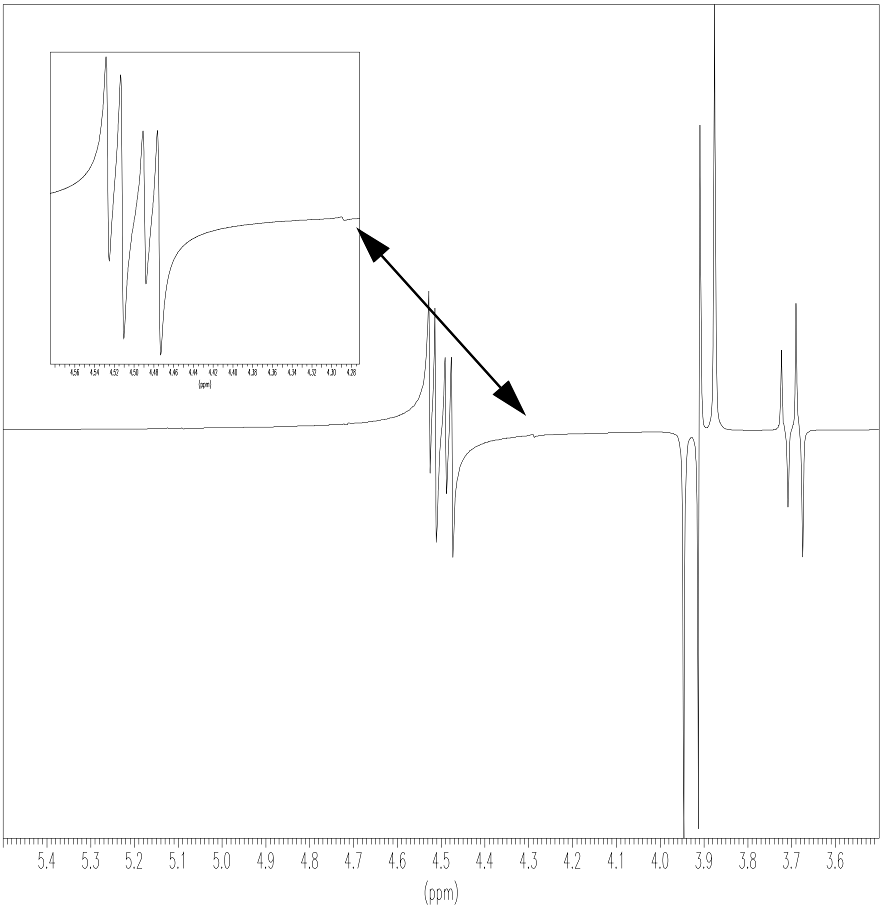


Figure 12.4 Selective COSY experiment. The length of the Gauss shaped pulse was 80 ms, the D13 delay ≈ 3.7 ms. Note the magnified parts of spectrum which shows small artifact, probably generated due the strong J-coupling in the spin system. The same artifact is also present in the real experiment.

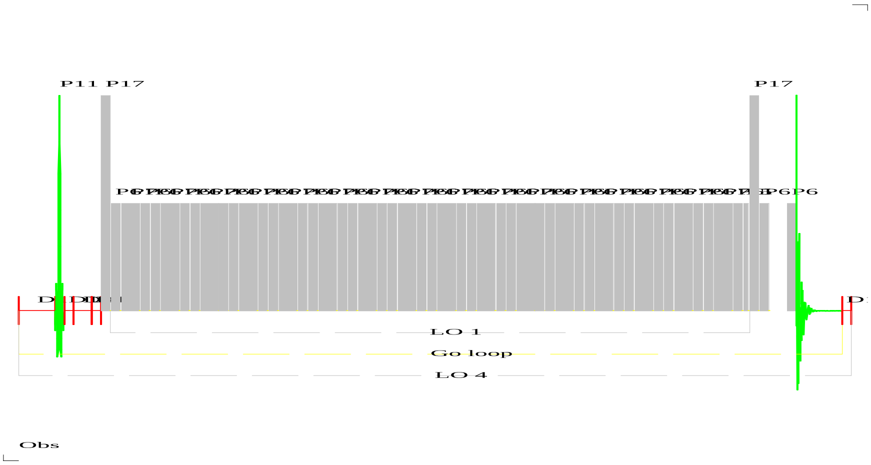


Figure 12.5 Schema of 1D HOHAHA z-filtered experiment

12.5 1D HOHAHA with z-filter

One of the most exciting areas in the NMR spectroscopy are the homo-nuclear Hartman Hahn experiments, which helps to elucidate the molecular structure. The next example shows the 1D version of such experiment, the configuration file is ***hohaha.cfg***.

This experiment shows the efficiency of the pulse program compilation in NMR-SIM. The first scan needs the most of the run-time.The shaped pulse for the selective excitation and the magnetization transfer sequence are compiled and saved in memory. Following scans use the previously compiled segments and execute much faster - the number of calculated pulses is reduced by a factor ~ 200.

The result of the short experiment with only one delay in the z-filter contains a large number of artifacts - Figure 12.6 a).
The “full” experiment with 8 delays in the z-filter exhibits the significant suppression of artifacts - Figure 12.6 b). The pulse program requires the delay table ***hoha_z.ld***.

The delays in the z-filter (hoha_z.ld) are calculated for the example ABC spin system and for the spectrometer frequency SF = 200 MHz. To use a different spin system or frequency, you should create a new delay list file. The delay values τ are calculated using formula

$$\frac{1}{\tau\pi} = \sum_{i<j} \pi\alpha_{ij}(\omega_i - \omega_j)$$

where ω_i,ω_j are the chemical shifts of the nuclei and α_{ij} π is 0 or 1. Every possible combination of 0 and 1 in this formula defines one delay time $\tau\pi$.

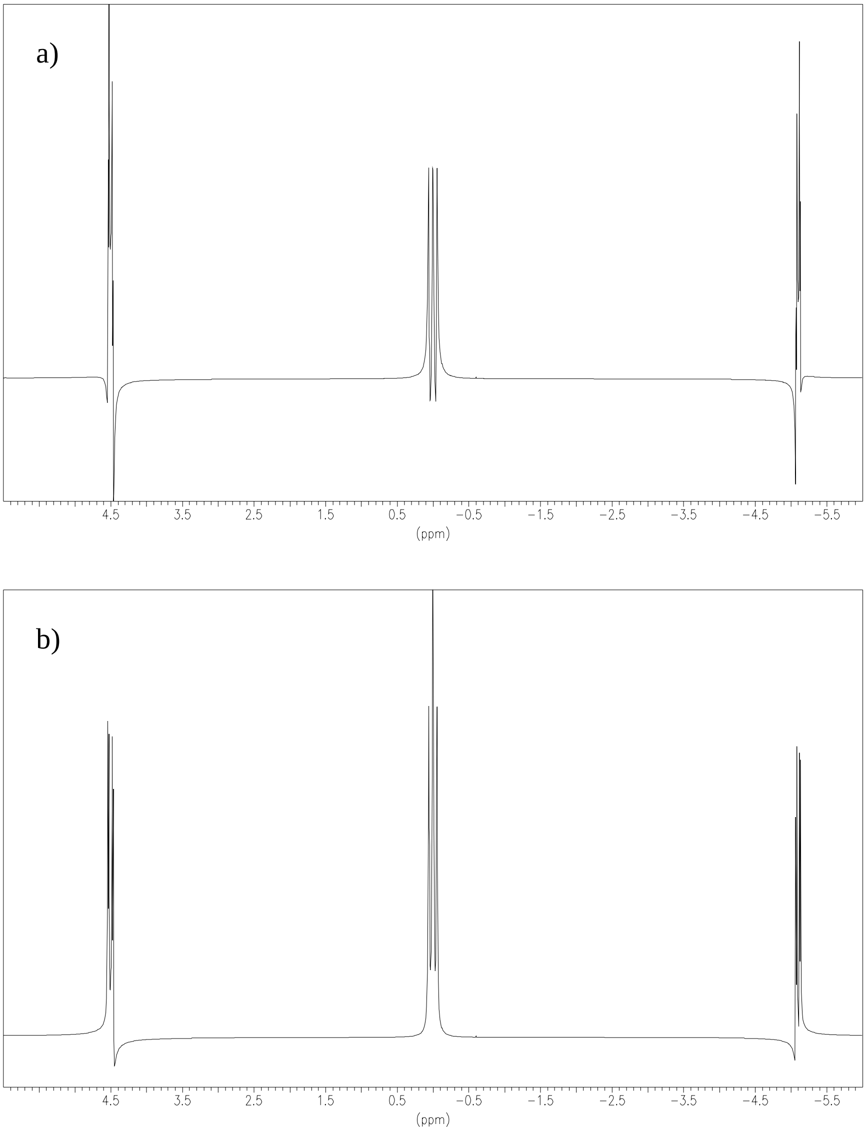

a)
4.5
3.5
2.5
1.5
0.5
−0.5
−1.5
−2.5
−3.5
−4.5
−5.5
(ppm)
b)
4.5
3.5
2.5
1.5
0.5
−0.5
−1.5
−2.5
−3.5
−4.5
−5.5
(ppm)

Figure 12.6

12.6 DEPT experiment

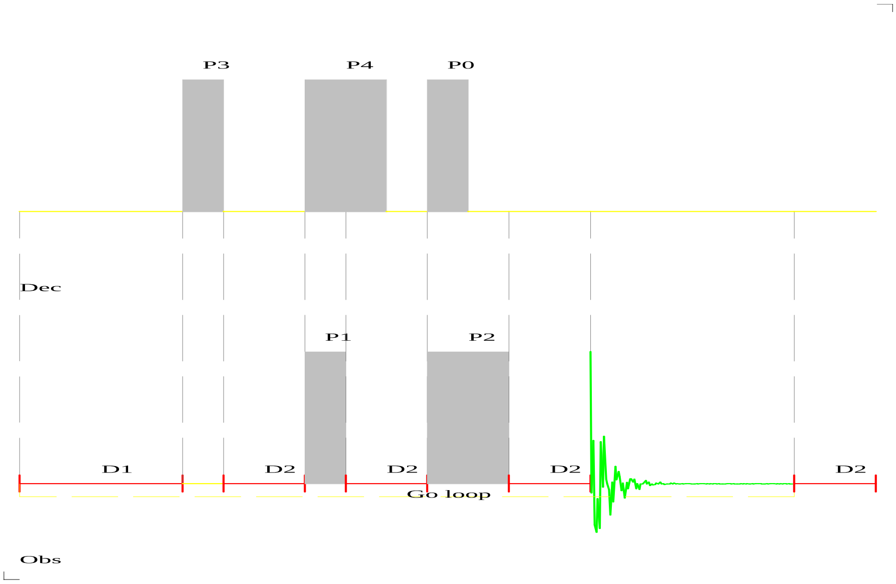


Figure 12.7 The scheme of DEPT pulse sequence

This example presents a simple heteronuclear experiment. The used spin system is a artificial CH3-CH2-CH molecule. The picture demonstrates the dependency of C13 spectra on the number of coupled protons and the tilt angle of the P0 pulse in the DEPT pulse sequence:

```
;deptnd
;dept polarization transfer
;no decoupling during acquisition
1 ze
2 d1 do s1
3 (p3 ph1):d
  d2
  (p4 ph2):d (p1 ph4 d2)
  (p0 ph3):d (p2 ph5)
  d2
  go=2 ph31
  wr #0
  d2 do
```

```
exit
ph1=0
ph2=0 2 1 3
ph3=1 1 1 1 3 3 3 3
ph4=0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1
    2 2 2 2 2 2 2 2 3 3 3 3 3 3 3 3
ph5=0 2 0 2 0 2 0 2 1 3 1 3 1 3 1 3
ph31=1 1 3 3 3 3 1 1 2 2 0 0 0 0 2 2
     3 3 1 1 1 1 3 3 0 0 2 2 2 2 0 0
;S1: ecoupler high power level
;p0 : 45, 90 or 135 degree decoupler high power pulse
;     45 degree - all positive
;     90 degree - XH only
;    135 degree - XH, XH3 positive, XH2 negative
;p1 :  90 degree transmitter high power pulse
;p2 : 180 degree transmitter high power pulse
;p3 :  90 degree decoupler high power pulse
;p4 : 180 degree decoupler high power pulse
;d1 : relaxation delay; 1-5 * T1
;d2 : 1/(2J(XH))
;NS: 4 * n
;DS: 4 or 8
```

The evolution delay D2 has been matched to the CH coupling 100 Hz. The phase distorsions in the resulting spectra results from the deviations of CH2 and CH3 coupling constants from this value.

You may try further experiments using the same setup and changing only the pulse program. The pulse program ***dept*** contains the same experiment, but with the decoupling during the acquisition. Another possibility is the pulse program ***ineptnd***. The evolution delays for the inept experiment are already set.

Experiment definition file dept.cfg

```
[NMR-Sim-Experiment]
sequence=deptn
hamiltonian=chmodel.ham
p0=-135
d2=0.005
Relaxation=1
TD=16384
NS=4
HL1=100000
HL2=200
SF=200
SFO1=50
SW=40
```

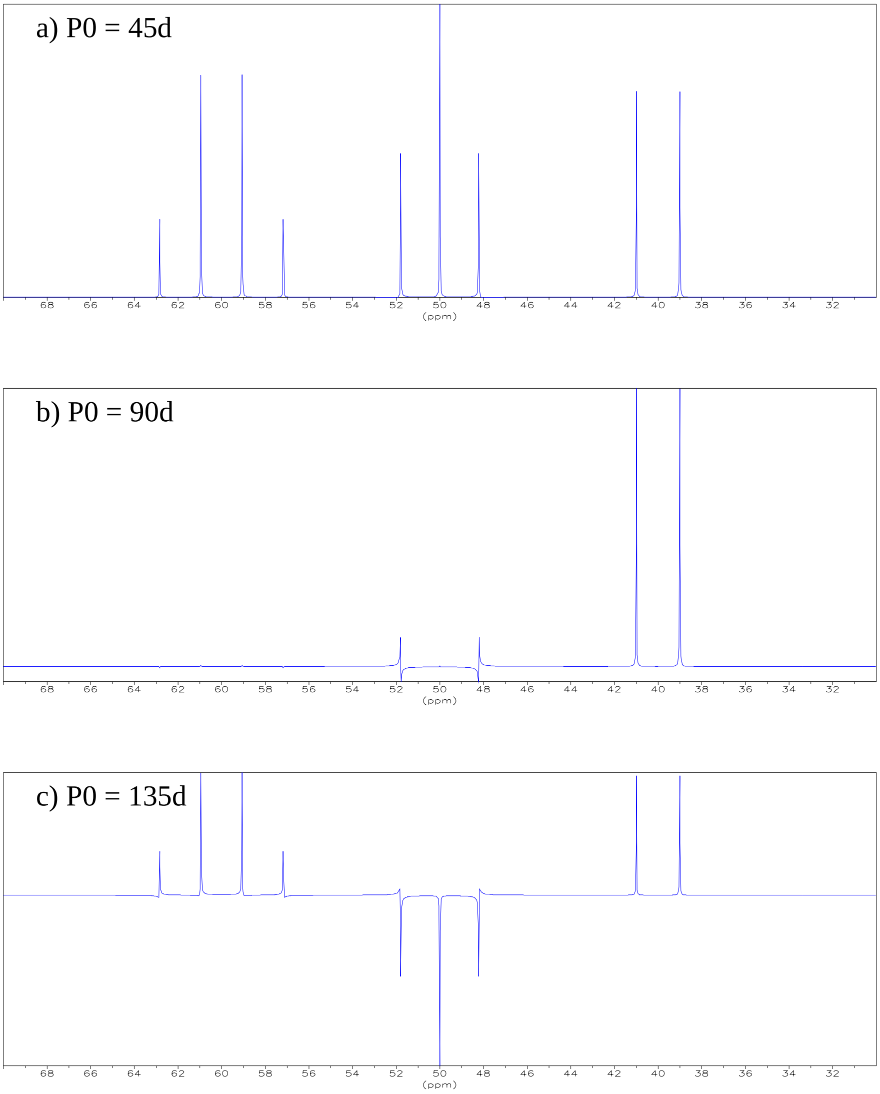


Figure 12.8 **Comparison of simulated *C^{13}* DEPT spectra for three different leading pulses *P0*.**

12.7 J resolved experiment

This simple 2D experiment shows the ability of NMR-SIM to calculate 2nd order spectra. The comparison of the same J-resolved spectra on 300 MHz and 600 MHz shows the significant reduction of strong coupling artifacts for the higher resonance frequency. Both spectra on the Figure 12.11 were processed using the *qsine* window function with SSB= 3.

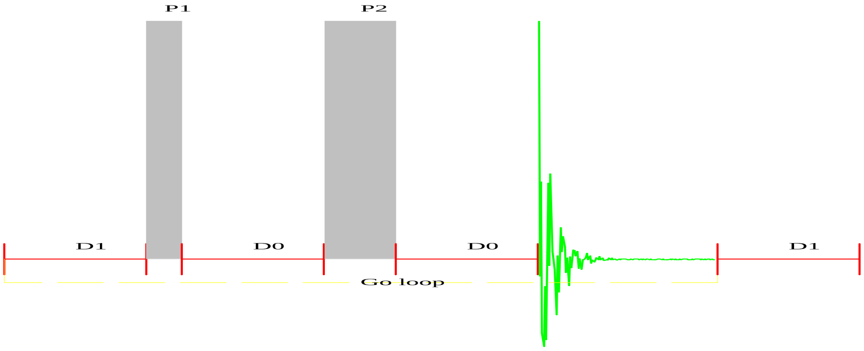


Figure 12.9

Experiment definition jres.cfg:

```
[NMR-Sim-Experiment]
sequence=jres
hamiltonian=dbpa.ham
in0=0.01
Relaxation=1
TD=1024
NS=4
HL1=100000
SF=300.13
SFO1=4.1
SW=1.2
```

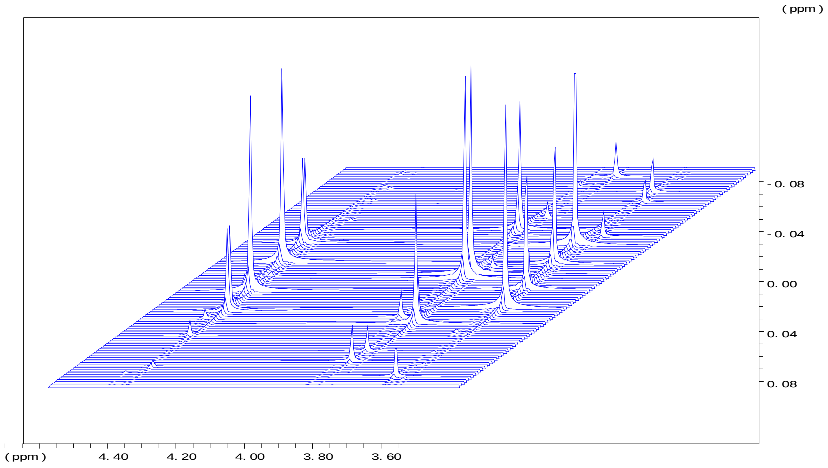
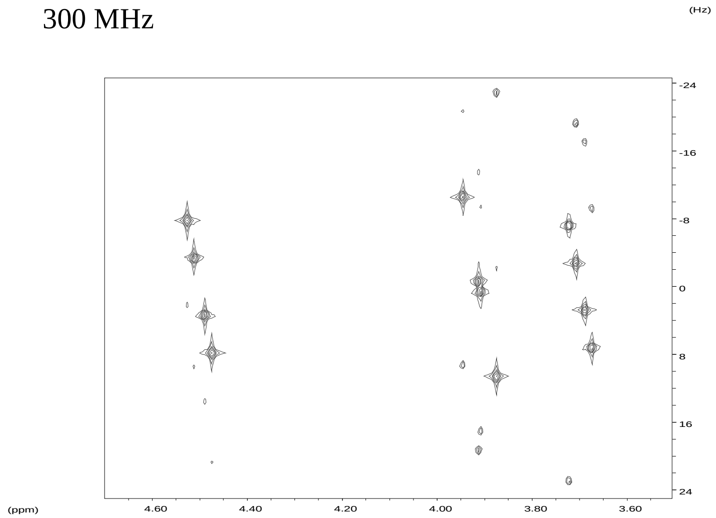


Figure 12.10 The 300 MHz spectrum shown as a stacked plot. The intensity of 2nd order artifacts is remarkable.

300 MHz



600 MHz

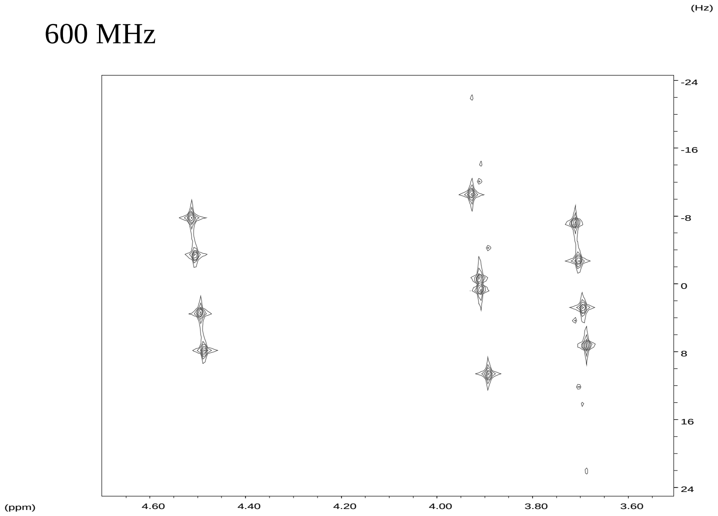


Figure 12.11 The comparison of J-resolved experiment for two different frequencies.

12.8 Phase sensitive DQ COSY experiment

Experiment definition is stored in ***cosydtp.cfg***.

```
[NMR-Sim-Experiment]
sequence=cosydftp
hamiltonian=dbpa.ham
in0=sw
Relaxation=1
TD=1024
NS=4
HL1=100000
SF=300.13
SFO1=4.1
SW=1.2
```

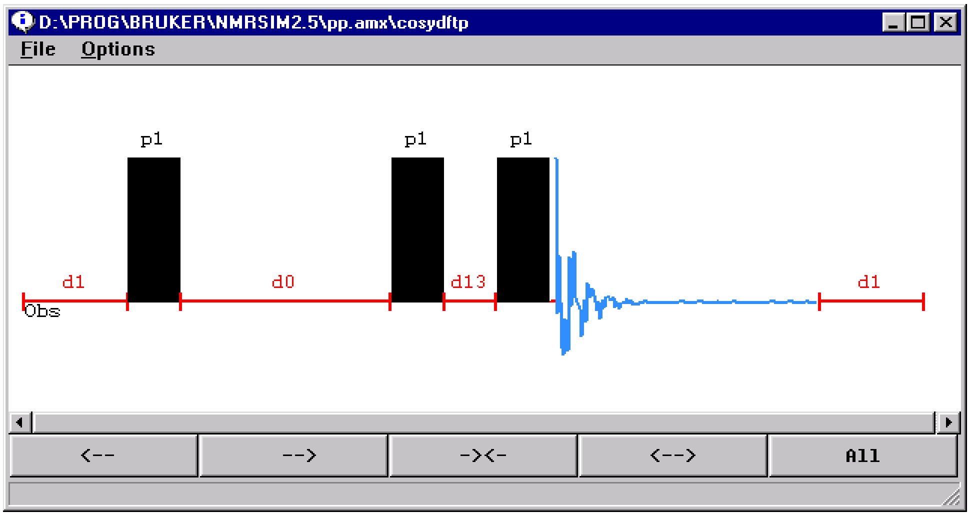


Figure 12.12 Double quantum cosy pulse program scheme.

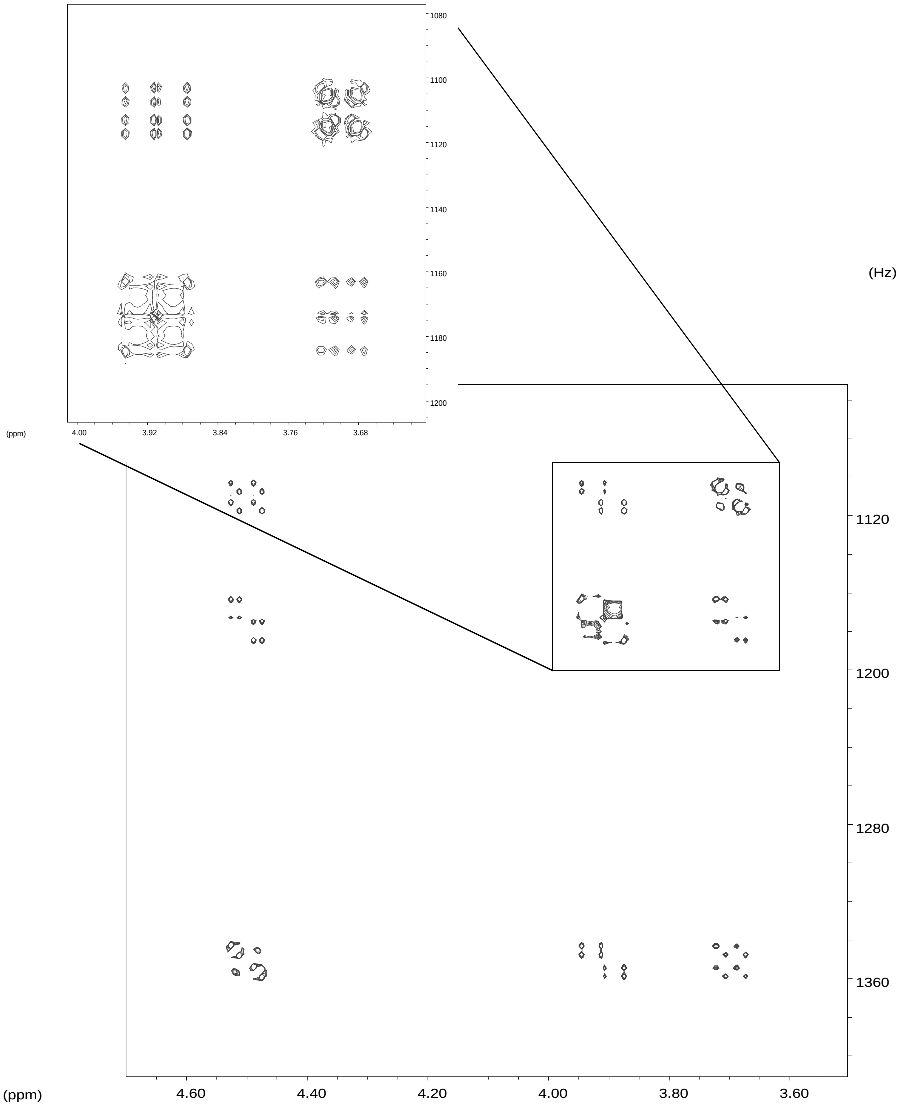


Figure 12.13 The DQ-COSY spectrum of di-brom propionic acid at 300 MHz

12.9 Inversion recovery experiment

The configuration file ***invreco.cfg*** contains a simple inversion recovery experiment setup. The picture shows the relaxation procedure on 10 1D spectra. It may be also possible to present the experiment in 2D form: just change the experiment type from 1D to 2D. Transforming the acquisition dimension f2, you will get a equivalent picture.

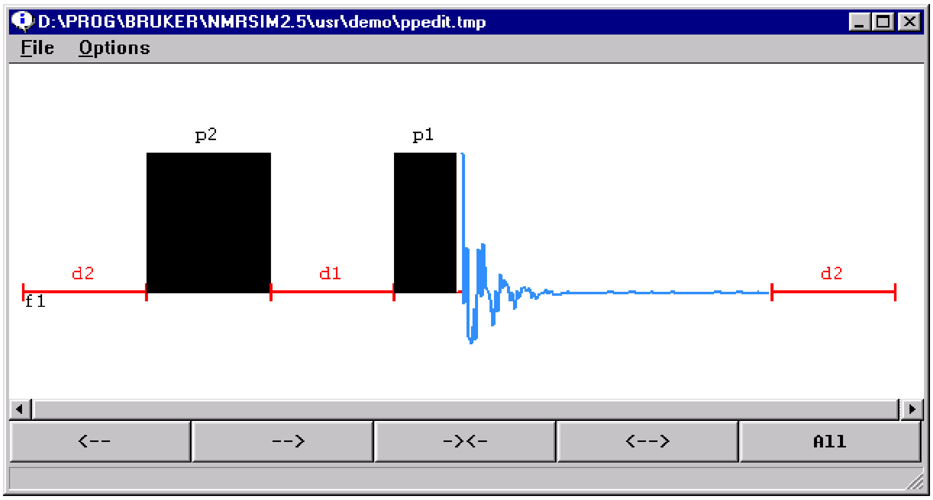


Figure 12.14

```
[NMR-Sim-Experiment]
sequence=$root$\usr\demo\invreco.seq
hamiltonian=$root$\usr\demo\abc.ham
p1=-90
p2=-180
d1=0.0
d2=10
in1=0.03
```

```
l1=1
Relaxation=2
TD=16304
NS=1
HL1=100000
SF=200
AQ_mod=1
SW=12
```

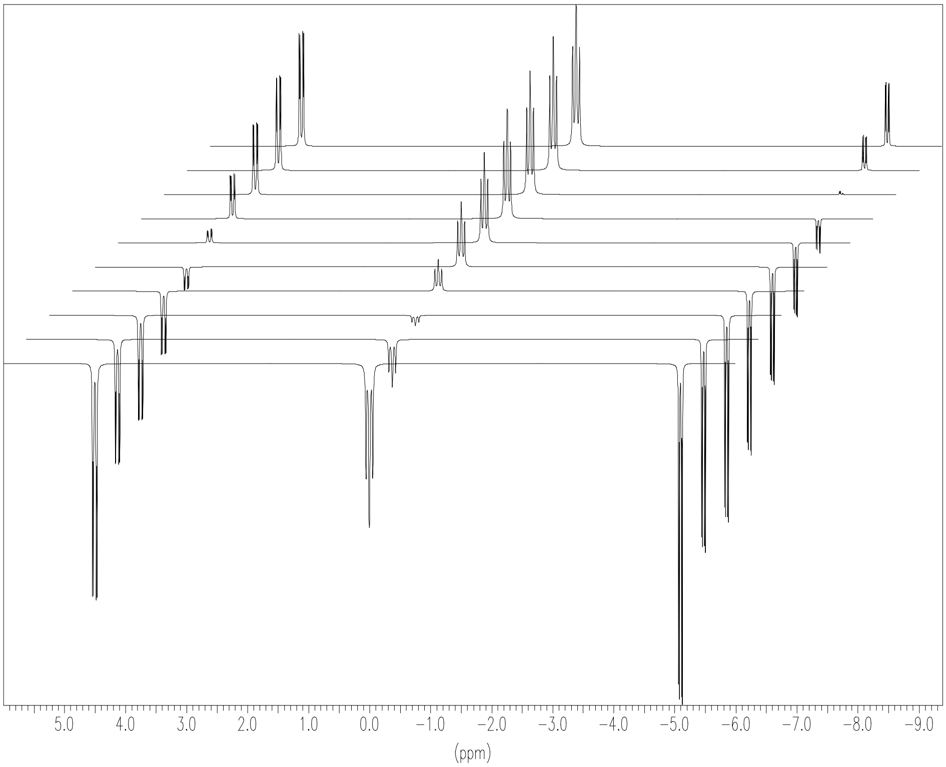


Figure 12.15 Inversion recovery experiment

12.10 Heteronuclear correlation

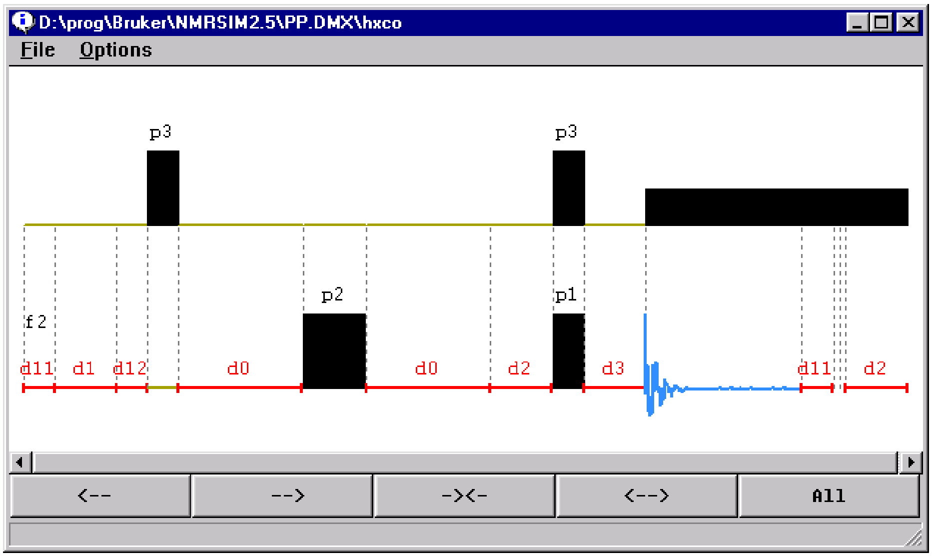


Figure 12.16 The ***hxco*** pulse program.

This example presents a simple heteronuclear correlation experiment. The sample CH3-CH2-CH spin system (***chmodel.ham***) was used. The result of the simulation is shown on Figure 12.17.

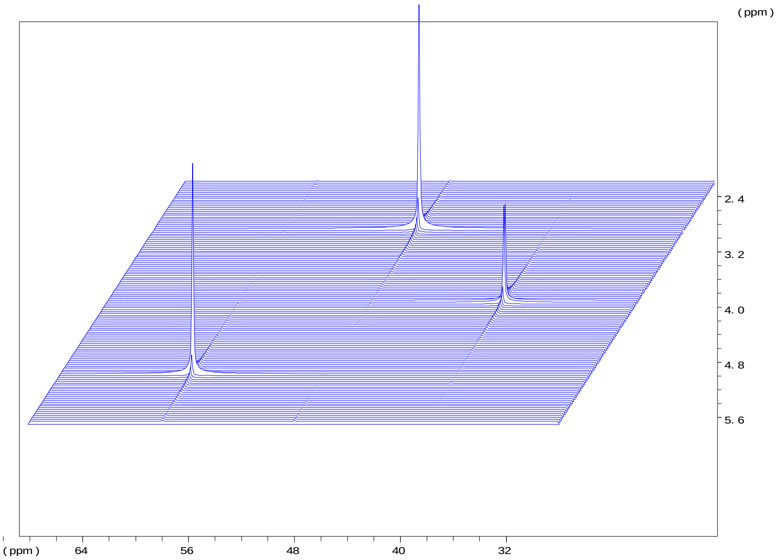


Figure 12.17 Result of the heteronuclear correlation experiment.

12.11 Inverse experiment

The configuration file ***invitp.cfg*** contains a setup for a sample inverse experiment.

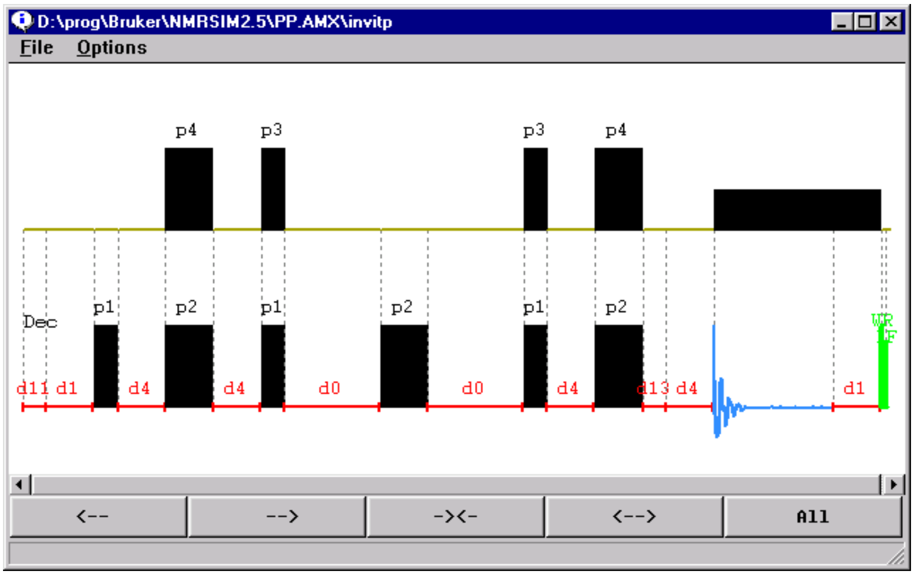


Figure 12.18 invitp pulse program **-** inverse correlation using the inept sequence.

The double inept sequence is used for the magnetization transfer.

The sample CH3-CH2-CH spin system was used. Figure 12.19 shows the result.

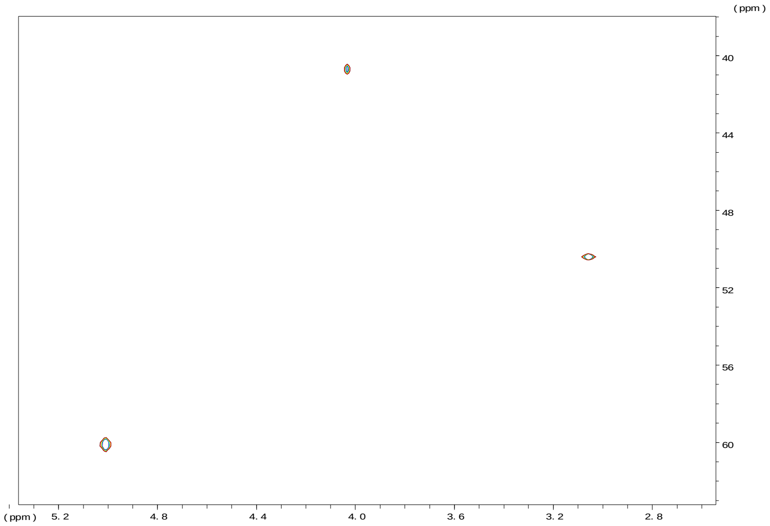


Figure 12.19

12.12 1D Heteronuclear correlation

The 1D inverse heteronuclear correlation experiment may be used to detect the protons attached to selected X nuclei.

There exist two version of this experiment: the “classical” one uses a phase cycle to do the selection of attached nuclei. The second one uses magnetic field gradient for the coherence selection.

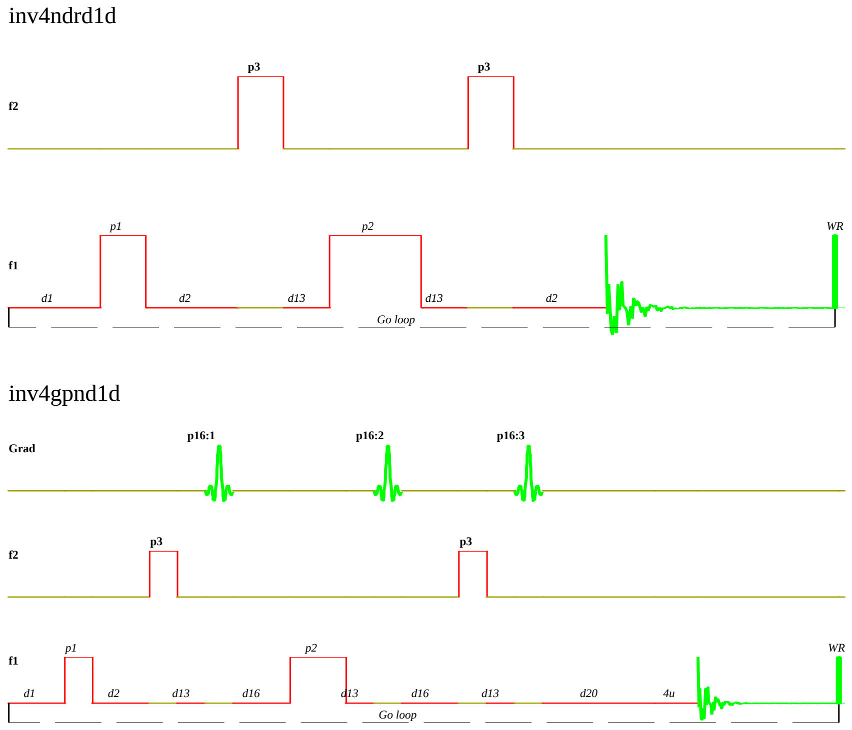


Figure 12.20 Comparison of the “classical” and gradient versions of the inverse 1D correlation experiment.

The experiment parameters are stored in the configuration file ***inv_1d.cfg***. We use the ethanol (***ethanol2.ham***) as a model spin system.

The gradient version should use the gradient intensity ratio 50:30:40. This ratio is valid for the H-C13 spin systems. Other X nuclei will require different values.

The results are shown on the next picture. The signals of protons without the C13 coupling are suppressed and we see only the C13 coupled nuclei. An 1D spectrum of the molecule is shown for the comparison.

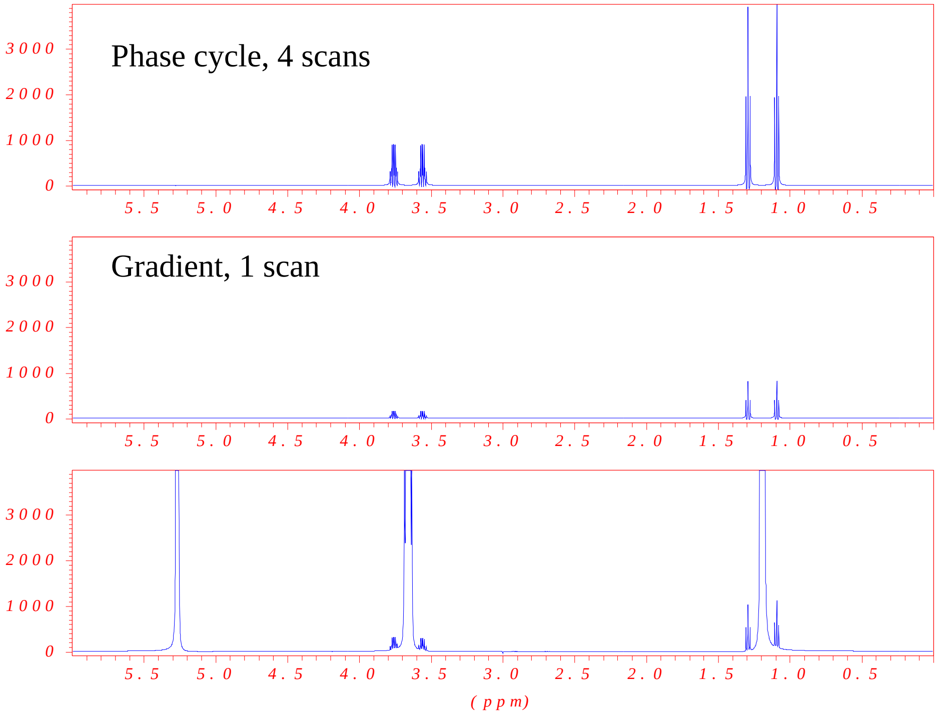


Figure 12.21 Comparison of the 1D inversion experiment using a traditional pulse program with phase cycling to gradient version. No decoupling was used during the acquisition. The gradient version uses only one scan, so the signal intensities are lower.

12.13 Gradient experiments

The details of the implementation of gradient spectroscopy are described in the chapter ***Gradient spectroscopy*** on page 101.

12.13.1 Gradient COSY experiment

The basic gradient experiment is the ***cosygp*** pulse program. Here we use the ***cosygpmftp*** pulse program: multiple quantum filtered COSY using gradients.

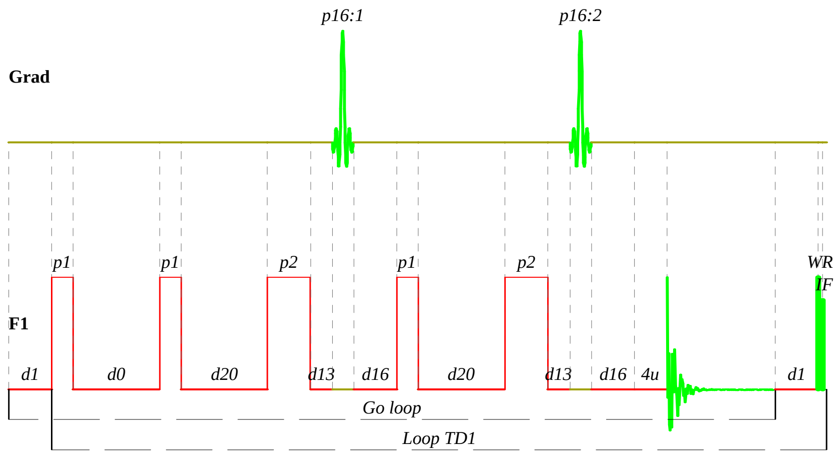


Figure 12.22 COSYGPMFTP pulse program

This pulse program may uses different gradient intensity ratios for the coherence selection. Ratio 10:20 gives a double-quantum filtered experiment, ratio 10:30 gives a triple quantum spectrum. The experiment is phase sensitive using the TPPI phase modulation, only one transient (scan) is required.

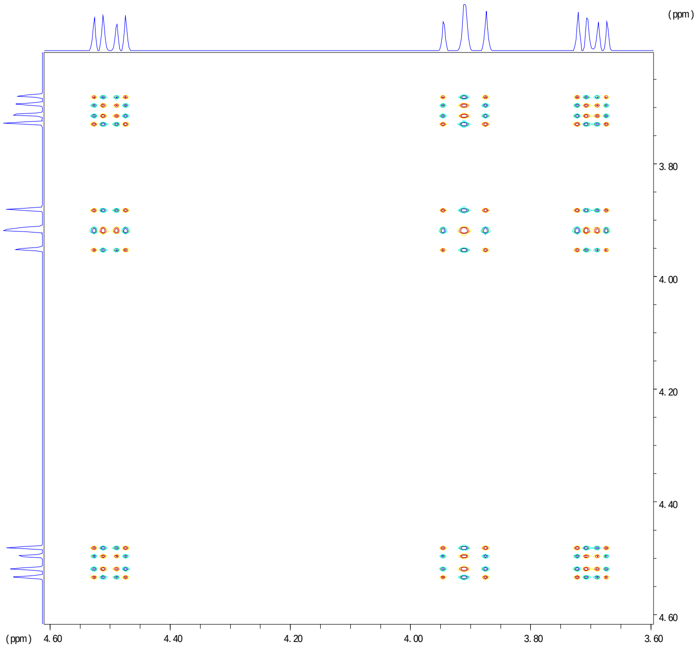


Figure 12.23 Triple-quantum filtered gradient cosy spectrum of a dibrompropionic acid.

12.13.2 Watergate

The watergate pulse program is used for the efficient suppression of solvent signals. The pulse sequence contains a "sandwich" of two gradients separated by a selective inversion pulse. The version presented here uses a popular binomial sequence of hard pulses as the inversion pulse.

The following pulse program calculates the excitation profile of the watergate sequence. It uses the NMR-SIM spin system manipulation commands to imitate the shift of the spectrometer carrier frequency which is necessary to measure such a dependence. The name of the pulse program is ***watergate.seq***, the configuration file is ***watergate.cfg***.

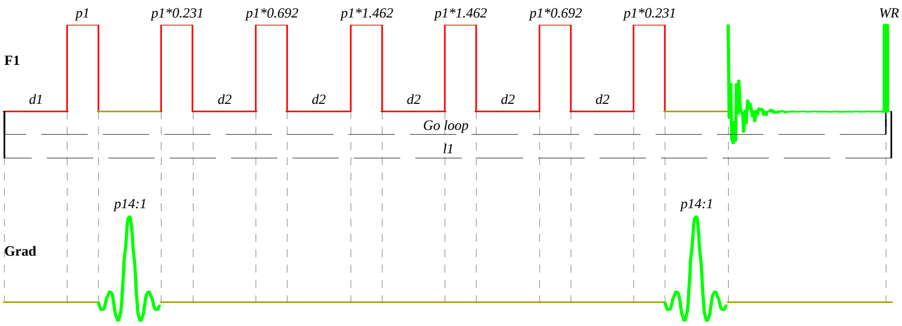


Figure 12.24 Watergate pulse program

```
;watergate
;avance-version
;
; Pulse program for the solvent suppression
; using the watergate pulse sequence
;
1     ze
2     d1
3     p1 ph1
      p14:gp1
;
; The binomial selective pulse starts here
      p1*0.231 ph1
      d2
      p1*0.692 ph1
      d2
      p1*1.462 ph1
      d2
      p1*1.462 ph2
      d2
      p1*0.692 ph2
      d2
      p1*0.231 ph2
      p14:gp1
      go=2 ph31
; this command increments the spin system variables
      ihc
```

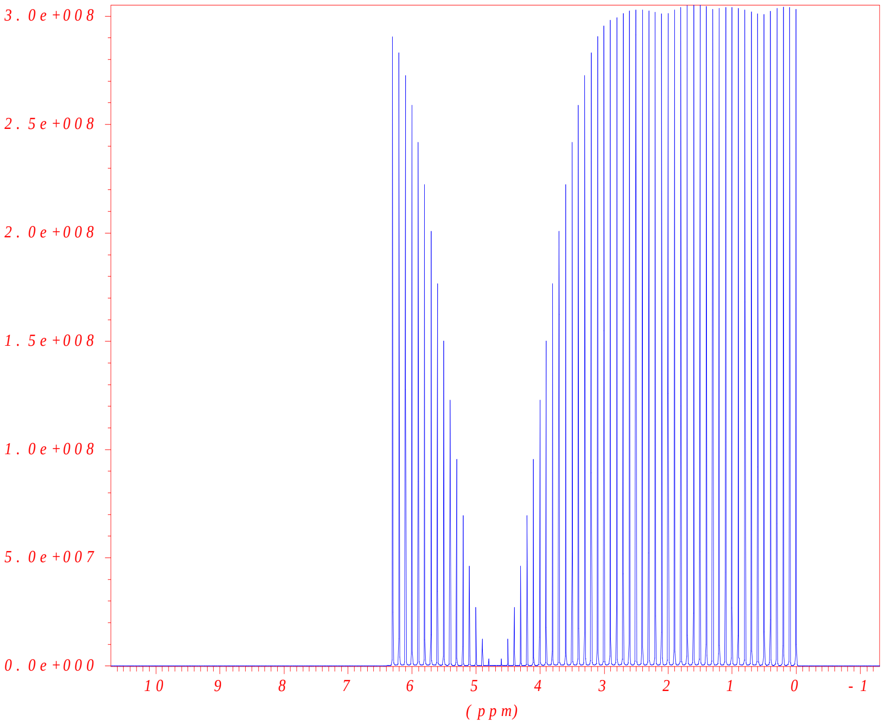


Figure 12.25

```
          lo to 2 times l1
          wr #0
    exit

    ph1=0 1 2 3
    ph2=2 3 0 1
    ph31=0 1 2 3

    ;NS: 4 * n
```

The experiment requires 4 transients (scans), the gradient pulse length was 2ms, the gradient power GPZ1 10%.

The delay D2 is a important parameter defining the periodicity of the binomial inversion pulse. The value 0.3 us used here guaranties, that the next minimum lies always outside of the spectrum bandwidth.

Chapter 13

Appendix

13.1 Important changes

This part of manual describes the important changes, which were implemented since the last release. The new developments are not described here.

- The multiplication of radio-frequency fields by gamma factor may be now switched on or off in *the Options/NMR-Sim settings* dialog box: ***Modify RF fields***.
- The shaped pulses now use the radio frequency field intensity defined in parameters TP0-7.
- There are now two modes for the **shaped pulses calculation**. You can switch it in *Options/NMR-Sim settings* dialog box. The new one (it is now default) ***Use Actual RF fields*** is a equivalent to the spectrometer: the shaped pulse is defined using the radio-frequency. intensity TP0-7 and the pulse duration.

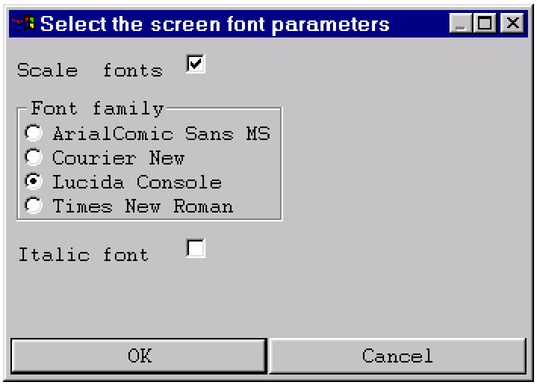
The option ***Normalize pulses*** uses the pulse length and the on-resonance flip angle (AW0-7) to calculate the effective radio frequency field, which is used for the pulse. This works very well, but only for pulses **without phase modulation**.

The hamiltonian variables HV1-32 are now defined in Hz, instead of ppm! The number of variables has been changed to 32.

13.2 Font selection

Windows

The font selection dialog allow you to select the font family used in the graphic windows and the font resizing policy.



Scale fonts ☑

Font family
- ○ ArialComic Sans MS
- ○ Courier New
- ● Lucida Console
- ○ Times New Roman

Italic font ☐

The option ***Scale fonts*** is used to switch the automatic font scaling on or off. When on, the font size is scaled when the height of the window change. The font family used in this case may be also selected here.

Switching the option ***Scale fonts*** off disables the automatic scaling and selects a standard font family present on all MS-WINDOWS installations.

13.3 Files and directories

All user files are stored in the user directory and its subdirectories. The user directory used on the UNIX system and on MS-WINDOWS NT is the ***NMRSIM_SESSION*** subdirectory in the user home directory. Typical path on the IRIX system is

/usr/people/<`user_name`>/NMRSIM_SESSION.

MS-WINDOWS NT uses something like

c:\users\<`user_name`>\NMRSIM_SESSION.

The home directory may be set or changed in the MS-WINDOWS NT user manager. File types used in the program have different file name extensions.

- ***.cfg*** configuration files defining the experiment
- ***.ham*** spin system definition
- ***.job*** job description
- ***.ld*** Delay list
- ***.lo*** offset list
- ***.lp*** pulse list
- ***.pr*** job protocol file
- ***.seq*** pulse sequence

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