

# WSolids1 — Solid State NMR Simulations

USER MANUAL

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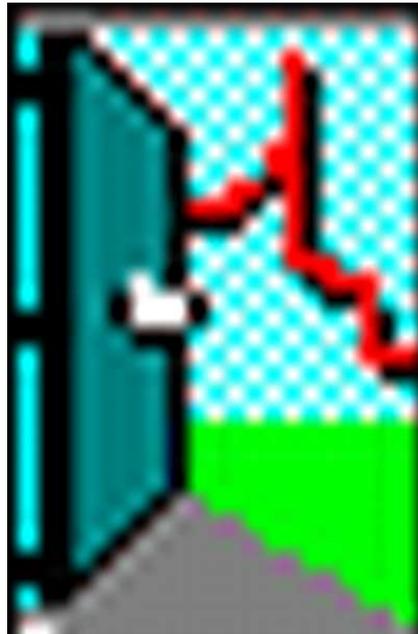


# Contents

<b>1</b>	<b>Getting Started</b>	<b>5</b>
1.1	Introduction	6
1.1.1	Purpose of the Program	6
1.1.2	Features	7
1.1.3	License	7
1.1.4	Trouble?	8
1.2	Overview	9
1.3	Revision History	10
1.3.1	Version 1.19.2 (21.08.2008)	10
1.3.2	Version 1.17.30 (23.05.2001)	10
1.3.3	Version 1.17.28 (27.09.2000)	10
1.3.4	Version 1.17.22 (17.03.1999)	10
1.3.5	Version 1.17.21 (09.10.1998)	10
1.3.6	Version 1.17	11
1.3.7	Version 1.16	11
1.4	Multiple Document Interface, MDI	12
1.4.1	The Multiple Document Interface	12
1.4.2	Menu Management	12
1.4.3	Keyboard Interface	13
1.5	Keyboard Accelerators	14
<b>2</b>	<b>Menus</b>	<b>15</b>
2.1	File Menu	18
2.1.1	New Window	18
2.1.2	Open Spectrum	18
2.1.3	Save Spectrum	22
2.1.4	Exit	23
2.2	Simulation Menu	24
2.2.1	Spectrum Default Parameters	25
2.2.2	Convolution Parameters	28
2.2.3	Derivative Mode	30
2.2.4	New Site	31
2.2.5	Select Calculation Model	31
2.2.6	Edit Sites	32
2.2.7	Calculate	33
2.2.8	Active Only	33
2.2.9	Cycle	33
2.2.10	Cycle Options	33
2.3	Tools Menu	34
2.3.1	Dipolar Coupling Constant	34
2.3.2	Table of Nuclear Properties	35
2.3.3	Periodic System of Elements	37
2.3.4	Convolute	37
2.3.5	Scale Spectrum	37
2.3.6	Add Constant	37
2.3.7	Reverse Spectrum	38
2.3.8	Absolute Value	38
2.4	Window Menu	39

2.5	Help Menu . . . . .	40
2.6	Known Problems . . . . .	41
<b>3</b>	<b>Spin Systems</b>	<b>43</b>
3.1	Static: Chemical Shift Anisotropy . . . . .	43
3.2	Static: Dipolar Chemical Shift (A2, AX) . . . . .	45
3.3	Static: Dipolar Chemical Shift (AB) . . . . .	48
3.4	Static: Quadrupolar Nucleus . . . . .	50
3.4.1	Implementation Details . . . . .	51
3.4.2	References . . . . .	52
3.5	MAS: Chemical Shift Anisotropy (HB) . . . . .	53
3.6	MAS: Quadrupolar Nucleus . . . . .	56
3.6.1	Implementation Details . . . . .	56
3.6.2	References . . . . .	57
3.7	MAS: Spin-1/2 – Spin-S (Diag.) . . . . .	58
3.7.1	Implementation Details . . . . .	59
3.8	MAS: Spin-1/2 – Spin-S (Stick) . . . . .	61
3.8.1	Implementation Details . . . . .	62
3.9	MAS: Spin-1/2 – Spin-S (Shape) . . . . .	64
3.10	VAS: Dipolar-Chemical Shift (A2, AX) . . . . .	66
3.11	VAS: Dipolar-Chemical Shift (AB) . . . . .	68
3.12	Spin System Parameters . . . . .	70
3.12.1	Relative Intensity . . . . .	70
3.12.2	Tie to previous site . . . . .	70
3.12.3	Convention . . . . .	70
3.12.4	Standard Convention . . . . .	70
3.12.5	Herzfeld-Berger Convention . . . . .	71
3.12.6	Haeberlen Convention . . . . .	71
3.12.7	Chemical Shift and Chemical Shielding . . . . .	72
3.12.8	Coupled To . . . . .	73
3.12.9	Natural Abundance . . . . .	73
3.12.10	Dipolar Coupling Constant D . . . . .	73
3.12.11	Indirect Spin-Spin Coupling J . . . . .	73
3.12.12	Anisotropy in Indirect Spin-Spin Coupling Delta-J . . . . .	74
3.12.13	Polar Angles . . . . .	74
3.12.14	Euler Angles . . . . .	75
3.12.15	Rotation Matrices . . . . .	75
3.12.16	The Swivel Chair . . . . .	78
3.12.17	Determining Euler Angles . . . . .	79
3.12.18	Electric Field Gradient Tensor . . . . .	79
3.12.19	Central Transition (CT) and Satellite Transitions (ST) . . . . .	80
3.12.20	Spinning Frequency . . . . .	80
3.12.21	Speedy Calculation . . . . .	80
<b>4</b>	<b>Acknowledgements</b>	<b>81</b>
4.1	Credits . . . . .	81
4.2	Trademark Acknowledgements . . . . .	82
4.3	Copyright Information . . . . .	82
4.4	Disclaimer of Warranty . . . . .	82

# 1 Getting Started



## Contents

---

<b>1.1 Introduction</b> . . . . .	<b>6</b>
1.1.1 Purpose of the Program . . . . .	6
1.1.2 Features . . . . .	7
1.1.3 License . . . . .	7
1.1.4 Trouble? . . . . .	8
<b>1.2 Overview</b> . . . . .	<b>9</b>
<b>1.3 Revision History</b> . . . . .	<b>10</b>
1.3.1 Version 1.19.2 (21.08.2008) . . . . .	10
1.3.2 Version 1.17.30 (23.05.2001) . . . . .	10
1.3.3 Version 1.17.28 (27.09.2000) . . . . .	10
1.3.4 Version 1.17.22 (17.03.1999) . . . . .	10
1.3.5 Version 1.17.21 (09.10.1998) . . . . .	10
1.3.6 Version 1.17 . . . . .	11
1.3.7 Version 1.16 . . . . .	11
<b>1.4 Multiple Document Interface, MDI</b> . . . . .	<b>12</b>
1.4.1 The Multiple Document Interface . . . . .	12
1.4.2 Menu Management . . . . .	12
1.4.3 Keyboard Interface . . . . .	13
<b>1.5 Keyboard Accelerators</b> . . . . .	<b>14</b>

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## 1.1 Introduction

### 1.1.1 Purpose of the Program

WSolids1 is a program for the visualization and analysis of processed one-dimensional solid-state NMR data. It is a simulation package initially developed at the [Department of Chemistry \(p. 6\)](#), [Dalhousie University \(p. 7\)](#), Halifax, Canada, in order to deal with the multitude of interactions observed in NMR spectra of static or spinning solid samples. The initial versions have been written in C++ using Borland C++ 4.5. However, in spring 2008 the developments, or the lack of such, at Borland made me change my programming tools to Microsoft Visual C++ 2008 Express Edition. Not that this development environment has everything that I would need to work efficiently, but it is for free (it's like they give you a free car without a seat for the driver—it's workable but a bit bumpy at times). WSolids1 succeeds its earlier FORTRAN version, Solids.

Although there are several "general purpose" programs or libraries available to calculate many interactions and for many different experiments, there is still room for programs with specially designed specific calculation models. The main reason is efficiency. A routine designed for one particular purpose will always be more efficient than a general purpose routine! Progress in computing power continually decreases the gap. However, calculation of a static powder pattern of an isolated spin pair using a general purpose program still requires several hours as compared to the few seconds using the less general implementation in WSolids (the "several hours" was written in the mid/end nineties; in 2008, this difference has dwindled). The advantage for the user is convenience rather than power; not every user has the knowledge to feel comfortable with, for example, Simpson (<http://www.bionmr.chem.au.dk/bionmr/software/simpson.php>).



Figure 1.1: The Department of Chemistry at Dalhousie University, Halifax, Canada



Figure 1.2: The logo of Dalhousie University, Halifax, Canada

### 1.1.2 Features

This section lists some of the features of *WSolids1*, the knowledge of which should enable the user to work more efficiently with *WSolids1*:

- *WSolids1* uses the [Multiple Document Interface \(p. 12\)](#) (MDI) specification. The user should familiarize himself with this specification. Often, the vendors of NMR spectrometers provide some means of analyzing or simulating experimental spectra, but often a mere simulation – to answer a question like “how would this look like?” – without an experimental spectrum is not possible. MDI as implemented in *WSolids1* allows to calculate spectra for different external magnetic fields, different derivative modes, or different experimental conditions simultaneously, using the same spin system parameters. This could help to answer a question like “does it make sense to go to a higher field?”
- Spin systems and spectra are allocated dynamically. One may have as many spectra and spin systems as the memory resources of the computer allow. In each case, the spectrum and spin system parameters are filled with sensible default values. This should allow for easy familiarization.
- *WSolids1* has no build-in features to support iterative fitting. In order to make the refinement of a calculated spectrum less painful, a so-called [Cycle \(p. 33\)](#) feature was implemented. Depending on the context and the selected Cycle options, pressing the Enter key will perform specific actions such as requesting spectrometer settings, requesting spin system parameters, requesting convolution parameters, performing a calculation, or switching to the next spectrum window.
- For several menu commands, [accelerator keys \(p. 14\)](#) have been defined (for example, pressing C starts a calculation). Also, holding down the ALT key and pressing any character key activates the corresponding menu item, edit control, list box, button, etc. for which the corresponding character is underlined.

Some of the description of features has already been formulated in the early nineties. Nowadays, with gigantic office software suites the user is certainly more accustomed to multiple documents etc., but I guess it doesn’t hurt to keep this description. Also, the look of *WSolids1* is now archaic, but remember: I am a one-man company and not making any money out of this software that I develop and maintain in the evening hours.

### 1.1.3 License

This program package can be used without any fee. However, if you find this program useful and publish results obtained by using *WSolids1*, we would appreciate a citation or acknowledgement of this program similar to:

*WSolids1*, K. Eichele, R. E. Wasylishen, Dalhousie University, Halifax, Canada.

Before reading on, you may also want to have a look at our [credits statement \(p. 81\)](#), [trademark acknowledgement \(p. 82\)](#), [copyright message \(p. 82\)](#), and obligatory [disclaimer \(p. 82\)](#).

#### 1.1.4 Trouble?

Although WSolids1 has been tested and used both in-house and by others, it is always possible that errors exist. Some errors may become apparent after detailed use on the wide variety of chemical systems. It is the responsibility of the user to determine the correctness of the results. If errors are noticed, please notify us of your problems, and the prescribed or suggested corrections, so that others may benefit from the improved code. Also, suggestions for improvements are welcome.

Inquiries about the use of this program or reports of problems can be directed via e-mail to:

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Also, you may address correspondence via snail mail to:

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## 1.2 Overview

The Overviews provided here are aimed at giving an outline of the steps required to achieve a particular task. Following a question in the left column, links to the relevant topics are provided. After catching up on any specific topic, use the **Back** feature of your reader to return to this screen.

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<b>How do I start?</b>	<a href="#">① Create a new spectrum window (p. 18)</a>
	<a href="#">② Read an experimental spectrum (p. 18)</a>
	<a href="#">③ Create a new spin system (p. 31)</a>
	<a href="#">④ Define convolution parameters (p. 28)</a>
	<a href="#">⑤ Calculate (p. 33)</a>
	<a href="#">⑥ Repeat as required (p. 33)</a>
	<a href="#">⑦ Save the results (p. 22)</a>

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<b>How do I work efficiently?</b>	<a href="#">Use keyboard accelerators (p. 14)</a>
	<a href="#">Use the cycle feature (p. 33)</a>

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## 1.3 Revision History

This page describes changes made to the WSolids1 program versus previous versions and provides a summary of new features.

### 1.3.1 Version 1.19.2 (21.08.2008)

- This is the first 32 bit release. Internally, Wsolids1 underwent some serious changes that will not be apparent to the user.
- Added reading of [TopSpin/XWinNMR \(p. 19\)](#), [JCAMP-DX \(p. 21\)](#), and [Simpson \(p. 22\)](#) files, removed handling of Antiope, NMRLAB and CC2X files.
- In addition to WinNMR format, spectra can also be saved as TopSpin or Solids files
- Incorporated the IUPAC Recommendations 2001 for the NMR properties of NMR active isotopes, the new Q values from Pyykkö; fixed spin of Nd-145 and U-235 and added U-233
- [MAS: Spin-1/2 Spin-S \(Diag.\) \(p. 58\)](#): added handling of general spin-5/2 case (any-chi, any-eta, any-orientation) and made some modifications to the spin-3/2 part also

### 1.3.2 Version 1.17.30 (23.05.2001)

- Included new Herzfeld-Berger tables that are more accurate at higher values of  $\mu$ . The tables were calculated using a home-made dedicated program on a Pentium 400 MHz PC and required almost a week of computer time.

### 1.3.3 Version 1.17.28 (27.09.2000)

- Changed the use of the [Relative intensity \(p. 70\)](#) parameter; it is now introduced after the calculation for that specific site has been carried out; sites using different calculational models should now have relative areas corresponding to their relative intensities. This also fixed bugs for some of the models where the relative intensity was not handled properly.
- Modified the model [Static: Quadrupolar Nucleus \(p. 50\)](#) to allow a homonuclear A2 spin system (it is up to the user to decide if the result makes sense). A division by zero for not initialized spectrometer frequency gets caught now.
- Modified the POWDER routine by Alderman (previously, the interpolation did not cover the half sphere completely).

### 1.3.4 Version 1.17.22 (17.03.1999)

- Fixed a bug related to the relative intensities of several sites when using the model [MAS: Quadrupolar nucleus \(p. 56\)](#).
- Made changes to the POWDER subroutine to deal with single-line lineshapes better (previously, no intensity got added).

### 1.3.5 Version 1.17.21 (09.10.1998)

- Changed the meaning of [SF \(p. 25\)](#) (spectrometer frequency): this parameter corresponds now to the frequency of the chemical shift standard.
- Fixed a bug in model [MAS Spin-1/2 – Spin-S \(Stick\) \(p. 61\)](#): the factor dealing with reference SF and different Larmor frequencies worked in the opposite sense of the intended direction.

- Added [Tools/Add constant](#) (p. 37) to allow for a very simple baseline correction.
- Added [Tools/Absolute value](#) (p. 38) to generate the absolute value representation.
- Added [Tools/Reverse spectrum](#) (p. 38) to reverse the sense of a spectrum.
- Problems with the [cycle feature](#) (p. 33) got probably fixed now.
- Introduced an option in the convolution of spectra to switch off the use of a [threshold value](#) (p. 27).
- Different sites calculated with the model [MAS: Chemical Shift Anisotropy \(HB\)](#) (p. 53) should have the proper relative intensities now.
- Added functions to read experimental spectra in Chemagnetics [SpinSight](#) (p. 21) format.
- Added functions to read [WinNMR ASCII](#) (p. 20) spectra directly, without the need to convert them into SOLIDS format.

### 1.3.6 Version 1.17

- Added a new calculation model: [MAS: Quadrupolar nucleus](#) (p. 56).
- Fixed a memory problem (bug) in model [MAS Spin-1/2 – Spin-S \(Stick\)](#) (p. 61) and modified processing.
- Changed the handling of spectrum files. WSolids1 now uses the NMRFILES dynamic link library developed for WSolids2, which allows for a greater variety of file formats.
- Fixed another error in model [MAS: Spin-1/2 Spin-S \(Diag.\)](#) (p. 58);  $\text{cup} = 1$  for  $\text{sth} = 0$
- Modified processing in model [MAS: Spin-1/2 Spin-S \(Shape\)](#) (p. 64)
- Added [Tools/Scale spectrum...](#) (p. 37) to allow scaling of spectrum
- Modified enabling/disabling of controls in convolution parameter box; changed layout of dialog box

### 1.3.7 Version 1.16

- Fixed cycle feature. (Actually, not really; fixed one problem, created a new one)
- Fixed MDI accelerators.
- Processing modified for the following dialog boxes: default parameters, convolution parameters, model selection, static chemical shift anisotropy, static dipolar chemical shift (A2, AX), static dipolar chemical shift (AB), static quadrupolar nucleus, MAS chemical shift anisotropy (HB), MAS spin-1/2 – spin-S (Diag.), About, Open file, Save file, Edit sites
- Fixed errors in model [Static: Dipolar–chemical shift \(A2, AX\)](#) (p. 45) and [VAS: Dipolar-chemical shift \(A2, AX\)](#) (p. 66): for A2 system, J is neglected now.
- Fixed two errors in model [MAS: Spin-1/2 Spin-S \(Diag.\)](#) (p. 58): sign error in sbsf term;  $\text{cet} = 1$  for  $\text{cth} = 1$ .
- Fixed update of BF1 in AQS file.
- Fixed file handling functions to use WinAPI exclusively (should allow to create and read more files).

## 1.4 Multiple Document Interface, MDI

This topic provides some information about the Multiple Document Interface in general and its implementation in WSolids1. Managing multiple documents is one of the key issues.

### 1.4.1 The Multiple Document Interface

The multiple document interface (MDI) has been designed for applications that need to simultaneously manage:

- more than one data set
- more than one view of a data set

In MDI, there are two fundamentally different type of windows:

- The main window of an MDI application is called a "**frame**" window. Frame windows usually have:
  - a title bar
  - a menu, a system menu
  - a sizing border
  - Minimize/Maximize buttons

The non client area of the frame window surrounds a portion of something called the application "**workspace**". The workspace can be larger than the frame window's client area, because a user can use scroll bars to scroll different portions of the workspace into view.

- An MDI application's workspace can contain zero or more child windows, which are referred to as "**documents**", "document windows", or "MDI children." In the case of WSolids1, a document window usually corresponds to a window with dual display of an experimental and a calculated spectrum. We shall call such a document window a **spectrum window**.

In general, document windows have:

- a title bar
- a sizing border
- a system menu bitmap
- Minimize/Maximize buttons
- scroll bars

Because document windows always have Minimize and Maximize buttons, they can be minimized and maximized. When minimized, they are represented as icons and displayed in the workspace of the frame window. When maximized, document windows are sized to fill the entire workspace of the frame window, not the entire Windows desktop. The title bar of a maximized document window disappears and its caption text is appended to the caption text in the frame window's title bar. In addition, the system menu bitmap of the document window becomes the first item in the menu bar of the frame window, and the button to restore the document window to normal size is positioned at the far right of the frame window's menu bar.

### 1.4.2 Menu Management

The frame window's menu bar has a popup menu bar item called Window near the right end of the menu (just left of the Help item). The Window popup menu contains items related to the arrangement of document windows within the workspace. These options include tiling and cascading of windows and arranging icons at the bottom of the workspace.

### 1.4.3 Keyboard Interface

The Windows MDI has its own keyboard interface that augments the keyboard interface for non-MDI applications. The MDI key sequences allow users to easily navigate between and manipulate document windows within an MDI application just as they can navigate between and manipulate applications on the Windows desktop (see also the section on [keyboard accelerators \(p. 14\)](#) in WSolids1).

- CTRL + F4 closes the currently active document window. (ALT + F4 closes an application's main window.)
- CTRL + F6 (or CTRL + TAB) switches among document windows in the MDI application's workspace (ALT + TAB switches among applications on the Windows desktop.)
- ALT + HYPHEN invokes the system menu of the active document window (ALT + SPACEBAR invokes the system menu of the active application's main window.)

## 1.5 Keyboard Accelerators

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ALT + F4	closes an application's main window
ALT + HYPHEN	invokes the system menu of the active document window
ALT + SPACEBAR	invokes the system menu of the active application's main window
ALT + TAB	switches among applications on the Windows desktop
CTRL + F4	closes the currently active document window
CTRL + F6	switches among document windows in the MDI application's workspace
CTRL + TAB	switches among document windows in the MDI application's workspace

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ENTER	perform the next step of the cycle feature
C	Calculate
E	Edit sites
N	New Site

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# 2 Menus



## Contents

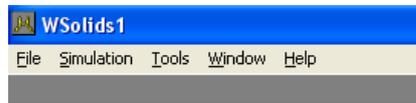
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<b>2.1</b>	<b>File Menu</b>	<b>18</b>
2.1.1	New Window	18
2.1.2	Open Spectrum	18
	Bruker TopSpin / XWinNMR	19
	Bruker WINNMR Generic	20
	Bruker WINNMR UNIX	20
	Bruker WINNMR ASCII	20
	Chemagnetics SpinSight	21
	SOLIDS	21
	JCAMP-DX	21
	Simpson	22
	Varian	22
2.1.3	Save Spectrum	22
2.1.4	Exit	23
<b>2.2</b>	<b>Simulation Menu</b>	<b>24</b>
2.2.1	Spectrum Default Parameters	25
	Observed Nucleus	25
	Spectrometer Frequency	25
	Spectrum Size	26
	ppm / Hz	26
	Spectrum Limits	26
	Use Relative Threshold Value	27
	Site-Dependent Broadening	27
2.2.2	Convolution Parameters	28
	Gaussian/Lorentzian Mixing	29
	Gaussian Convolution	29
	Lorentzian Convolution	29
2.2.3	Derivative Mode	30
2.2.4	New Site	31
2.2.5	Select Calculation Model	31
2.2.6	Edit Sites	32
2.2.7	Calculate	33
2.2.8	Active Only	33
2.2.9	Cycle	33
2.2.10	Cycle Options	33

<b>2.3</b>	<b>Tools Menu</b>	<b>34</b>
2.3.1	Dipolar Coupling Constant	34
2.3.2	Table of Nuclear Properties	35
2.3.3	Periodic System of Elements	37
2.3.4	Convolute	37
2.3.5	Scale Spectrum	37
2.3.6	Add Constant	37
2.3.7	Reverse Spectrum	38
2.3.8	Absolute Value	38
<b>2.4</b>	<b>Window Menu</b>	<b>39</b>
<b>2.5</b>	<b>Help Menu</b>	<b>40</b>
<b>2.6</b>	<b>Known Problems</b>	<b>41</b>

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The menu system of WSolids1 consists of the following pop-up menus:



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<a href="#">File (p. 18)</a>	File and document management
<a href="#">Simulation (p. 24)</a>	Simulation models and parameters management
<a href="#">Tools (p. 34)</a>	Calculational tools
<a href="#">Window (p. 39)</a>	Multiple document management
<a href="#">Help (p. 40)</a>	Help and program version information

---

## 2.1 File Menu

The File pop-up menu consists of the following items:




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<a href="#">New Window (p. 18)</a>	Opens a new spectrum window
<a href="#">Open Spectrum (p. 18)</a>	Retrieves an experimental spectrum
<a href="#">Save Spectrum (p. 22)</a>	Saves a spectrum
<a href="#">Exit (p. 23)</a>	Exits WSolids1

---

### 2.1.1 New Window

The **New window** item of the [File \(p. 18\)](#) pop-up menu creates a new spectrum window in the MDI client area of WSolids1.

A spectrum window is required to display experimental and calculated spectra. All actions are usually performed for the currently active spectrum window. For example, retrieving a spectrum file from hard disk automatically replaces the experimental spectrum of the currently active spectrum window.

Some actions automatically generate a new window, if they require a spectrum window in order to succeed and no active window exists. For example, retrieving a spectrum file will automatically load the spectrum into a new window, if no window has the input focus. However, if a spectrum window has the focus, WSolids1 will load and display the spectrum in this window.

### 2.1.2 Open Spectrum

The **Open Spectrum** item of the [File \(p. 18\)](#) pop-up menu retrieves an experimental spectrum into the [Spectrum Window \(p. 18\)](#) having the focus.

If the currently active spectrum window already contains an experimental spectrum, it is replaced by the new one. If no active spectrum window exists, a new spectrum window is created automatically.

Reading an experimental spectrum automatically changes the [default parameters \(p. 25\)](#) for the theoretical spectrum (of course, they can be modified afterwards).

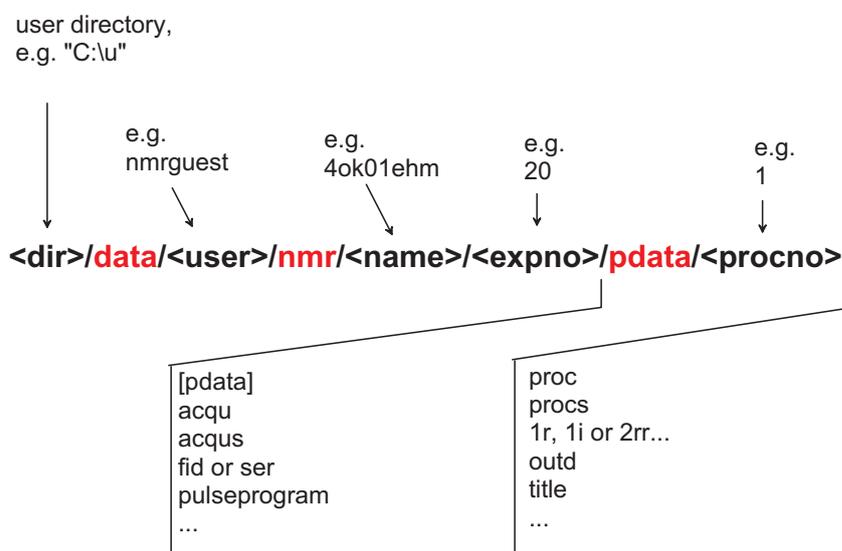
Various formats of experimental spectra are automatically recognized by WSolids1. Please note that the file type option only determines which files are listed in the selection window and does not affect the way the selected file is treated. WSolids1 will always rely on its own strategy to determine the file type. Thus, in order to be recognized, the spectrum needs to follow a certain pattern, as detailed below for each file format.

These are the file formats recognized by WSolids:

Spectrum format	Characteristics
<a href="#">TopSpin/XWinNMR (p. 19)</a>	Requires an 1r file in floating point (or integer) format and the parameter files <code>acqus</code> and <code>procs</code> in JCAMP-DX format.
<a href="#">WINNMR generic (p. 20)</a>	Requires an <code>.1R</code> or <code>.FID</code> file in floating point format and the parameter files <code>.aqs</code> and <code>.fqs</code> in binary format.
<a href="#">WINNMR UNIX (p. 20)</a>	Requires an <code>.1R</code> or <code>.FID</code> file in floating point format and the parameter files <code>.AQS</code> and <code>.FQS</code> in ASCII format
<a href="#">WINNMR-ASCII (p. 20)</a>	Reads a spectrum file in ASCII format generated by Bruker's WinNMR version 5.1 or later; it requires a single file, usually with the extension <code>.TXT</code>
<a href="#">Spinsight (p. 21)</a> <a href="#">SOLIDS (p. 21)</a>	Reads a Chemagnetics Spinsight file requires an ASCII file with header, followed by intensity data (preferred extension <code>.dat</code> )
<a href="#">JCAMP-DX (p. 21)</a>	requires an ASCII file that follows the JCAMP-DX standard (preferred extension <code>.dx</code> )
<a href="#">Simpson (p. 22)</a> <a href="#">Varian (p. 22)</a>	

### Bruker TopSpin / XWinNMR

Spectra stored in Bruker's TopSpin or XWinNMR file format consist of a series of files stored in a convoluted directory structure, as indicated in this figure:



Those parts of the path name written in red letters are fixed names that are required by TopSpin/XWinNMR. A data set of name `<name>` consists of one or more spectra, each characterized by its experiment number `<expno>`, an integer. Each spectrum can have different processed data, stored in the `pdata` subdirectory under a specific processing number `<procno>`, an integer that is usually 1.

In order to be recognized by WSolids as TopSpin/XWinNMR file, the data files need to adhere to the following format:

- `1r` in binary floating point format needs to be present;

- **procs** needs to be present in the same directory, and **acqus** two levels higher; both are ASCII parameter files of variable record length and start with **##** (JCAMP-DX format), the **acqus** file contains the parameters **SFO1, SW\_h, O1, AQ\_mod, BYTORDA, TD, DECIM, DSPFVS, NC, NUCLEUS** and **procs** contains **OFFSET, SI, XDIM, BYTORDP, NC\_proc**.

### Bruker WINNMR Generic

This was the file format used by BRUKER's WIN-NMR version 4.0 (1D version), and is still produced by Bruker's GetFile utility if conversion of Aspect files is selected (basically, the parameter files are in binary format).

In order to be recognized by WSolids1 as a generic WINNMR file, the data files need to adhere to the following format, where *eee* stands for the three-digit **experiment number** and *ppp* for the three-digit **processing number**, each zero-padded if necessary. Thus, an experiment number of 2 and a processing number of 1 would result in the file name 002001. (WSolids1 itself doesn't care about the *eeppp* format).

- *eeppp.1R* or *eeppp.FID* in binary floating point format need to be present (currently, WSolids1 does not read FID's)
- *eeppp.AQS* and *eeppp.FQS* need to be present in the same directory; these parameter files are in binary format of fixed record length and start with **A000**, the AQS file contains the parameters **SFO1, SW\_h, O1** and FQS contains **SR**

### Bruker WINNMR UNIX

This file format is similar to the [generic WIN-NMR \(p. 20\)](#) file format, however, the parameter files are of ASCII type and correspond to those generated by UXNMR and XWin-NMR. **WSolids1 uses this file format itself to store calculated spectra.**

In order to be recognized by WSolids as UNIX-type WINNMR file, the data files need to adhere to the following format:

- *eeppp.1R* or *eeppp.FID* in binary floating point format need to be present (Note that generic UXNMR files have these data stored as long integers; potentially, if coming from an SGI, the Endianness could also be different. If such a file is read, WSolids1 attempts to detect and convert them automatically; currently, WSolids1 does not read FID's)
- *eeppp.AQS* and *eeppp.FQS* need to be present in the same directory; they are ASCII parameter files of variable record length and start with **##** (JCAMP-DX format), the AQS file contains the parameters **SFO1, SW\_h, O1**, and FQS contains **OFFSET**

### Bruker WINNMR ASCII

WinNMR is able to export spectra in ASCII format; depending on the version of WinNMR, slight differences arise. The file starts with some parameters, one on each line, and is then followed by pure intensity data, each point on its own line. Here is the beginning of such a file:

```
Data file: D:\NMR\ASP3000\KOPOPH3\101001.TXT
Starting Point: 0
Ending Point: 4095
Point Count: 4096
Real Data
SF01: 81.018000 MHz
SF: 81.023633 MHz
Offset: 444.735199 ppm
Decim: 0
Dspfvs: 0
```

```
FW: 100000.000000 Hz
Sweep Width: 83333.333332 Hz
Hz/Pt: 20.345052
First Point: 36034.061368 Hz
Last Point: -47299.271964 Hz
First Point: 444.735199 PPM
Last Point: -583.771308 PPM
AQmod: 2
-5759
-1961
...
```

### Chemagnetics SpinSight

The Spinsight data format consists of several component files all contained within one directory.

In order to be recognized by WSolids as SpinSight file, the data files need to adhere to the following format:

- **data**: this is a binary file which contains the actual NMR data. The storage order is: all real values followed by all imaginary values, i.e., the data are unshuffled. No formatting, end of row or end of file characters are present in this file.
- **acq**: this is a text file describing the acquisition parameters used in acquiring the data file. These parameters can also be used for a prescription on how to acquire NMR data. The meaning of the acquisition parameters depends on the definitions used in the associated pulse program. WSolids1 is mainly interested in **SF** and **SW**.
- **proc**: this is a text file containing parameters which describe the current state of the data file and the previous operations that have been performed on the data since it was acquired. WSolids1 is mainly interested in **datatype**, **domain1**, **current\_size1**, **rmp1**, **rmv1**, **rmvunits1**.

### SOLIDS

This type of file format is produced by Solids, the FORTRAN predecessor of WSolids1, and was created to allow a slightly more general interface in terms of file formats. ASCII files created by WIN-NMR require only minor editing of the file header in order to conform to this format (the text and some lines need to be deleted).

In order to be recognized by WSolids1 as SOLIDS file, the **ASCII** data file need to adhere to the following format, where each parameter is on a separate row:

- number of points (SI)
- spectrometer frequency in MHz (SF)
- digital resolution in Hz per point  $((F1 - F2) / SI)$
- highest frequency, i.e. frequency of first point in Hz (F1)
- lowest frequency, i.e. frequency of last point in Hz (F2)
- intensity data as integers or floating point numbers, each in a separate row

### JCAMP-DX

The JCAMP-DX (Joint Committee on Atomic and Molecular Physical Data Exchange) format has been initiated by IUPAC to achieve better long-term archival and exchange of spectroscopic data. The main features [1] are:

- first non-binary approach ever

- vendor independent, JCAMP is not owned by anybody
- printable characters only (important for e-mail etc.)
- reasonable compression rates (long before LHARC etc. did show up)
- extendable and open definitions to allow further improvements

In my opinion, this was a good idea, in principle. However, in practice, the standard is too unclear in several aspects, thus writing an import filter for such data is a royal pain.

WSolids1 checks for the following parameters: **TITLE**, **JCAMP-DX** (with values of 4.24, 5.00, or 5.01), **DATA TYPE**, **NPOINTS**, **.OBSERVE FREQUENCY**, **FIRSTX**, **LASTX**, **XFACTOR**, **DATA CLASS**. Currently, only XY-DATA are supported.

#### References:

- (1) posting by Dr. Michael Grzonka in the newsgroup bionet.structural-nmr, Subject: The JCAMP standard of spectroscopic data transfer - a summary, on 29 January 1996.
- (2) McDonald, Wilks, *Appl. Spectrosc.* **1988**, *42*, 151
- (3) Davies, Lampen, *Appl. Spectrosc.* **1993**, *47*, 1093
- (4) Lampen, Lambert, Lancashire, McDonald, McIntyre, Rutledge, Fröhlich, Davies, *Pure Appl. Chem.* **1999**, *71*, 1549

#### Simpson

“SIMPSON: A General Simulation Program for Solid-State NMR Spectroscopy” was the title of the paper [1] that introduced SIMPSON. Its output is an ASCII text file, usually with extension **.SPE**. WSolids1 requires the parameters **SIMP**, **NP**, **SW** and, in newer versions, **REF**.

#### Reference:

- (1) M. Bak, J. T. Rasmussen, N. C. Nielsen, *J. Magn. Reson.* **2000**, *147*, 296

#### Varian

Reading of Varian files is planned but not implemented yet. Basically, I would need some example files.

### 2.1.3 Save Spectrum

The **Save Spectrum** item of the **File** (p. 18) pop-up menu saves a spectrum from the active **Spectrum Window** (p. 18). If the spectrum window contains only an experimental spectrum, the experimental spectrum is saved. If there is a calculated spectrum available, the calculated spectrum is always saved.

There are several output formats available: (1) a **WinNMR** (p. 20) file with UNIX-type ASCII parameter files; (2) in **TopSpin/XWinNMR** (p. 19) format; (3) in **Solids** (p. 21) format. ASCII and JCAMP are planned but not implemented yet.

When writing WinNMR files, the file name should adhere to the **eeeepp.\*** (p. 20) convention.

When writing Topspin files, please consider that the dialog was written initially for WinNMR. Therefore, if you want to create the file **d:\u\data\nmrguest\nmr\simulation\11\pdata\20\1r**, you should point the path to the **...simulation** subdirectory and enter the file name **011020** (file type Topspin). WSolids1 extracts from this file name the corresponding experiment and processing numbers.

<p><b>Note:</b> When displaying experimental spectra and spectra calculated by WSolids1 in WinNMR, use the “relative intensities” scaling mode of the dual/multiple display window.</p>
---

#### 2.1.4 Exit

The **Exit** item of the [File \(p. 18\)](#) pop-up menu quits WSolids1. All existing data will be lost, if not saved prior to selecting Exit.

## 2.2 Simulation Menu

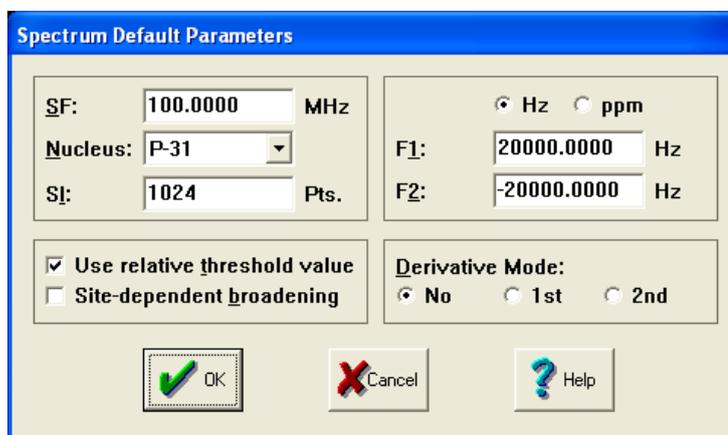
The Simulation pop-up menu consists of the following items:



Item	Purpose
<a href="#">Default parameters</a> (p. 25)	Invokes a dialog box to retrieve parameters for the calculated spectrum
<a href="#">New site</a> (p. 31)	Allocates and adds a new site to the calculational model
<a href="#">Edit sites</a> (p. 32)	Manage sites, modify parameters etc.
<a href="#">Calculate</a> (p. 33)	Performs a calculation using the currently selected simulation models and parameters
<a href="#">Active window only</a> (p. 33)	Perform calculation for currently active spectrum window only or for all spectrum windows
<a href="#">Cycle through</a> (p. 33)	Calls the next step in the Input–Calculate–Display cycle
<a href="#">Cycle options</a> (p. 33)	Customize the cycle steps

## 2.2.1 Spectrum Default Parameters

The **Default parameters** item of the [Simulation](#) (p. 24) popup menu invokes the Spectrum Default Parameters dialog box. The default parameters characterize the appearance of the calculated spectrum; they apply to all sites.



The default parameters define:

Parameter	Purpose
<a href="#">Nucleus</a> (p. 25)	Observed nucleus
<a href="#">SF</a> (p. 25)	Spectrometer frequency (Larmor frequency) in MHz
<a href="#">SI</a> (p. 26)	Size of calculated spectrum in points
<a href="#">ppm/Hz</a> (p. 26)	Toggles input for F1/F2 between Hz or ppm
<a href="#">F1</a> (p. 26)	High-frequency limit of calculated spectrum
<a href="#">F2</a> (p. 26)	Low-frequency limit of calculated spectrum
<a href="#">Use relative threshold value</a> (p. 27)	Toggle between use of a threshold value in the convolution or doing the full convolution
<a href="#">Site-dependent broadening</a> (p. 27)	Individual or global line broadening
<a href="#">Derivative Mode</a> (p. 30)	Absorption or derivative display

### Observed Nucleus

The kind of observed nucleus is selected in the [Spectrum Default Parameter](#) (p. 25) box.

In many cases, the actual selection here is not important. Exceptions are, for example:

- Observation of a quadrupolar nucleus (here, the nuclear spin quantum number is important)
- If a quadrupolar nucleus is coupled to the observed nucleus, the ratio of magnetogyric ratios of both nuclei is used to calculate the Larmor frequency of the quadrupolar nucleus

### Spectrometer Frequency

The parameter SF defines the spectrometer or Larmor frequency in MHz and is set in the [Spectrum Default Parameter](#) (p. 25) box.

Actually, this value corresponds to the frequency of the chemical shift reference compound, and is thus not SF or SFO1 as used in Bruker parameter files.

If an experimental spectrum is available, this parameter is set by default and should not be changed.

This value is used in the conversion of ppm into Hz and vice versa. For the direct observation of quadrupolar nuclei, its magnitude relative to the quadrupolar coupling constant is important for the observed line shape.

Valid values for the Larmor frequency are any positive, non-zero floating point numbers.

**Note:**

All calculations assume that the Zeeman interaction is the dominant interaction (high-field approximation). For example, calculation of a Pake doublet with a dipolar coupling constant of 1 kHz and a spectrometer frequency of 100 Hz will not give the proper result! The high-field approximation is slightly relaxed in cases involving quadrupolar nuclei, but one should always be aware of the approximations behind any type of calculation!

### Spectrum Size

The spectrum size **SI** defines the size of the calculated spectrum in points and is set in the [Spectrum Default Parameter \(p. 25\)](#) box. Traditionally, its values are multiples of two, but it is not limited to these numbers. If an experimental spectrum is available, this parameter is set by default.

Together with the high- and low-frequency limits, [F1 \(p. 26\)](#) and [F2 \(p. 26\)](#), the spectrum size determines the spectral resolution. Often, it is sufficient to use the same spectral resolution as the experimental spectrum. However, in cases involving “stick” approaches, a higher digital resolution for the calculated spectrum is advisable.

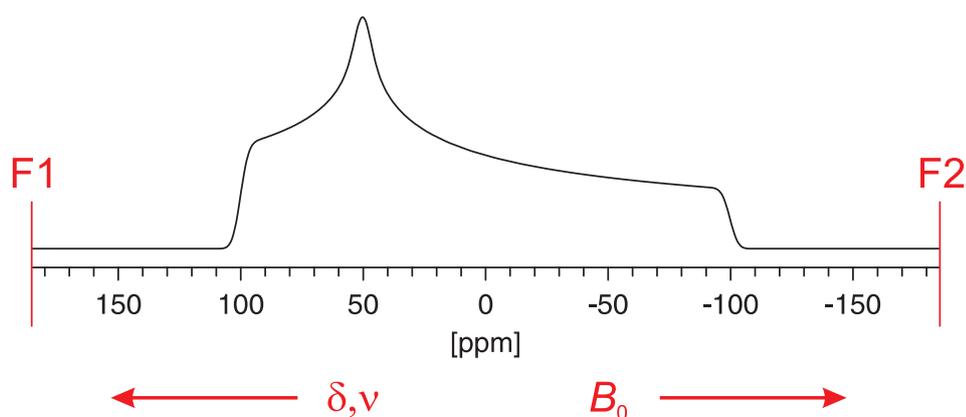
The spectrum size affects the time required for calculating a spectrum, i.e., the performance of the interpolation routine for the powder averaging or the convolution routine depends on the digital resolution.

Valid values for the spectrum size are positive integers greater than or equal to 16. Additionally, the letter **K** can be used to indicate Kilo-points, 1K = 1024 points.

### ppm / Hz

The two mutually exclusive radio buttons **ppm** and **Hz** in the [Spectrum Default Parameter \(p. 25\)](#) box allow to toggle the input between frequency (Hz) or chemical shift (ppm) units. In order to perform the conversion, the value presently selected for the [spectrometer frequency \(p. 25\)](#) is used.

### Spectrum Limits



The spectrum limits are specified by the high-frequency limit (in conventional NMR, the “left” limit), **F1**, and the low-frequency limit, **F2**, in the [Spectrum Default Parameter \(p. 25\)](#) box. Dependent on the state of the radio buttons [ppm/Hz \(p. 26\)](#), the input is taken in units of ppm or Hz. To perform the conversion between ppm and Hz, the current value of [SF \(p. 25\)](#) is taken. In combination with [SI \(p. 26\)](#), these parameters determine the digital resolution.

### Use Relative Threshold Value

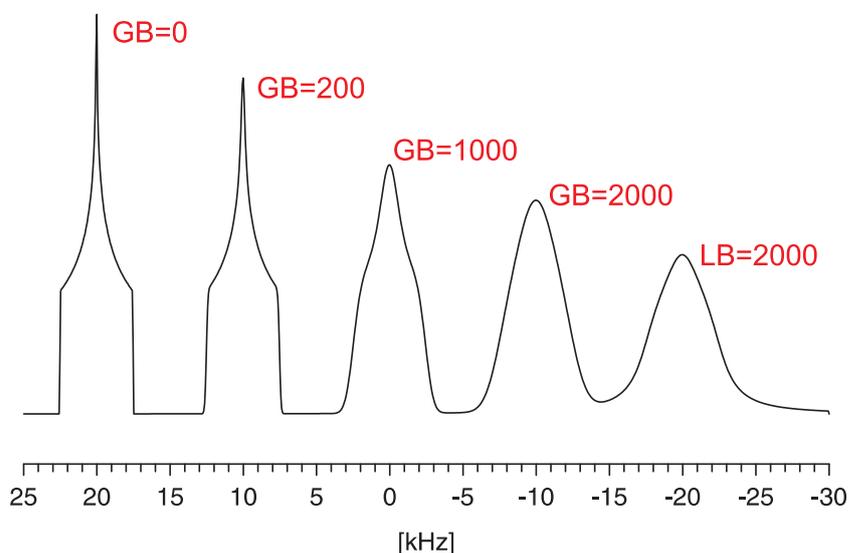
In the [Spectrum Default Parameter \(p. 25\)](#) box, the status of the checkbox for using relative threshold values determines the time required to do a convolution.

Checkbox status	Meaning
<input type="checkbox"/>	The mixed Gaussian-Lorentzian line shape used in the convolution process is used until the intensity of the wings reaches zero. This is the more lengthy process but may be required if weak peaks are to be displayed in the presence of very strong peaks.
<input checked="" type="checkbox"/>	The mixed Gaussian-Lorentzian line shape used in the convolution process is used until the intensity of the wings reaches 1/10000 of the greatest spectral intensity. This reduces calculation time but may produce funny looking line shapes for weak peaks.

### Site-Dependent Broadening

In the [Spectrum Default Parameter \(p. 25\)](#) box, the status of the checkbox for **site-dependent broadening** determines whether each site requires its own set of [convolution parameters \(p. 28\)](#). Because the Gaussian / Lorentzian peaks used for convolution are normalized, the relative areas of each site are approximately preserved.

Checkbox status	Meaning
<input type="checkbox"/>	Usually, the selection of no site-dependent broadening will do. In this case, only one set of convolution parameters will be necessary. The convolution routine is activated only once, after all site specific spectra have been calculated.
<input checked="" type="checkbox"/>	In this case, each site requires its own set of line broadening parameters. Also, the convolution routine is invoked each time after a site specific spectrum has been generated.



**Note:**

Although the convolution parameters belong to the spectrum window (spectra at different spectrometer frequencies will require different broadening), the actual parameters are accessible via the spin system.

## 2.2.2 Convolution Parameters



The convolution parameters determine the amount of “line broadening” added to the calculated spectrum.

The convolution parameters should not be mixed up with the LB/GB parameters used in apodization functions applied to experimental spectra. Here, they take into account the sum of all line broadening effects intrinsic to the sample and the spectrometer (and processing). Such effects can be inhomogeneity of the external magnetic field, homonuclear dipolar couplings, unresolved indirect couplings, interactions with quadrupolar nuclei, degree of crystallinity (chemical shift dispersion), insufficient decoupling power, temperature gradients, etc. etc., and finally the actual window function applied to the experimental data. In short, the convolution parameters represent all these effects in a phenomenological manner.

Convolution is done in the frequency domain, rather than in the time domain. Exponential multiplication in time domain requires for  $N$  points  $N$  multiplications; in contrast, the equivalent in the frequency domain — convolution with a Lorentzian peak — requires  $N \times (N - 1)$  multiplications, unless a threshold value is specified!

Although considered part of the spectrum parameters rather than of the spin system, access to convolution parameters is gained by editing the spin system. Convolution also depends on the setting of the [site-dependent convolution \(p. 27\)](#) check box in the [Spectrum Default Parameter \(p. 25\)](#) box.

Parameter	Purpose
<a href="#">GB/LB mixing (p. 29)</a>	The GB/LB mixing in percent determines the amount of Gaussian- Lorentzian character of the convolution function: 0: pure Gaussian 100: pure Lorentzian
<a href="#">GB (p. 29)</a>	Gaussian broadening in Hz
<a href="#">LB (p. 29)</a>	Lorentzian broadening in Hz

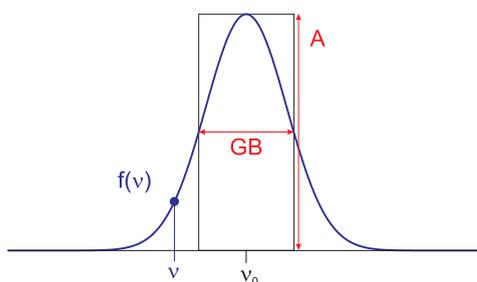
### Gaussian/Lorentzian Mixing

In the [Convolution Parameters \(p. 28\)](#) dialog box, the Gaussian/Lorentzian mixing determines the weighting of Gaussian and Lorentzian line shapes in the convolution subroutine. A value of 0 % corresponds to a pure Gaussian line shape, a value of 100 % yields a pure Lorentzian line shape. In the case of mixed line shapes, both Gaussian broadening, [GB \(p. 29\)](#), and Lorentzian broadening, [LB \(p. 29\)](#), must be specified, but can be different.

#### Note:

if calculations are performed in the frequency domain, Lorentzian line shapes require considerably longer computation times because their wings extend much farther than those of Gaussian peaks. For time domain convolution, both line shapes require the same time. This different behaviour arises from the fact that in the case of frequency domain convolution, the subroutine uses a threshold value, 0.00001 of the maximum intensity, to reduce computation time.

### Gaussian Convolution



In the [Convolution Parameters \(p. 28\)](#) dialog box, the value of **GB**, in Hz, specifies the full width at half maximum-height of a Gaussian peak. This line shape will be employed in the convolution of spectra.

The intensity at a given frequency is given by the following expression for an absorption-mode Gaussian:

$$f(v) = A \exp \left[ \frac{-4 \ln(2)(v - v_0)^2}{GB^2} \right]$$

where:

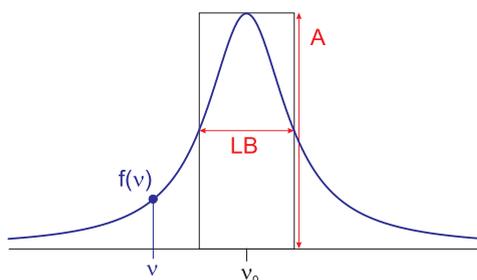
$A$  : peak maximum amplitude

$v_0$  : peak centre frequency

$GB$  : full width at half maximum-height

In order to preserve the relative areas of sites with different line broadening parameters, the convolution procedure takes into account that the area of a Gaussian peak can be approximated by  $\sqrt{\pi/4 \ln 2} \times A \times GB = (1.064467 \times A \times GB)$ .

### Lorentzian Convolution



In the [Convolution Parameters \(p. 28\)](#) dialog box, the value of **LB**, in Hz, specifies the full width at half maximum-height of a Lorentzian peak. This line shape will be employed in the convolution of spectra.

The intensity at a given frequency is given by the following expression for an absorption-mode Lorentzian:

$$f(\nu) = \frac{A}{\left[1 + \frac{4(\nu - \nu_0)^2}{LB^2}\right]}$$

where:

$A$  : peak maximum amplitude

$\nu_0$  : peak centre frequency

$LB$  : full width at half maximum-height

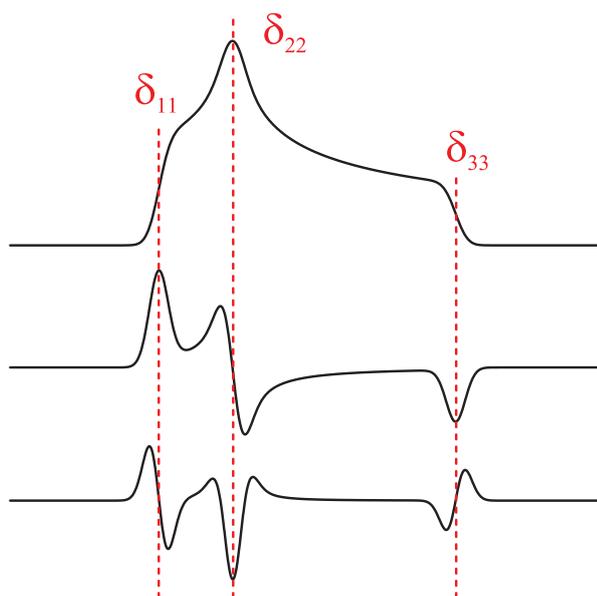
In order to preserve the relative areas of sites with different line broadening parameters, the convolution procedure takes into account that the area of a Lorentzian peak can be approximated by  $[(\pi/2) \times A \times LB] = 1.570796 \times A \times LB$ .

### 2.2.3 Derivative Mode

In the [Spectrum Default Parameter \(p. 25\)](#) box, the status of the mutually exclusive radio buttons **Derivative: No/1st/2nd** determine whether the calculated spectrum will be displayed in normal (absorption) mode or as the first or second derivative.

**Note:**

The experimental spectrum remains unaffected by this setting. Use your favourite NMR processing program to manipulate the experimental spectrum. (Taking the derivative of a spectrum dramatically decreases the signal-to-noise ratio. Modern processing software has usually some sort of digital filtering, e.g. Savitzky-Golay, implemented for generating derivatives of spectra. For calculated spectra, one can get away with a much simpler procedure.)



There are certain advantages in fitting the line shape in one of the derivative modes. In this mode, the frequencies of the singularities can be determined more accurately. As indicated in the picture,

the points of inflection (e.g.  $\delta_{11}$  and  $\delta_{33}$ ) correspond to peaks in the first derivative, while the discontinuities (e.g.  $\delta_{22}$ ) reveal themselves as peaks in the second derivative. The width of the peaks in the first derivative line shape indicates the natural line width, a parameter which can be employed in the convolution of the calculated spectrum.

### References

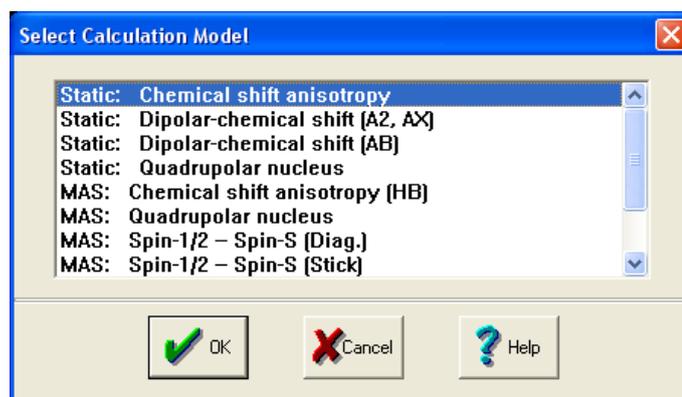
- T. G. Oas, C. J. Hartzell, T. J. McMahon, G. P. Drobny, F. W. Dahlquist, *J. Am. Chem. Soc.* **1987**, *109*, 5956.
- T. G. Oas, C. J. Hartzell, F. W. Dahlquist, G. P. Drobny, *J. Am. Chem. Soc.* **1987**, *109*, 5962.
- C. J. Hartzell, M. Whitfield, T. G. Oas, G. P. Drobny, *J. Am. Chem. Soc.* **1987**, *109*, 5966.

## 2.2.4 New Site

A site is an independent part of a spectrum with a line shape uniquely defined by parameters (e.g. chemical shifts, couplings etc.) specific to the calculational model selected for this site.

The feature **New Site** of the [Simulation](#) (p. 24) popup menu adds a new site to the calculation model. It calls the [Select Calculation Model](#) (p. 31) dialog box and requests the user to select a model. Afterwards, it initiates the input of the appropriate site specific parameters.

## 2.2.5 Select Calculation Model

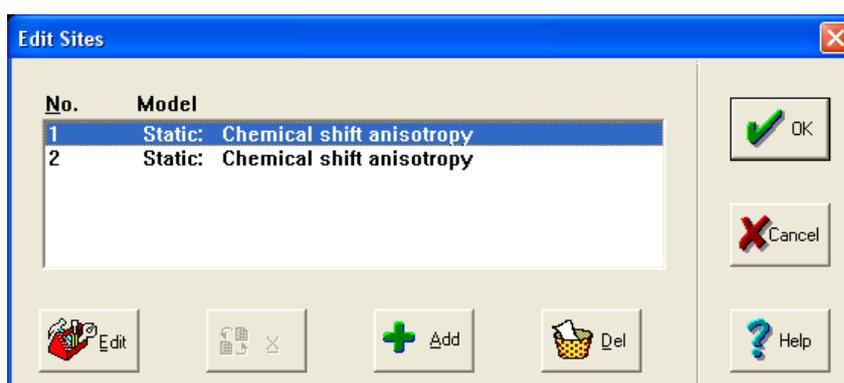


The **Select Calculation Model** dialog box, available from the [New Site](#) (p. 31) item of the [Simulation](#) (p. 24) popup menu, allows the user to select a calculational model from a list of available models. Each model is, in its performance, tailored to a specific situation. Currently, the following models are supported:

Model	Characteristics
<a href="#">Static: Chemical shift anisotropy</a> (p. 43)	Spectrum of a static powder sample showing chemical shift anisotropy (“powder pattern”)
<a href="#">Static: Dipolar-chemical shift (A2, AX)</a> (p. 45)	Chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling for a homonuclear pair of equivalent spin-1/2 nuclei or a heteronuclear spin pair in a static powder sample (A2 or AX approximation)
<a href="#">Static: Dipolar-Chemical Shift (AB)</a> (p. 48)	Chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling for a homonuclear pair of spin-1/2 nuclei, including “second-order” effects, in a static powder sample (AB)

Static: Quadrupolar Nucleus (p. 50)	Quadrupolar interaction up to second order for the observed nucleus, including chemical shift anisotropy, for a static powder sample. Optionally, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus)
MAS: Chemical shift anisotropy (HB) (p. 53)	Spectrum of a powder sample spinning at the magic angle, showing chemical shift anisotropy; uses Herzfeld-Berger tables
MAS: Quadrupolar nucleus (p. 56)	Spectrum of central transition of a quadrupolar nucleus in a powder sample spinning fast at the magic angle
MAS: Spin-1/2 – Spin-S (Diag.) (p. 58)	Considers spin-spin interactions with a quadrupolar nucleus under magic-angle spinning, using full matrix diagonalization
MAS: Spin-1/2 – Spin-S (Stick) (p. 61)	Considers spin-spin interactions with quadrupolar nuclei under magic-angle spinning, using first-order perturbation theory and “stick” approach
MAS: Spin-1/2 – Spin-S (Shape) (p. 64)	Considers spin-spin interactions with a quadrupolar nucleus under magic-angle spinning, using first-order perturbation theory to calculate line shape
VAS: Dipolar-chemical shift (A2, AX) (p. 66)	Considers chemical shift and spin-spin interactions for a homo- or heteronuclear pair of nuclei, i.e., A2 or AX approximation, under variable-angle spinning
VAS: Dipolar-chemical shift (AB) (p. 68)	Considers chemical shift and spin-spin interactions for a homonuclear pair of nuclei, i.e., AB approximation, under variable-angle spinning

### 2.2.6 Edit Sites



The item **Edit Sites** of the [Simulation](#) (p. 24) popup menu allows to manage the sites constituting the calculational model. A dialog box provides a list of currently available sites.

Selection	Action
<b>Edit</b>	Highlight the desired site in the list box using mouse or keyboard and select the <b>Edit</b> button to obtain access to the parameters for this site. You can also <b>double-click</b> on the desired site to trigger this action.

---

<b>Add</b>	Select the <b>Add</b> button to add a new site to the calculational model.
<b>Delete</b>	Select the <b>Delete</b> button to delete the site highlighted in the list box. A dialog box requesting confirmation pops up before the site gets actually deleted. <b>There is no Undo function!</b>

---

**Note:**

Access to editing the parameters of a spin system might be easier by using the [cycle \(p. 33\)](#) feature, i.e., hitting the Enter key the appropriate number of times.

### 2.2.7 Calculate

The item **Calculate** of the [Simulation \(p. 24\)](#) popup menu starts calculation of a theoretical spectrum, using the selected calculation models and site-specific parameters. If not all parameters were initialized, it calls the appropriate parameter dialog boxes. After a successful calculation, the calculated spectrum will be displayed. If there is no spectrum window currently active, this procedure also opens a spectrum window and asks for default spectrum parameters. The detailed calculation mode depends on the state of the [Active only \(p. 33\)](#) menu item.

### 2.2.8 Active Only

The item **Active only** of the [Simulation \(p. 24\)](#) popup menu determines if a calculation is performed for the currently active window only or for all available spectrum windows.

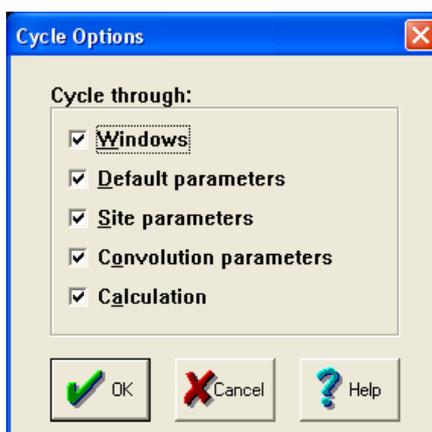
### 2.2.9 Cycle

The item **Cycle** of the [Simulation \(p. 24\)](#) popup menu automatically initiates the next step in the generation of a calculated spectrum to refine the agreement between experimental and theoretical spectra. The detailed course of the cycle feature depends on the selections made under [Cycle options \(p. 33\)](#).

**Note:**

The **Enter** key is the accelerator key for this action.

### 2.2.10 Cycle Options

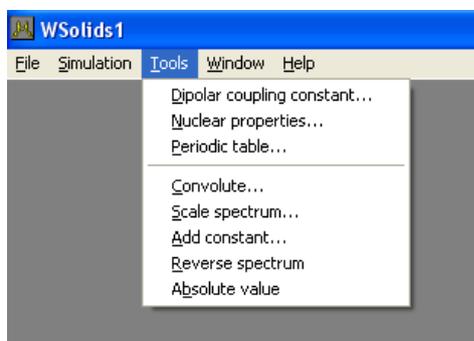


The item **Cycle options** of the [Simulation \(p. 24\)](#) popup menu allows to customize the detailed course of the [Cycle \(p. 33\)](#) feature. This cycle consists of:

Selection	Action
<b>Windows</b>	After all other cycle steps were performed for a window, switch to the next spectrum window
<b>Default parameters</b>	Edit the spectrum default parameters for the currently active spectrum window
<b>Site parameters</b>	Edit the site-specific parameters for each available site
<b>Convolution parameters</b>	Edit the convolution parameters
<b>Calculation</b>	Perform calculation of a theoretical spectrum and display the result

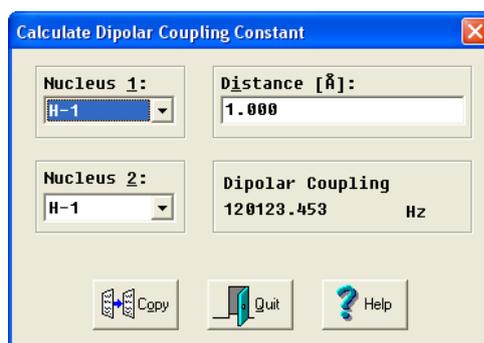
## 2.3 Tools Menu

The Tools pop-up menu consists of the following items:



Item	Purpose
<a href="#">Dipolar coupling constant (p. 34)</a>	Invokes a dialog box to calculate dipolar coupling constants
<a href="#">Nuclear properties (p. 35)</a>	Displays a table of nuclear properties
<a href="#">Periodic table (p. 37)</a>	Displays a periodic system of elements relevant to NMR
<a href="#">Convolute (p. 37)</a>	Performs an additional convolution of experimental or theoretical spectra
<a href="#">Scale spectrum (p. 37)</a>	Scale a spectrum by a given factor
<a href="#">Add constant (p. 37)</a>	Adds the specified value to the intensity of the spectrum
<a href="#">Reverse spectrum (p. 38)</a>	Reverses the frequency direction of the spectrum
<a href="#">Absolute value (p. 38)</a>	Generates the absolute-value representation of the spectrum

### 2.3.1 Dipolar Coupling Constant



Selection of the **Tools|Dipolar coupling constant** menu item invokes this dialog box.

**To calculate the dipolar coupling constant, follow these steps:**

- Select from the two list boxes **Nucleus 1** and **Nucleus 2** the two nuclei constituting the spin pair (use mouse, arrow keys, or first letter of nucleus).
- Enter the internuclear separation in Angstrom.
- Hit **Enter** to display the calculated dipolar coupling constant

- If required, copy the result to the clipboard by pushing the **Copy** button (or ALT-O). This can be used to **paste** (typically CTRL-V or SHIFT-INSERT) the result into appropriate edit controls
- Exit the dialog by selecting **Quit** (or ESC)

For information on the source of the nuclear data, refer to [Table of Nuclear Properties](#) (p. 35).

### 2.3.2 Table of Nuclear Properties

No.	Nucleus	Spin	Gamma [1E07]	N.A. [%]	Q [1E-28]	Frequency
1	H-1	1/2	26.75221	99.9880	0.00000	950.1301
2	H-2	1	4.10663	0.0115	0.00286	145.8508
3	H-3	1/2	28.53498	0.0000	0.00000	1013.4466
4	He-3	1/2	-20.38016	0.0001	0.00000	-723.8206
5	Li-6	1	3.93717	7.5900	-0.00081	139.8323
6	Li-7	3/2	10.39770	92.4100	-0.04010	369.2841
7	Be-9	3/2	-3.75967	100.0000	0.05288	-133.5281
8	B-10	3	2.87468	19.9000	0.08459	102.0969
9	B-11	3/2	8.58470	80.1000	0.04059	304.8939
10	C-13	1/2	6.72828	1.0700	0.00000	238.9613
11	N-14	1	1.93378	99.6320	0.02044	68.6800
12	N-15	1/2	-2.71262	0.3680	0.00000	-96.3412
13	O-17	5/2	-3.62808	0.0380	-0.02558	-128.8547
14	F-19	1/2	25.18148	100.0000	0.00000	894.3440
15	Ne-21	3/2	-2.11308	0.2700	0.10155	-75.0480

Sort for: **No.**      Magnetic Field [T] **22.3153**

Buttons: Quit, Help

This dialog box, accessible from the **Tools|Nuclear properties** menu item, lists nuclear properties for many of the known NMR active nuclei:

#### The Properties:

- nuclear **spin** quantum number
- magnetogyric ratio, **Gamma**, in units of  $10^7 \text{ rad s}^{-1} \text{ T}^{-1}$
- natural abundance, **N.A.**, in %
- nuclear electric quadrupole moment, **Q**, in units of  $10^{-28} \text{ m}^2$
- frequency, in MHz, of the reference compound for that nucleus at the selected magnetic field strength

#### Sorting:

By default, the nuclei are listed according to their position in the periodic table of elements (i.e. for increasing mass number). Using the **Sort for:** list box, the display can be sorted alphabetically for the labels of the nuclei, the spin, the magnetogyric ratio (Gamma), the natural abundance, or the nuclear electric quadrupole moment.

#### Magnetic Field:

The strength of the magnetic field, affects the frequency of the reference compound. The following values produce the given values of the  $^1\text{H}$  NMR frequency of TMS:

$B_0 / T$	$^1\text{H}$ frequency of TMS / MHz
2.348661	100.00
4.700374	200.13
5.874703	250.13
7.049034	300.13
9.397695	400.13
11.746354	500.13
14.0950140	600.13
16.443674	700.13
18.792334	800.13
21.140994071	900.13
22.3153239	950.13

**Copying Data:**

Note that it is possible to high-light parts of the table and to copy the highlighted parts to the clipboard using standard Windows editing techniques (CTRL-INSERT or CTRL-C to copy the selected part).

**Modifications:**

Most nuclear data have originated from Mason's extremely useful book on *Multinuclear NMR* [1]. The current version of R has been updated according to data from the *IUPAC Recommendations 2001* [6]. The following data differ from those in reference [1], all magnetogyric ratios are according to [6]:

- the nuclear quadrupole moment values are from the "Year 2001 Q Values" collected by Pekka Pyykkö [3];
- the magnetogyric ratios of Sn-119 and Sn-117 could be 3 % less than the accepted value [2], i.e.,  $9.997559 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$  and  $9.552955 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$  instead of  $10.021 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$  and  $9.589 \times 10^7 \text{ rad s}^{-1} \text{ T}^{-1}$ .
- Nd-145 apparently has a spin of 7/2 instead of 5/2 [4,5]. Similarly, U-235 has a spin of 7/2 instead of 5/2 [4,5]. U-233 has been added to the tables [4,5].

**References:**

- (1) Joan Mason, *Multinuclear NMR*, Plenum Press, New York, 1987.
- (2) A. Laaksonen and R. Wasylishen, *J. Am. Chem. Soc.* **1995**, *117*, 392–400.
- (3) P. Pyykkö, *Mol. Phys.* **2001**, *99*, 1617–1629
- (4) *Quantities, Units and Symbols in Physical Chemistry (IUPAC)*
- (5) *CRC Handbook of Chemistry and Physics*
- (6) R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Solid State Nucl. Magn. Reson.* **2002**, *22*, 458–483.



### 2.3.7 Reverse Spectrum

This option, available from the **Tools|Reverse spectrum** menu, enables one to reverse the frequency direction of the spectrum.

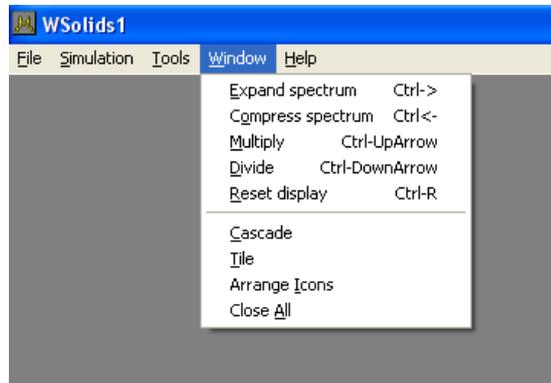
Physically, for a spectrum consisting of  $n$  points, this exchanges the intensity of the first and  $n$ -th point, the second and  $(n-1)$ -th point, and so on. Some versions of WinNMR do not provide such a functionality to swap the high- and low-frequency halves of the spectrum, although some Bruker spectrometers produce(d) spectra for which this is (was) necessary.

### 2.3.8 Absolute Value

This option, available from the **Tools|Absolute value** menu, enables one to generate the absolute value representation of the spectrum.

## 2.4 Window Menu

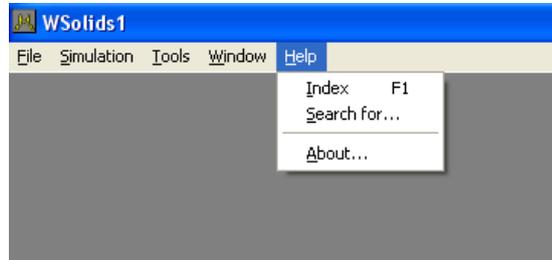
The Window menu allows management of spectrum windows and select display regions. It consists of the following items:



Item	Action
<b>Expand spectrum</b>	Horizontally expand spectra (frequency scale) in the currently active spectrum window
<b>Compress spectrum</b>	Horizontally contract spectra (frequency scale) in the currently active spectrum window
<b>Multiply</b>	Scale up the intensities of spectra in the currently active spectrum window
<b>Divide</b>	Scale down the intensities of spectra in the currently active spectrum window
<b>Reset display</b>	Resets the display limits such that the spectra are fully visible
<b>Cascade</b>	Cascade all open spectrum windows
<b>Tile</b>	Arrange all open spectrum windows so that each has the same area
<b>Arrange Icons</b>	Arrange the icons of minimized spectrum windows
<b>Close All</b>	Close all spectrum windows

## 2.5 Help Menu

The Help menu allows access to a variety of information. It consists of the following items:



---

Item	Action
<b>Index</b>	Open the WSolids1 help file on its table of contents page
<b>Search for</b>	Call the WSolids1 help file and search for a specific keyword in a list of predefined keywords. Note that the help file also provides a full-text search feature, activated with the <b>Search++</b> button
<b>About</b>	Displays information about the current version and build number of WSolids1.

---

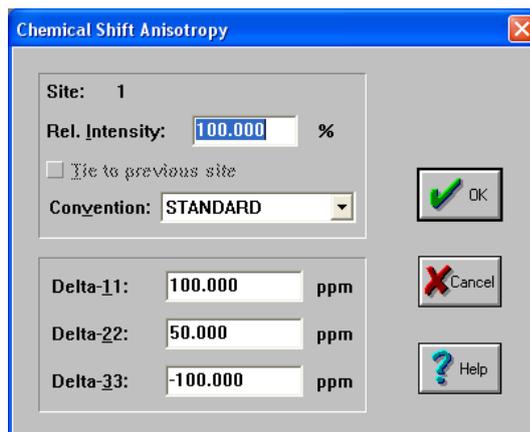
## 2.6 Known Problems

Usually, I will try to keep the content of this page as small as possible ;-)

- There is a problem in the [MAS: Spin-1/2 – Spin-S \(Diag.\) \(p. 58\)](#) model when the observed nucleus has a negative magnetogyric ratio. In these cases it might appear that the quadrupolar coupling constant has the opposite sign. There is no quick fix right now; contact me if you need more information.

## 3 Spin Systems

### 3.1 Static: Chemical Shift Anisotropy

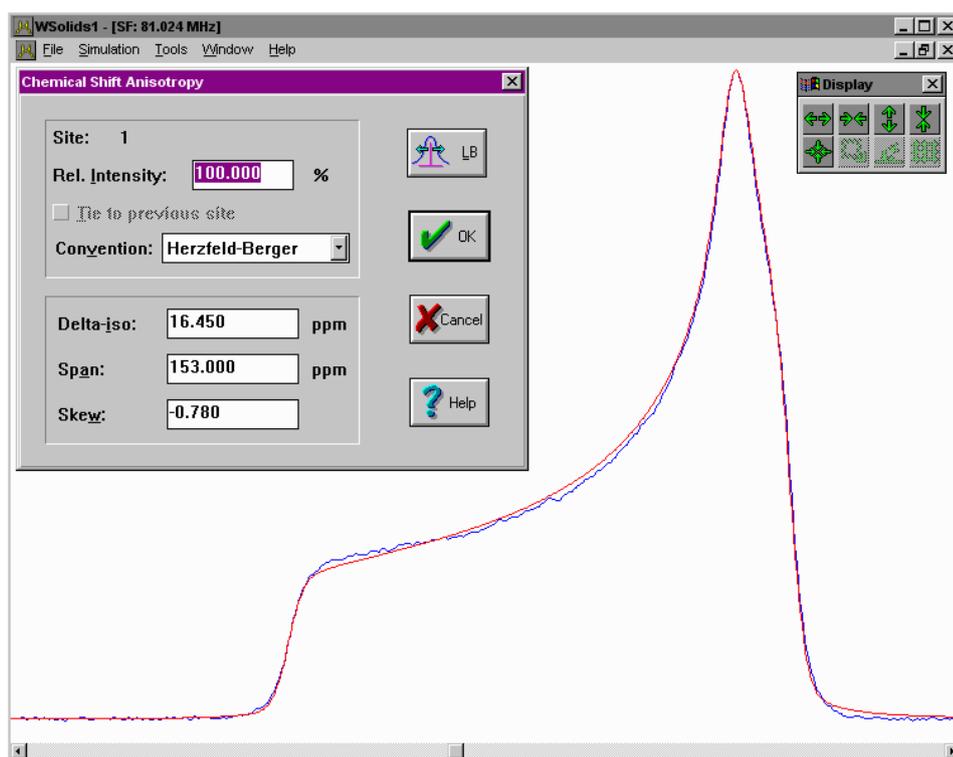


This model calculates the spectrum of a static powder sample showing only chemical shift anisotropy (“powder pattern”).

Parameter	Purpose
<a href="#">Rel. Intensity (p. 70)</a>	Relative intensity of this site in percent
<a href="#">Tie to previous site (p. 70)</a>	Ties parameters to those of the previous site
<a href="#">Convention (p. 70)</a>	Convention used for chemical shift tensor components
<a href="#">Delta-11, Delta-22, Delta-33 (p. 70)</a>	Principal components of chemical shift tensor (standard convention) in ppm
<a href="#">Delta-iso, Span, Skew (p. 70)</a>	Principal components of chemical shift tensor (Herzfeld-Berger convention)
<a href="#">Delta-iso, Anisotropy, Asymmetry (p. 70)</a>	Principal components of chemical shift tensor (Haeberlen convention)
<a href="#">LB (p. 28)</a>	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box

#### Background

Depending on the local symmetry at the nuclear site, the magnitude of the chemical shift will vary as a function of the orientation of the molecule with respect to the external magnetic field. This orientation dependence of the chemical shift is referred to as chemical shift anisotropy (CSA). Mathematically, the chemical shift anisotropy is described by a second-rank tensor (a 3 by 3 matrix), which in the case of the symmetric part of the chemical shift (CS) tensor consists of six independent components. Generally, one is able to express the chemical shift tensor in a coordinate frame where all off-diagonal elements vanish. In this principal axis system, the chemical shift tensor is fully described by the three diagonal elements, the principal components, and the three eigenvectors or Euler angles describing



**Figure 3.1:** Experimental and calculated  $^{31}\text{P}$  NMR spectra of a static powder sample of a molybdenum phosphine complex.

the orientation of the principal axes with respect to an arbitrary frame.

Due to the chemical shift anisotropy, the spectrum of a static powder sample, where statistically all orientations of the molecule with respect to the magnetic field are present, will consist of a broad line shape with three distinct features, corresponding to the principal components. However, note that for a powder sample there is no information about the orientation of the principal components in the molecular frame of reference.

### Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

K. Eichele, R. E. Wasylshen, *J. Magn. Reson. A* **106** (1994) 46–56

This model employs the POWDER space tiling and interpolation procedure.

Figure 3.1 shows an example of the successful simulation of a spectrum arising from the chemical shift anisotropy of a powder sample. It is the  $^{31}\text{P}$  NMR spectrum of a molybdenum phosphine complex and the results have been published in:

K. Eichele, R.E. Wasylshen, K. Maitra, J.H. Nelson, J.F. Britten:  
Single-Crystal  $^{31}\text{P}$  NMR and X-ray Diffraction Study of a Molybdenum Phosphine Complex: (5-Methyldibenzophosphole)pentacarbonylmolybdenum(0).  
*Inorg. Chem.* 1997, 36, 3539-3544.

## 3.2 Static: Dipolar Chemical Shift (A2, AX)

Calculates the spectrum of a static powder sample containing an isolated spin pair considering chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling. The spin pair can be a homonuclear pair of magnetically equivalent spin-1/2 nuclei or a heteronuclear pair (A2 or AX approximation). It is assumed that the dipolar interaction and the anisotropy are both collinear and axially symmetric.

Parameter	Purpose
Rel. Intensity (p. 70)	Relative intensity of this site in percent
Tie to previous site (p. 70)	Ties parameters to those of the previous site
Convention (p. 70)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 70)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 70)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 70)	Principal components of chemical shift tensor (Haebleren convention)
Coupled to (p. 73)	Specifies the nucleus the observed nucleus is coupled to. If this is the same isotope as the observed nucleus, the checkbox <b>homonuclear</b> becomes checked
N.A. (p. 73)	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
D (p. 73)	Direct dipole-dipole coupling constant, in Hz
J (p. 73)	Indirect spin-spin coupling constant, in Hz
Delta-J (p. 74)	Anisotropy of the indirect spin-spin coupling, in Hz
Alpha (p. 74)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
Beta (p. 74)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
LB (p. 28)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box

## Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation.

For historical reasons, this model works slightly different from the other models. Via the parameters relative intensity and natural abundance, one can calculate coupled and uncoupled spectra directly, without defining a separate spin system for each. This is ok for spin systems where the observed nucleus is coupled to an NMR active isotope and an NMR passive isotope. However, to deal with situations where the observed nucleus is coupled to an NMR passive isotope and several different NMR active isotopes, the generation of several spin systems is required.

**Example: P-31 coupled to cadmium (Cd-111: 12.75%, Cd-113: 12.26%, passive: 74.99%).**

- One could use three different sites, with the relative intensity reflecting the natural abundancies of each isotope (and tying the parameters of the sites together), while the natural abundance parameter is set to 100% (except for the passive site, where this parameter should be zero).
- Or, one could use two different sites. The first site should correspond to coupling with one of the active cadmium isotopes, say Cd-111 (rel. intensity: 12.75%, nat. abund.: 100%). The second site reflects both coupling to Cd-113 as well as the passive cadmium, thus rel. intensity = 87.25%, nat. abund. = 14.05% - because 14.05% of 87.25% corresponds to 12.26% in total)

## Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

K. Eichele, R. E. Wasylshen, *J. Magn. Reson. A* **106** (1994) 46-56

Furthermore, this article describes the technique of analyzing spectra using the dipolar-splitting-ratio method and outlines the background behind the program DSR.

This model employs the POWDER space tiling and interpolation procedure.

Figure 3.2 shows an example of the succesful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear dipolar coupling in a powder sample. It is the <sup>31</sup>P NMR spectrum of tetraethyl diphosphine disulfide, shown as absorption and first derivative spectrum, and the results have been published in:

K. Eichele, G. Wu, R. E. Wasylshen, J. F. Britten:

Phosphorus-31 NMR Studies of Solid Tetraethyldiphosphine Disulfide. A Reinvestigation of the <sup>31</sup>P,<sup>31</sup>P Spin-Spin Coupling Tensor.

*J. Phys. Chem.* 1995, 99, 1030-1037.

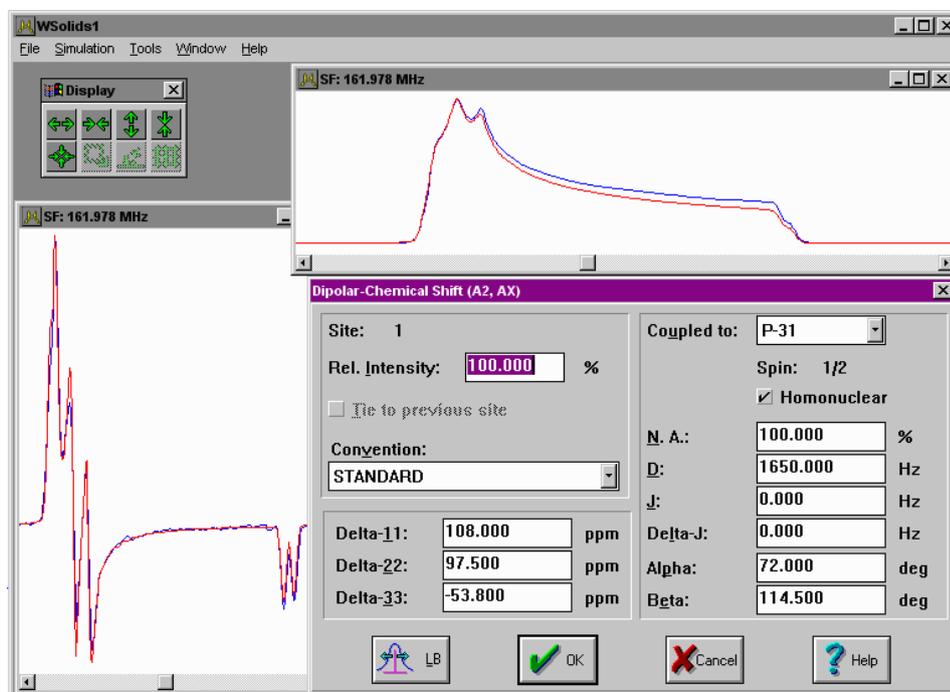


Figure 3.2: Experimental and calculated  $^{31}\text{P}$  NMR spectra of a static powder sample of tetraethyl diphosphine disulfide.

### 3.3 Static: Dipolar Chemical Shift (AB)

**Homonuclear Two-Spin System (AB)**

Site: 3  
 Rel. Intensity: 100.000 %  
 Tie to previous site  
 Convention: STANDARD

D: 730.000 Hz  
 J: 0.000 Hz  
 Delta-J: 0.000 Hz  
 Alpha: 0.000 deg  
 Beta: 0.000 deg

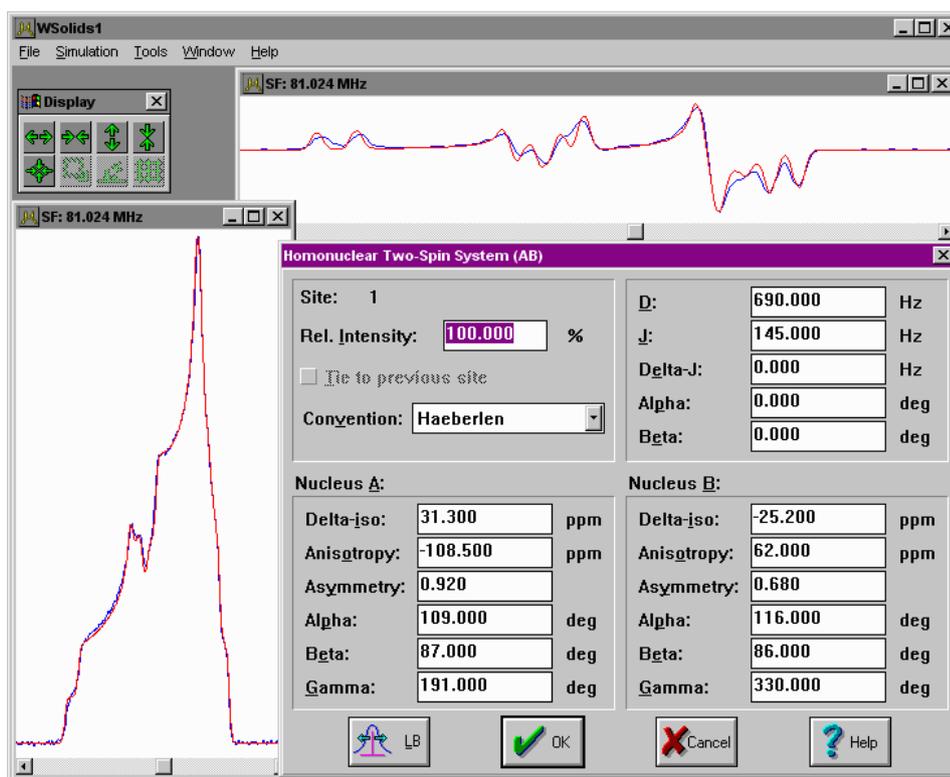
**Nucleus A:**  
 Delta-11: 269.000 ppm  
 Delta-22: 114.000 ppm  
 Delta-33: -39.000 ppm  
 Alpha: 0.000 deg  
 Beta: 90.000 deg  
 Gamma: -25.000 deg

**Nucleus B:**  
 Delta-11: 269.000 ppm  
 Delta-22: 114.000 ppm  
 Delta-33: -39.000 ppm  
 Alpha: 0.000 deg  
 Beta: 90.000 deg  
 Gamma: -25.000 deg

OK Cancel Help

Calculates the spectrum of a static powder sample containing an isolated spin pair of homonuclear spin-1/2 nuclei, considering chemical shift anisotropy, direct dipole-dipole coupling and indirect spin-spin coupling, including second order effects. It is assumed that the dipolar and indirect coupling tensors are colinear and axially symmetric.

Parameter	Purpose
Rel. Intensity (p. 70)	Relative intensity of this site in percent
Tie to previous site (p. 70)	Ties parameters to those of the previous site
Convention (p. 70)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 70)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 70)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 70)	Principal components of chemical shift tensor (Haeberlen convention)
Alpha, Beta, Gamma (p. 75)	Euler angles, in degrees, for going from the crystal frame to the principal axis system of the chemical shift tensors
D (p. 73)	Direct dipole-dipole coupling constant, in Hz
J (p. 73)	Indirect spin-spin coupling constant, in Hz
Delta-J (p. 74)	Anisotropy of the indirect spin-spin coupling, in Hz
Alpha (p. 74)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
Beta (p. 74)	Polar angle, in degrees, of the internuclear vector in the principal axis system of the chemical shift tensor
LB (p. 28)	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box



**Figure 3.3:** Experimental and calculated  $^{31}\text{P}$  NMR spectra of a static powder sample of tetraethyl diphosphine disulfide.

## Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. In contrast to the  $A_2$  and AX first-order spin systems, the line shape of a general homonuclear AB spin system may also depend on the relative orientations of the two chemical shift tensors.

## Implementation Details

For an introduction, see for example the following reference and the literature quoted there-in:

K. Eichele, R. E. Wasylishen, *J. Magn. Reson. A* **106** (1994) 46-56

This model employs the POWDER space tiling and interpolation procedure.

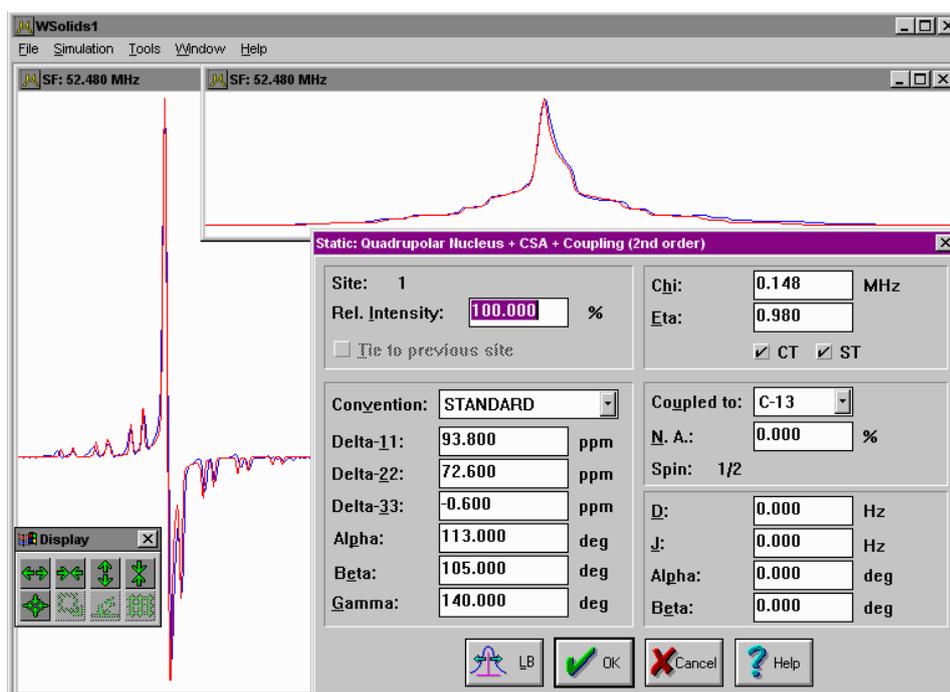
Figure 3.3 shows an example of the successful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear dipolar coupling in a powder sample. It is the  $^{31}\text{P}$  NMR spectrum of pentacarbonyl molybdenum [bis(diphenylphosphino) methane], shown as absorption and first derivative spectrum, and the results have been published in:

K. Eichele, G. Ossenkamp, R. E. Wasylishen, T. S. Cameron, J. F. Britten:  
Phosphorus-31 Solid-State NMR Studies of Homonuclear Spin Pairs in Molybdenum Phosphine Complexes: Single-Crystal, Dipolar-Chemical Shift, Rotational-Resonance and 2D Spin-Echo NMR Experiments  
*Inorg. Chem.* 1999, 38, 639-651.

### 3.4 Static: Quadrupolar Nucleus

Calculates the static powder spectrum of a quadrupolar nucleus, considering the quadrupolar interaction up to second order. Additionally, chemical shift anisotropy, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Parameter	Purpose
Rel. Intensity (p. 70)	Relative intensity of this site in percent
Tie to previous site (p. 70)	Ties parameters to those of the previous site
Convention (p. 70)	Convention used for chemical shift tensor components
Delta-11, Delta-22, Delta-33 (p. 70)	Principal components of chemical shift tensor (standard convention) in ppm
Delta-iso, Span, Skew (p. 70)	Principal components of chemical shift tensor (Herzfeld-Berger convention)
Delta-iso, Anisotropy, Asymmetry (p. 70)	Principal components of chemical shift tensor (Haberlen convention)
Alpha, Beta, Gamma (p. 75)	Euler angles, in degrees, for going from the electric field gradient tensor frame to the principal axis system of the chemical shift tensor
Chi (p. 79)	Quadrupolar coupling constant, in MHz
Eta (p. 79)	Asymmetry parameter of the electric field gradient tensor, $0 \leq \eta \leq 1$
CT,ST (p. 80)	Select central transition (CT) or satellite transitions (ST)
Coupled to (p. 73)	Specifies the nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
N.A (p. 73)	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
D (p. 73)	Direct dipole-dipole coupling constant, in Hz
J (p. 73)	Indirect spin-spin coupling constant, in Hz
Delta-J (p. 74)	Anisotropy of the indirect spin-spin coupling, in Hz
Alpha (p. 74)	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor



**Figure 3.4:** Experimental and calculated  $^{133}\text{Cs}$  NMR spectra of a static powder sample of cesium cadmium thiocyanate.

[Beta \(p. 74\)](#)

Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor

[LB \(p. 28\)](#)

Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the [Spectrum Default Parameters \(p. 25\)](#) box

## Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a quadrupolar nucleus will also depend on the nuclear quadrupolar interaction and the relative orientation of both interactions. The quadrupolar interaction is considered up to second order for the observed nucleus. Optionally, dipolar and indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

### 3.4.1 Implementation Details

Specifically, we use the following conventions:

- the NQR notation is used for labelling the axes of the EFG tensor:  $|VZZ| \geq |VYY| \geq |VXX|$
- the orientation of the field is given by the polar angle beta (wrt. VZZ) and the azimuth alpha, the angle between the projection of B into the VXX-VYY plane and VXX (cf. Abragam)
- direction cosines of the shielding tensor with respect to the EFG frame are obtained via the Euler angles following Arfken's convention, with the initial alignment 11-XX, 22-YY, 33-ZZ

Figure 3.4 shows an example for the successful simulation of a spectrum of a quadrupolar nucleus that shows the combined effect of chemical shift anisotropy and quadrupolar interaction in a powder sample. It is the  $^{133}\text{Cs}$  NMR spectrum of cesium cadmium thiocyanate,  $\text{CsCd}(\text{SCN})_3$ , and the results

have been published in:

S. Kroeker, K. Eichele, R.E. Wasylshen, J.F. Britten:

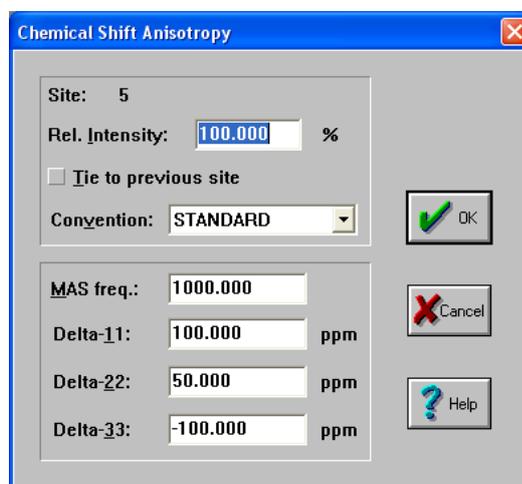
Cesium-133 NMR Study of CsCd(SCN)<sub>3</sub>: Relative Orientation of the Chemical Shift and Electric Field Gradient Tensors.

J. Phys. Chem. B 1997, 101, 3727-3733.

### 3.4.2 References

- (1) The first-order expression is taken from Amoureux's treatment, which follows Abragam and Taulelle:  
Amoureux, Fernandez, Granger, In *Multinuclear Magnetic Resonance in Liquids and Solids - Chemical Applications*; Granger, Harris, eds.; Kluwer Academic Publishers, 1990; Ch. 22, p 409
- (2) The second-order expression is taken from:  
G. H. Stauss, *J. Chem. Phys.* **1964**, *40*, 1988.
- (3) Related papers:  
K. Narita, J.-I. Umeda, H. Kusumoto, *J. Chem. Phys.* **1966**, *44*, 2719.  
J. F. Baugher, P. C. Taylor, T. Oja, P. J. Bray, *J. Chem. Phys.* **1969**, *50*, 4914.

### 3.5 MAS: Chemical Shift Anisotropy (HB)



This model calculates the spectrum of a powder sample spinning at the magic angle showing only chemical shift anisotropy. Spinning sideband intensities are obtained from precomputed Herzfeld-Berger Tables.

Parameter	Purpose
<a href="#">Rel. Intensity (p. 70)</a>	Relative intensity of this site in percent
<a href="#">Tie to previous site (p. 70)</a>	Ties parameters to those of the previous site
<a href="#">MAS freq. (p. 80)</a>	Spinning frequency in Hz
<a href="#">Convention (p. 70)</a>	Convention used for chemical shift tensor components
<a href="#">Delta-11, Delta-22, Delta-33 (p. 70)</a>	Principal components of chemical shift tensor (standard convention) in ppm
<a href="#">Delta-iso, Span, Skew (p. 70)</a>	Principal components of chemical shift tensor (Herzfeld-Berger convention)
<a href="#">Delta-iso, Anisotropy, Asymmetry (p. 70)</a>	Principal components of chemical shift tensor (Haerberlen convention)
<a href="#">LB (p. 28)</a>	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box

#### Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin in a powder sample under magic angle spinning will depend on the spinning frequency, if the spinning frequency is lower than the width of the chemical shift powder pattern. In this case, the isotropic peak (center peak) is flanked by spinning sidebands spaced at integer multiples of the spinning rate. The intensities of the spinning sidebands are intimately related to the principal components of the chemical shift tensor. For efficiency reasons, WSolids uses look-up tables of precomputed spinning sideband intensities.

Figure 3.5 shows an example for the successful simulation of a spectrum arising from chemical shift anisotropy in a powder sample under magic-angle spinning. It is the  $^{31}\text{P}$  CP/MAS NMR spectrum of a phosphinidene ruthenium cluster, nido- $\text{Ru}_4(\text{CO})_{13}(\text{m}^3\text{-PPh})$ , and the results have been published in:

K. Eichele, R. E. Wasylshen, J. F. Corrigan, N. J. Taylor, A. J. Carty:  
Phosphorus-31 Chemical Shift Tensors of Phosphinidene Ligands in Ruthenium Carbonyl Cluster

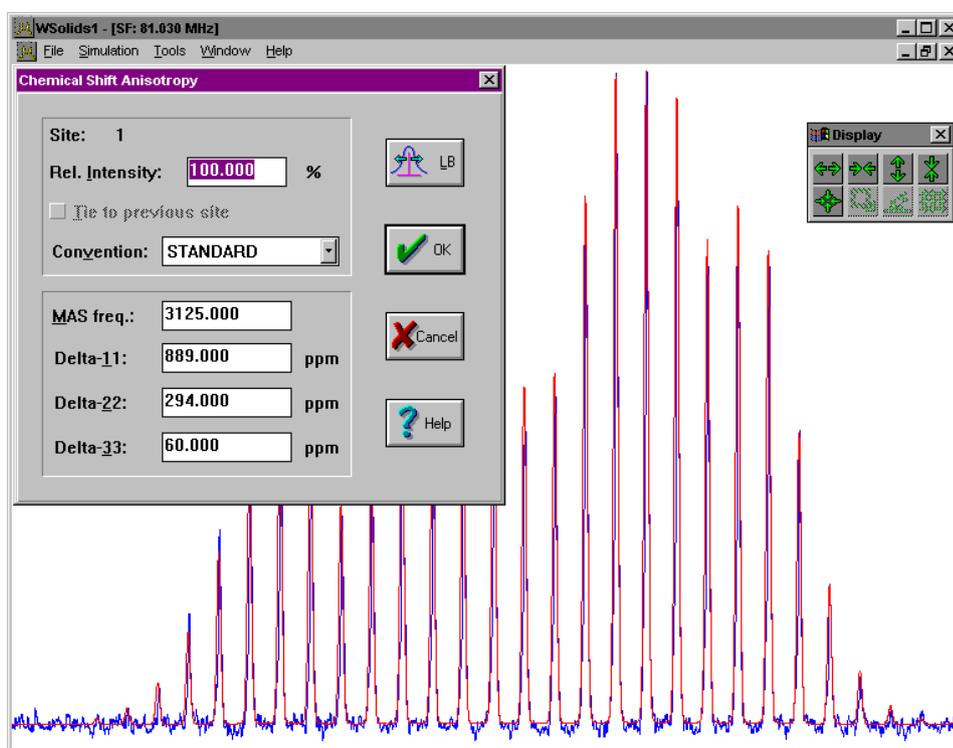
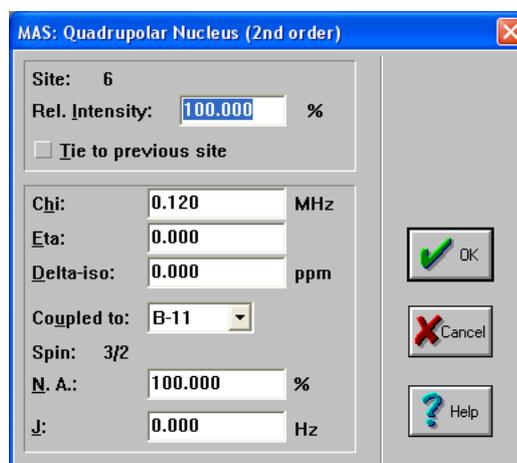


Figure 3.5: Experimental and calculated  $^{31}\text{P}$  MAS NMR spectra of a powder sample of a phosphinidene ruthenium cluster.

Compounds: A  $^{31}\text{P}$  Single-Crystal and CP/MAS NMR Study.  
J. Am. Chem. Soc. 1995, 117, 6961-6969.

## 3.6 MAS: Quadrupolar Nucleus



Calculates powder MAS spectrum of the central transition of a quadrupolar nucleus, considering the quadrupolar interaction to second order. Additionally, indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

Parameter	Purpose
<a href="#">Rel. Intensity (p. 70)</a>	Relative intensity of this site in percent
<a href="#">Tie to previous site (p. 70)</a>	Ties parameters to those of the previous site
<a href="#">Delta-iso (p. 70)</a>	Isotropic chemical shift, in ppm
<a href="#">Chi (p. 79)</a>	Quadrupolar coupling constant, in MHz
<a href="#">Eta (p. 79)</a>	Asymmetry parameter of the electric field gradient tensor, $0 \leq \eta \leq 1$
<a href="#">Coupled to (p. 73)</a>	Specifies the nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
<a href="#">N.A (p. 73)</a>	Natural abundance, in percent, of the coupled nucleus. If smaller than 100%, WSolids1 automatically includes calculation of the spectrum of the uncoupled spin species
<a href="#">J (p. 73)</a>	Indirect spin–spin coupling constant, in Hz
<a href="#">LB (p. 28)</a>	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box

### Background

If the nuclear quadrupolar coupling for a quadrupolar nucleus is sufficiently large, MAS cannot remove its effect on the line shape of the central transition and causes second-order broadening with characteristic lineshapes as well as a second-order shift. In order to obtain correct chemical shifts for the quadrupolar nucleus, simulation of the spectra is required. Optionally, indirect coupling to a heteronucleus can be added (note: quadrupolar interaction, if any, is neglected for the coupled heteronucleus).

### 3.6.1 Implementation Details

Specifically, we use the following convention:

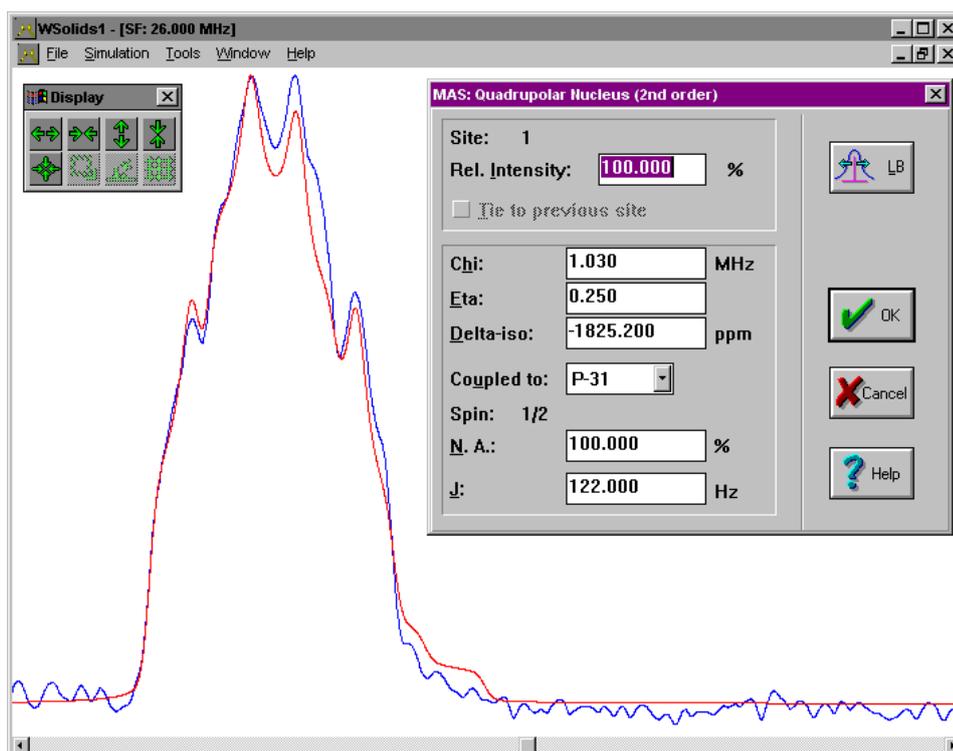


Figure 3.6: Experimental and calculated  $^{95}\text{Mo}$  MAS NMR spectra of a powder sample of a molybdenum phosphine complex.

- the NQR notation is used for labelling the axes of the EFG tensor:  $|VZZ| \geq |VYY| \geq |VXX|$

Figure 3.6 shows an example for the successful simulation of a MAS spectrum of a quadrupolar nucleus that shows the combined effect of quadrupolar interaction and spin-spin coupling to a spin-1/2 nucleus in a powder sample. It is the  $^{95}\text{Mo}$  NMR MAS spectrum of pentacarbonyl-5-methyldibenzophosphole molybdenum(0),  $\text{Mo}(\text{CO})_5(\text{MeDBP})$ , and the results have been published in:

K. Eichele, R. E. Wasylshen, J. H. Nelson:

Solid-State  $^{95}\text{Mo}$  NMR Studies of Some Prototypal Molybdenum Compounds: Sodium Molybdate Dihydrate, Hexacarbonylmolybdenum, and Pentacarbonyl Phosphine Molybdenum (0) Complexes. *J. Phys. Chem. A* 1997, 101, 5463-5468.

### 3.6.2 References

- (1) The second-order expression is taken from Amoureux's treatment, which follows Taulelle: Amoureux, Fernandez, Granger, In *Multinuclear Magnetic Resonance in Liquids and Solids - Chemical Applications*; Granger, Harris, eds.; Kluwer Academic Publishers, 1990; Ch. 22, p 409

## 3.7 MAS: Spin-1/2 – Spin-S (Diag.)

MAS: Spin-1/2 Coupled to Quadrupolar Nucleus (Diag.)

Site: 2  Tie to previous site

Coupled to: S-33  Speedy calculation

N. A.: 100.000 % Spin: 3/2

Delta-iso: 0.000 ppm D: 510.000 Hz

Alpha[D]: 0.000 deg J: -20.000 Hz

Beta[D]: 0.000 deg Delta-J: 0.000 Hz

Chi: -73.000 MHz Eta: 0.000

LB OK Cancel Help

Spectrum of a powder sample under magic-angle spinning containing a spin-1/2 nucleus dipolar and indirect coupled to a quadrupolar nucleus. The expectation values for the spin states of the quadrupolar nucleus are evaluated using full matrix diagonalization. Only the center peak in the spectrum is calculated (i.e. high-spinning frequency limit).

**Note:** Don't forget to define the observed nucleus (this is required to evaluate the Larmor frequency of the quadrupolar nucleus).

**Note:** For  $\eta = 0$ ,  $S$  can be 1, 3/2, 5/2, and 7/2; for  $\eta > 0$ ,  $S$  can be 3/2

**Note:** There can be a [problem \(p. 41\)](#) if the observed nucleus has a negative magnetogyric ratio.

Parameter	Purpose
<a href="#">Coupled to (p. 73)</a>	Specifies the quadrupolar nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
<a href="#">N.A (p. 73)</a>	Natural abundance, in percent, of the coupled nucleus
<a href="#">Tie to previous site (p. 70)</a>	Ties parameters to those of the previous site
<a href="#">Speedy calculation (p. 80)</a>	If checked, less crystallite orientations are included into the calculation
<a href="#">Delta-iso (p. 70)</a>	Isotropic chemical shift in ppm
<a href="#">Alpha (p. 74)</a>	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
<a href="#">Beta (p. 74)</a>	Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
<a href="#">D (p. 73)</a>	Direct dipole-dipole coupling constant, in Hz
<a href="#">J (p. 73)</a>	Indirect spin-spin coupling constant, in Hz
<a href="#">Delta-J (p. 74)</a>	Anisotropy of the indirect spin-spin coupling, in Hz
<a href="#">Chi (p. 79)</a>	Quadrupolar coupling constant, in MHz
<a href="#">Eta (p. 79)</a>	Asymmetry parameter of the electric field gradient tensor, $0 \leq \eta \leq 1$

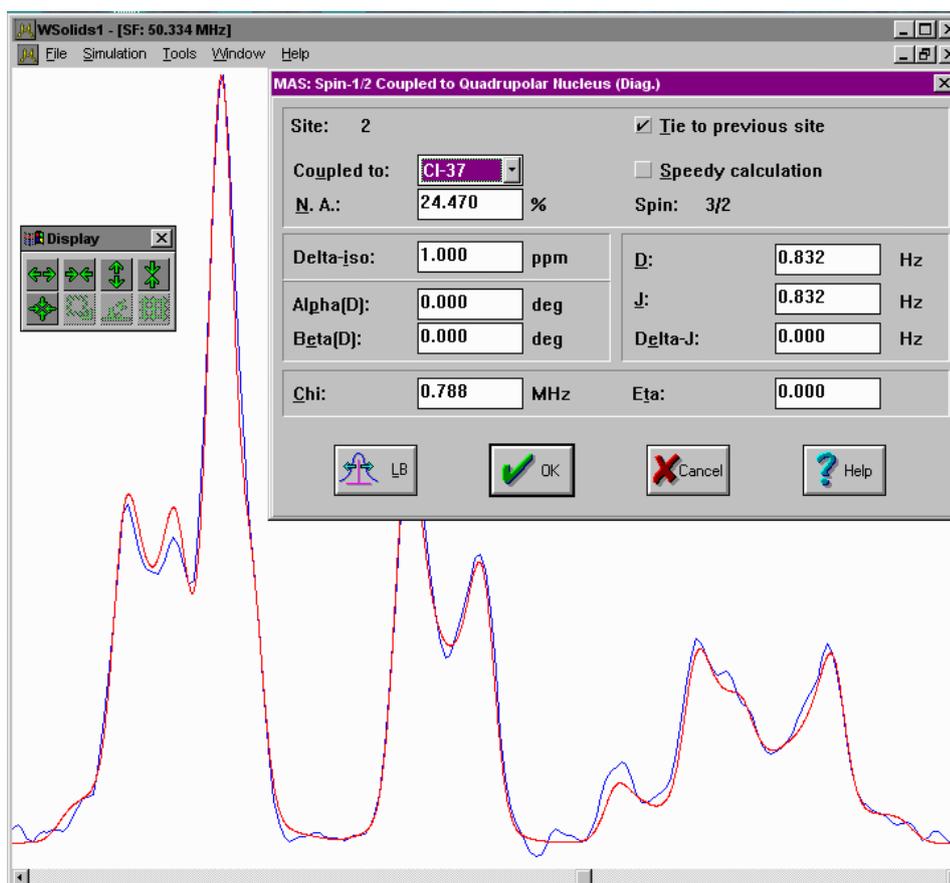


Figure 3.7: Experimental and calculated  $^{13}\text{C}$  MAS NMR spectra of a carbon coupled to  $^{35/37}\text{Cl}$ .

LB (p. 28)

Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the [Spectrum Default Parameters \(p. 25\)](#) box

## Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum.

### 3.7.1 Implementation Details

Specifically, we use the following conventions:

- the NQR notation is used for labelling the axes of the EFG tensor:  $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$

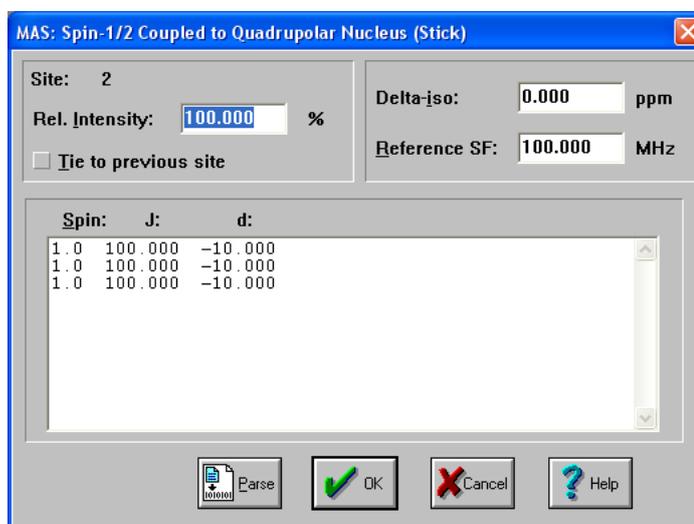
Figure 3.7 shows an example for the successful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to a quadrupolar nucleus in a powder sample. It is the  $^{13}\text{C}$  MAS NMR spectrum of a

chloroketosulfone, where carbon is coupled to Cl-35 and Cl-37, and the results have been published in:

K. Eichele, R. E. Wasylshen, J. S. Grossert, A. C. Olivieri:  
The Influence of Chlorine-Carbon Dipolar and Indirect Spin-Spin Interactions on High-Resolution Carbon-13 NMR Spectra of Chloroketosulfones in the Solid State.  
J. Phys. Chem. 1995, 99, 10110-10113.

This picture also illustrates the workings of the Tie to previous site feature: the parameters of the C-13,Cl-37 isotopomer are tied to those of the C-13,Cl-35 isotopomer by using the ratios of the magnetic ratios and nuclear quadrupole moments as factors.

### 3.8 MAS: Spin-1/2 – Spin-S (Stick)



Calculates the centerband (i.e. high-spinning frequency limit) in the MAS spectrum of a powder sample containing a spin-1/2 nucleus spin-spin coupled to several heteronuclei, typically quadrupolar nuclei. (Actually, one could also calculate solution H-1 NMR spectra of >10 protons coupled to each other, when the spectra are purely first order.) The break-down of the high-field approximation is taken into account using first-order perturbation theory, where the quadrupolar interaction is the perturbation. Each coupling interaction can be described by an indirect spin-spin coupling constant, *J*, and a field-dependent residual dipolar coupling, *d*, as well as the number of nuclei coupled and their respective spins.

The program calculates the frequency of each transition and puts some intensity (a “stick”) into the corresponding bin of the spectrum array. One may want to use a higher resolution for the calculated spectrum than for the experimental spectrum (e.g. increase the number of points and decrease the spectral width), as the center position of each peak is “quantized” according to the digital resolution.

Parameter	Purpose
Rel. Intensity (p. 70)	Relative intensity of this site in percent
Tie to previous site (p. 70)	Ties parameters to those of the previous site. Except for relative intensity and the spins of the coupled nuclei, all other parameters are affected by the setting of this flag. Always have the site with the most coupled nuclei as first site, followed by decreasing numbers. Otherwise, the result will be unpredictable
Delta-iso (p. 70)	Isotropic chemical shift in ppm
Reference SF	The residual dipolar coupling is field dependent. The value entered for <i>d</i> in the edit box is for the spectrometer frequency entered as reference frequency (of the observed nucleus), in MHz. Spectra at different fields can be calculated from the same set of parameters based on different observe frequencies.
Coupled nuclei	In the edit box, enter parameters for each coupled nucleus on a separate line. The parameters <b>spin</b> , <b>J</b> , and <b>d</b> should be separated by blank spaces. To check for proper format, use the Parse button to see the result of how WSolids1 interprets the input

---

Spin	Nuclear spin of the coupled nucleus. This parameter is not affected by the state of the "Tie to previous site" flag
J	Indirect spin-spin coupling constant, in Hz
d	Residual dipolar coupling, in Hz
<a href="#">LB (p. 28)</a>	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box
Parse	Use this button to check if the parameters for the coupled nuclei have been entered correctly

---

### Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum. However, if the quadrupolar and dipolar coupling are small relative to the indirect spin-spin coupling, this so-called breakdown of the high-field approximation causes no significant broadening of the individual peaks, only unequal spacings between the peaks of the multiplet. Such spectra can be simulated using first-order perturbation theory with a stick approach, where the patterns are characterized by an indirect spin-spin coupling constant, J, and a residual dipolar coupling, d.

### 3.8.1 Implementation Details

The theory behind this model is outlined in:

- A. C. Olivieri, *J. Magn. Reson.* **1989**, *81*, 201-205
- R. K. Harris, A. C. Olivieri, *Progr. NMR Spectrosc.* **1992**, *24*, 435-456.
- An introduction into applications, with several examples, is also given in:  
K. Eichele, R. E. Wasylishen, *Inorg. Chem.* **1994**, *33*, 2766-2773

Figure 3.8 shows an example for the successful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to several quadrupolar nuclei in a powder sample. It is the  $^{113}\text{Cd}$  MAS NMR spectrum of  $(\text{NMe}_4)_2[\text{Cd}(\text{SCN})_4]$ , where the octahedral cadmium is coupled to four N-14 nuclei, and the results have been published in:

K. Eichele, R. E. Wasylishen:

High-Resolution  $^{113}\text{Cd}$  CP/MAS NMR Studies of Cadmium Thiocyanate Coordination Compounds. Direct Observation of  $^{113}\text{Cd}$ ,  $^{14}\text{N}$  Spin-Spin Coupling Constants in the Solid State. *Inorg. Chem.* 1994, *33*, 2766-2773.

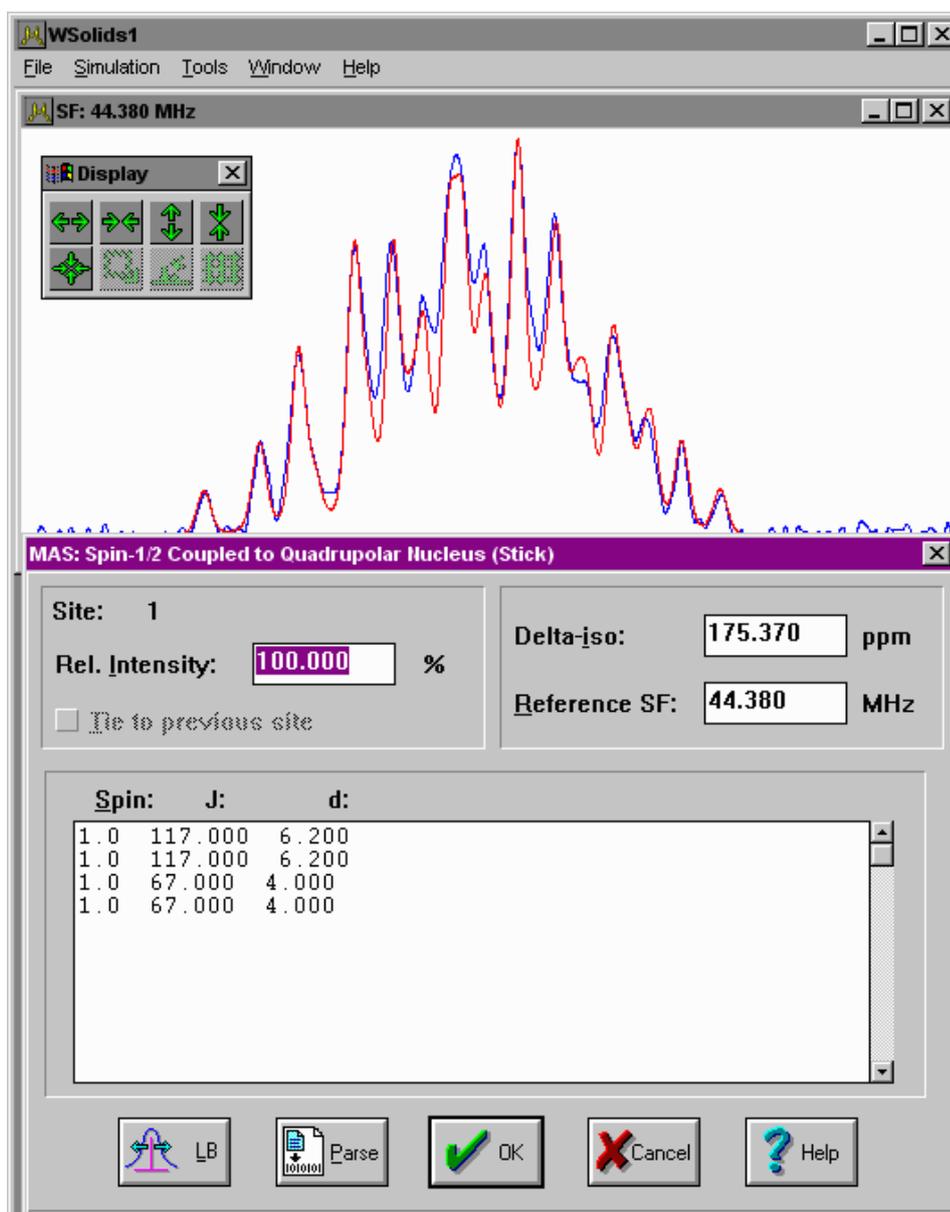


Figure 3.8: Experimental and calculated  $^{113}\text{Cd}$  MAS NMR spectra showing coupling to  $^{14}\text{N}$ .

### 3.9 MAS: Spin-1/2 – Spin-S (Shape)

Spectrum of a powder sample under magic-angle spinning containing a spin-1/2 nucleus spin-spin coupled to a quadrupolar nucleus. The expectation values for the spin states of the quadrupolar nucleus are evaluated using first-order perturbation theory, where the quadrupolar interaction is the perturbation. Only the center peak in the spectrum is calculated (i.e. high-spinning limit).

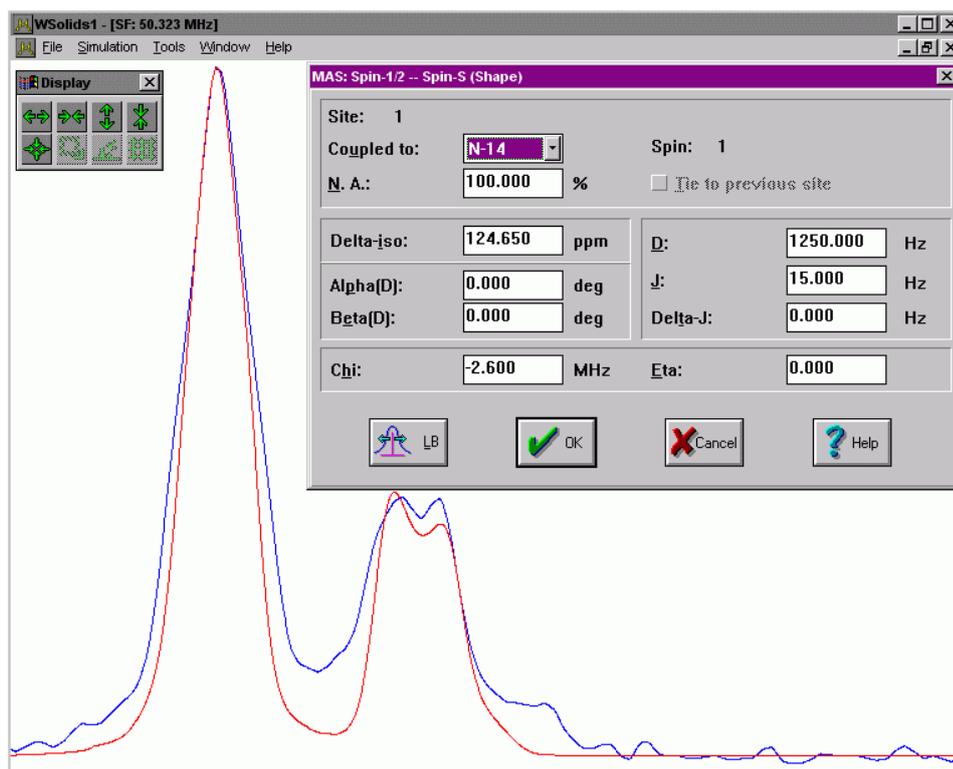
**Note:** Don't forget to define the observed nucleus (this is required to evaluate the Larmor frequency of the quadrupolar nucleus).

**Note:** For a nucleus with a nuclear spin of 3, a warning will appear that the spectrum contains a single line subspectrum. According to the line shape equation, this will generally be true of two transitions and independent of the parameters used.

Parameter	Purpose
<a href="#">Coupled to (p. 73)</a>	Specifies the quadrupolar nucleus the observed nucleus is coupled to. Only heteronuclear coupling will be considered
<a href="#">N.A (p. 73)</a>	Natural abundance, in percent, of the coupled nucleus
<a href="#">Tie to previous site (p. 70)</a>	Ties parameters to those of the previous site
<a href="#">Delta-iso (p. 70)</a>	Isotropic chemical shift in ppm
<a href="#">Alpha (p. 74)</a>	Azimuth angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
<a href="#">Beta (p. 74)</a>	Polar angle, in degrees, of the internuclear vector in the principal axis system of the electric field gradient tensor
<a href="#">D (p. 73)</a>	Direct dipole-dipole coupling constant, in Hz
<a href="#">J (p. 73)</a>	Indirect spin-spin coupling constant, in Hz
<a href="#">Delta-J (p. 74)</a>	Anisotropy of the indirect spin-spin coupling, in Hz
<a href="#">Chi (p. 79)</a>	Quadrupolar coupling constant, in MHz
<a href="#">Eta (p. 79)</a>	Asymmetry parameter of the electric field gradient tensor, $0 \leq \eta \leq 1$
<a href="#">LB (p. 28)</a>	Provides access to the convolution parameters for the current site. To have individual convolution parameters for each site, specify this in the <a href="#">Spectrum Default Parameters (p. 25)</a> box

#### Background

The quadrupolar interaction at a quadrupolar nucleus causes its axis of quantization to be tilted away from the direction of the external magnetic field. This also modifies the spatial dependence of the dipolar interaction, so that magic-angle spinning is not able to suppress the heteronuclear dipolar coupling in the spectrum of the spin-1/2 nucleus, resulting in splittings and broadenings. Similar effects can be transmitted through the indirect spin-spin coupling. If the nuclear quadrupolar coupling constant is on the same order of magnitude as the Larmor frequency of the quadrupolar nucleus, the combined Zeeman-quadrupolar Hamiltonian must be diagonalized at each orientation and averaged over a rotor period to calculate a theoretical spectrum. However, if the quadrupolar coupling is relatively small, this so-called breakdown of the high-field approximation causes lineshapes that can be simulated using first-order perturbation theory. If the broadening is small, such lineshapes can also be analyzed



**Figure 3.9:** Experimental and calculated  $^{13}\text{C}$  MAS NMR spectra showing coupling to  $^{14}\text{N}$ .

using a “stick” approach.

Figure 3.9 shows an example for the successful simulation of a MAS spectrum of a spin-1/2 nucleus that is coupled to several quadrupolar nuclei in a powder sample. It is the  $^{13}\text{C}$  MAS NMR spectrum of  $(\text{NH}_4)\text{SeCN}$ , where carbon is coupled to a N-14 nucleus, and the results have been published in:

G. M. Bernard, K. Eichele, G. Wu, C. Kirby, R. E. Wasylshen:  
 Nuclear Magnetic Shielding Tensors for the Carbon, Nitrogen and Selenium Nuclei of Selenocyanates  
 - A Combined Experimental and Theoretical Approach.  
 Can. J. Chem. 2000, 78, 614-625.

### 3.10 VAS: Dipolar-Chemical Shift (A2, AX)

Site:	2	Coupled to:	Ir-193
Rel. Intensity:	100.000 %	Spin:	3/2
<input type="checkbox"/> Tie to previous site		N. A.:	34.000 %
Convention:	STANDARD	<input type="checkbox"/> Homonuclear	
VAS angle:	60.000 deg	D:	1500.000 Hz
Delta-11:	100.000 ppm	J:	60.000 Hz
Delta-22:	50.000 ppm	Delta-J:	0.000 Hz
Delta-33:	-100.000 ppm	Alpha:	0.000 deg
		Beta:	20.000 deg

Spectrum of a powder sample under variable-angle spinning containing a spin pair where AX or A2 approximation is valid.

#### Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. Spinning the powder sample rapidly about an axis that forms an angle different from the magic angle with respect to the external magnetic field, the resulting lineshape will look like that of a static powder sample, but scaled by a factor that depends on the spinning angle. This scaling factor ranges from 1.0 (for spinning parallel to the field) to -0.5 (for spinning perpendicular to the magnetic field).

Figure 3.10 shows an example for the successful simulation of a spectrum arising from the combined effect of chemical shift anisotropy, and heteronuclear indirect and dipolar coupling in a powder sample under fast variable-angle spinning. It is the  $^{31}\text{P}$  NMR spectrum of a cadmium phosphine complex.

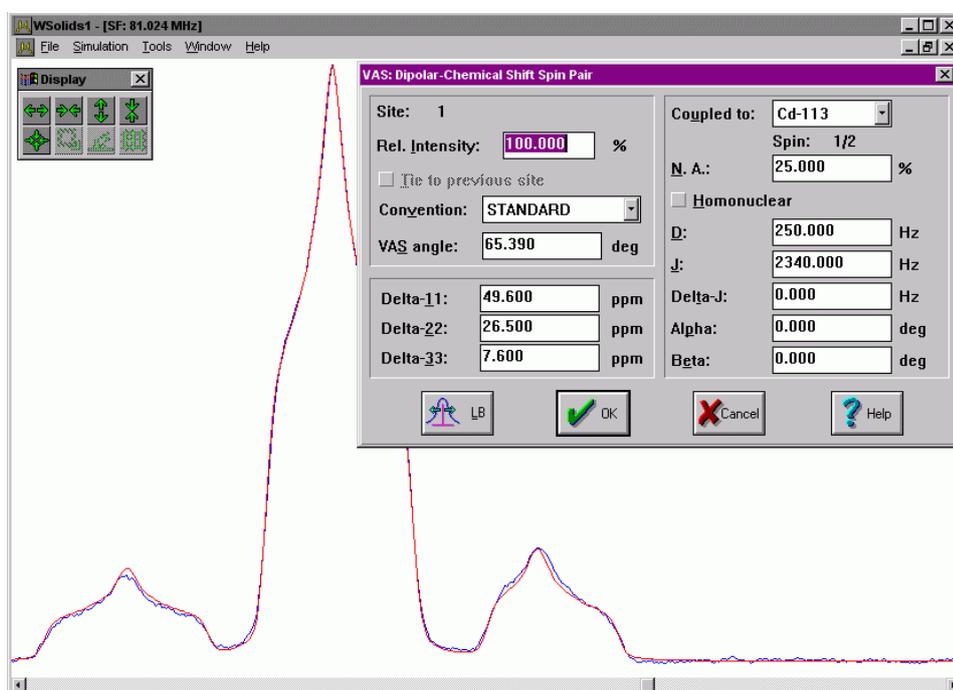


Figure 3.10: Experimental and calculated  $^{31}\text{P}$  VAS NMR spectra of a cadmium phosphine complex.

### 3.11 VAS: Dipolar-Chemical Shift (AB)

The screenshot shows a software dialog box titled "VAS: Homonuclear Two-Spin System (AB)". It contains the following parameters and values:

- Site: 3
- Rel. Intensity: 100.000 %
- Tie to previous site
- Convention: STANDARD
- VAS angle: 60.000 deg
- D: 1500.000 Hz
- J: 60.000 Hz
- Delta-J: 0.000 Hz
- Alpha: 10.000 deg
- Beta: 40.000 deg

Parameters for Nucleus A:

- Delta-11: 100.000 ppm
- Delta-22: 50.000 ppm
- Delta-33: -100.000 ppm
- Alpha: 0.000 deg
- Beta: 20.000 deg
- Gamma: 0.000 deg

Parameters for Nucleus B:

- Delta-11: 100.000 ppm
- Delta-22: 50.000 ppm
- Delta-33: -100.000 ppm
- Alpha: 0.000 deg
- Beta: -20.000 deg
- Gamma: 0.000 deg

Buttons: OK, Cancel, Help

Spectrum of a powder sample under variable-angle spinning containing a homonuclear spin pair, using AB equation.

#### Background

In addition to the chemical shift anisotropy (CSA), the spectrum of a spin pair will also depend on the direct dipolar coupling and potentially the indirect spin-spin coupling between both nuclei. Because both, the CSA and dipolar interaction, are tensorial interactions, the actual line shape also depends on their relative orientation. Spinning the powder sample rapidly about an axis that forms an angle different from the magic angle with respect to the external magnetic field, the resulting lineshape will look like that of a static powder sample, but scaled by a factor that depends on the spinning angle. This scaling factor ranges from 1.0 (for spinning parallel to the field) to -0.5 (for spinning perpendicular to the magnetic field).

Figure 3.11 shows an example for the successful simulation of a spectrum arising from the combined effect of chemical shift anisotropy and homonuclear indirect and dipolar coupling in a powder sample under fast variable-angle spinning. It is the  $^{31}\text{P}$  NMR spectrum of *fac*-(OC) $_3$ (h $_2$ -phen)Mo(h $_1$ -Ph $_2$ P-PP $_2$ ), and the results have been published in:

K. Eichele, G. Ossenkamp, R. E. Wasylshen, T. S. Cameron, J. F. Britten:  
Phosphorus-31 Solid-State NMR Studies of Homonuclear Spin Pairs in Molybdenum Phosphine Complexes: Single-Crystal, Dipolar-Chemical Shift, Rotational-Resonance and 2D Spin-Echo NMR Experiments  
*Inorg. Chem.* 1999, 38, 639-651.

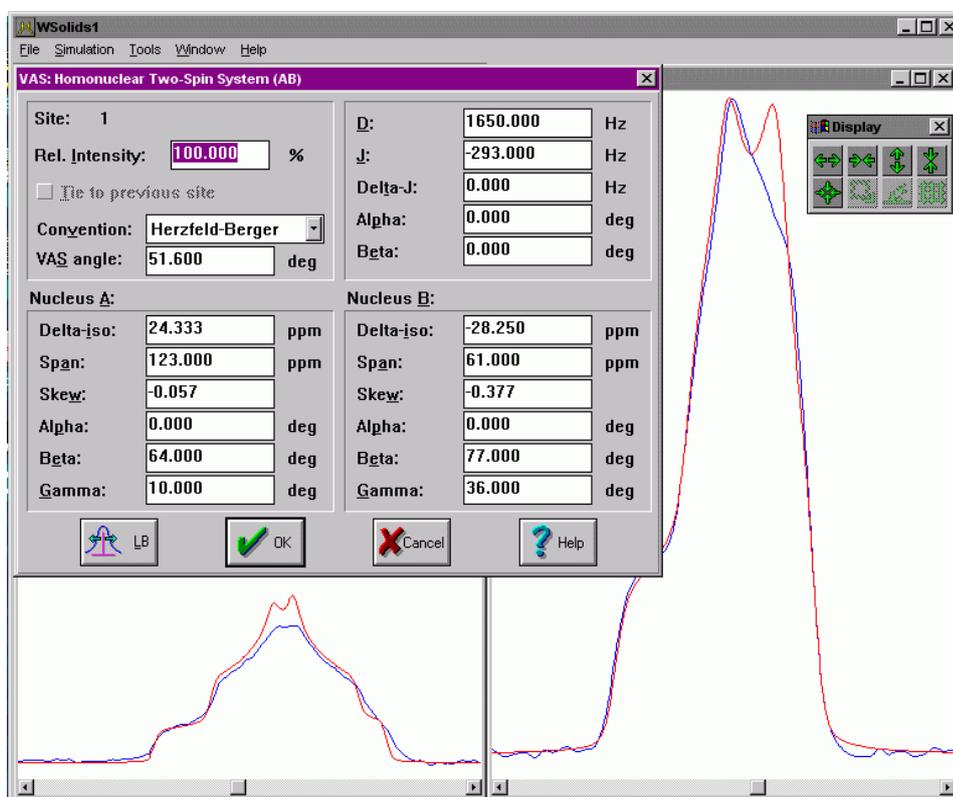


Figure 3.11: Experimental and calculated  $^{31}\text{P}$  VAS NMR spectra of a molybdenum phosphine complex.

## 3.12 Spin System Parameters

### 3.12.1 Relative Intensity

The **relative intensity** of each site determines the relative area this site contributes to the total line shape. Allowed values are 0-100, but there is no check whether the relative intensities of all sites sum up to 100 %. Considered as a mere scaling factor.

To exclude a site momentarily from a calculation without deleting it, set the relative intensity of this site to zero.

### 3.12.2 Tie to previous site

This feature allows to tie the parameters of a site to the parameters of the previous site, using fixed factors. Such a feature is useful if the spectrum is made up of a variety of different isotopomers and the site specific parameters differ only by ratios of nuclear constants. Because such cases are rather rare, the implementation here does not offer a high degree of sophistication.

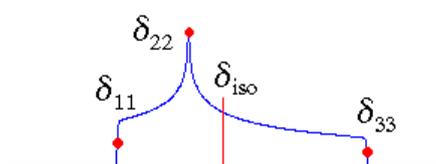
There are a few points to keep in mind:

- More than one site needs to be available, and this feature will not be available for the first site (obviously)
- The simulation models for the sites tied together should be the same. This is not checked! Tying together different models may produce unexpected results
- Once sites are tied together, one cannot change the convention used for tensor components
- Parameters not affected by the state of the **Tie** check box are grouped together with this check box in one shaded area; all parameters outside this area depend on the state of the check box (exceptions are, e.g., spin quantum numbers)

### 3.12.3 Convention

Unfortunately, there are many different conventions around in the literature for labeling the principal components of chemical shift tensors. Most of the conventions have advantages for certain situations but drawbacks in others. Often, it is not obvious which convention has been chosen. The collection given here attempts to summarize some of the most frequently used conventions.

### 3.12.4 Standard Convention



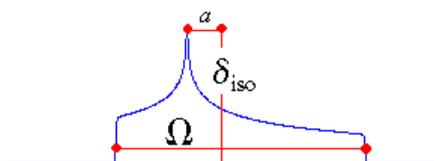
<b>Principal Components</b>	$\delta_{11} \geq \delta_{22} \geq \delta_{33}$
	$\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$
<b>Isotropic Value</b>	$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
	$\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$

In what we shall call the standard convention, the principal components of the chemical shift tensor,  $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$ , are labeled according to the IUPAC rules [3]. They follow the high frequency-positive order. Thus,  $\delta_{11}$  corresponds to the direction of least shielding,  $\sigma_{11}$ , with the highest frequency, while  $\delta_{33}$  corresponds to the direction of highest shielding,  $\sigma_{33}$ , with the lowest frequency. The isotropic values,  $\delta_{\text{iso}}$  or  $\sigma_{\text{iso}}$ , are the average values of the principal components, and correspond to the center of gravity of the line shape.

In many cases, the spectrum or calculation will not depend on any given order, and the values can be entered in any order. However, in some cases where the orientation of the tensors is also important,

the assignment of values to the principal axes will affect the spectrum.

### 3.12.5 Herzfeld-Berger Convention



<b>Isotropic Value</b>	$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
<b>Span</b>	$\Omega = \delta_{11} - \delta_{33} \quad (\Omega \geq 0)$
<b>Skew</b>	$\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega; (-1 \leq \kappa \leq 1)$

In the Herzfeld-Berger notation [4], a tensor is described by three parameters, which are combinations of the principal components in the standard notation:

The **isotropic value**, i.e., the center of gravity, is the average value of the principal components.

The **span** describes the maximum width of the powder pattern.

The **skew** of the tensor is a measure of the amount and orientation of the asymmetry of the tensor. As indicated,  $\kappa$  is given by  $3a / \Omega$ . Depending on the position of  $\delta_{22}$  with respect to  $\delta_{\text{iso}}$ , the sign is either positive or negative. If  $\delta_{22}$  equals  $\delta_{\text{iso}}$ ,  $a$  and the skew are zero. In the case of an axially symmetric tensor,  $\delta_{22}$  equals either  $\delta_{11}$  or  $\delta_{33}$  and  $a = \Omega / 3$ . Hence, the skew is  $\pm 1$ .

The parameter  $\mu$  used with the Herzfeld-Berger tables is related to the span of a tensor by:

$$\mu = \Omega * \text{SF} / \text{spinning rate}$$

The parameter  $\rho$  used with the Herzfeld-Berger tables corresponds to the skew of a tensor described here. For "historical" reasons we used  $\rho$  throughout this manual, but generally we prefer  $\kappa$  [3].

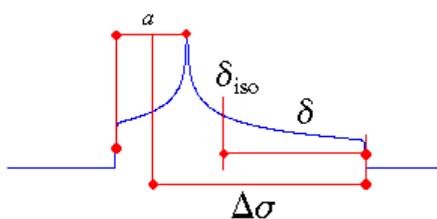
The Herzfeld-Berger convention is related to the Standard convention via:

$$\delta_{22} = \delta_{\text{iso}} + (\kappa \Omega / 3)$$

$$\delta_{33} = (3 \delta_{\text{iso}} - \delta_{22} - \Omega) / 2$$

$$\delta_{11} = 3 \delta_{\text{iso}} - \delta_{22} - \delta_{33}$$

### 3.12.6 Haeberlen Convention



<b>Principal Components</b>	$ \delta_{zz} - \delta_{\text{iso}}  \geq  \delta_{xx} - \delta_{\text{iso}}  \geq  \delta_{yy} - \delta_{\text{iso}} $
<b>Isotropic Value</b>	$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
<b>Reduced Anisotropy</b>	$\delta = \delta_{zz} - \delta_{\text{iso}}$
<b>Anisotropy</b>	$\Delta\sigma = \delta_{zz} - (\delta_{xx} + \delta_{yy})/2 = 3\delta/2$
<b>Asymmetry</b>	$\eta = (\delta_{yy} - \delta_{xx})/\delta; (0 \leq \eta \leq +1)$

The Haeberlen-Mehring [5] convention uses different combinations of the principal components to describe the line shape. This convention requires that the principal components are ordered according to their separation from the isotropic value.

The center of gravity of the line shape is described by the **isotropic value**, which is the average value of the principal components.

The **anisotropy** and **reduced anisotropy** describe the largest separation from the center of gravity. (The term reduced anisotropy is not used in the literature, but we introduce it here in order to be able to distinguish between  $\delta$  and  $\Delta\sigma$ .) The sign of the anisotropy indicates on which side of the isotropic value one can find the largest separation.

The **asymmetry** parameter indicates by how much the line shape deviates from that of an axially symmetric tensor. In the case of an axially symmetric tensor,  $a = (\delta_{yy} - \delta_{xx})$  will be zero and hence  $\eta = 0$ .

The Haeberlen-Mehring convention is related to the Standard convention via:

for $\delta > 0$ (i.e. $\delta_{zz} = \delta_{11}$ )	for $\delta < 0$ (i.e. $\delta_{zz} = \delta_{33}$ )
$\delta_{11} = \delta_{\text{iso}} + \delta$	$\delta_{33} = \delta_{\text{iso}} + \delta$
$\delta_{22} = \delta_{\text{iso}} - \delta(1 - \eta)/2$	$\delta_{22} = \delta_{\text{iso}} - \delta(1 - \eta)/2$
$\delta_{33} = \delta_{\text{iso}} - \delta(1 + \eta)/2$	$\delta_{11} = \delta_{\text{iso}} - \delta(1 + \eta)/2$

## References

- [1] *Pure Appl. Chem.* **1972**, 29, 627; **1976**, 45, 217.
- [2] Some examples for established shielding scales:
- Carbon:*  
A. K. Jameson, C. J. Jameson, *Chem. Phys. Lett.* **1987**, 134, 461.  
W. T. Raynes, R. McVay, S. J. Wright, *J. Chem. Soc., Faraday Trans. 2* **1989**, 85, 759.
- Silicon:*  
C. J. Jameson, A. K. Jameson, *Chem. Phys. Lett.* **1988**, 149, 300.
- Phosphorus:*  
C. J. Jameson, A. De Dios, A. K. Jameson, *Chem. Phys. Lett.* **1990**, 167, 575.
- Tin:*  
A. Laaksonen, R. E. Wasylshen, *J. Am. Chem. Soc.* **1995**, 117, 392.
- [3] J. Mason, *Solid State Nucl. Magn. Reson.* **1993**, 2, 285.
- [4] J. Herzfeld, A. E. Berger, *J. Chem. Phys.* **1980**, 73, 6021.
- [5] U. Haeberlen, In *Advances in Magnetic Resonance*; Suppl. 1; J. S. Waugh, Ed.; Academic Press: New York, 1976.
- M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd. ed.; Springer Verlag: Berlin, 1983.

### 3.12.7 Chemical Shift and Chemical Shielding

It is recommended that the IUPAC conventions [1] are obeyed:

- The **absolute chemical shielding**,  $\sigma$ , in ppm is the difference in shielding between the frequency of the bare nucleus,  $\nu_{\text{nucl}}$ , and the frequency of the same nucleus in the species under investigation,  $\nu_{\text{s}}$ :  
$$\sigma / \text{ppm} = 10^6 * (\nu_{\text{nucl}} - \nu_{\text{s}}) / \nu_{\text{nucl}}$$
- The **chemical shift**,  $\delta$ , is the difference in shielding between the nucleus in the species under investigation,  $\sigma_{\text{s}}$ , and the shielding of the same nucleus in a reference compound,  $\sigma_{\text{ref}}$ :  
$$\delta / \text{ppm} = (\sigma_{\text{ref}} - \sigma_{\text{s}}) / (1 - \sigma_{\text{ref}})$$
- Because  $\sigma_{\text{ref}}$  is often a small number compared to 1, frequently the following approximation is used:

Shifts, commonly used in solution and solid state NMR studies, are thus positive to high frequency. Absolute shieldings are positive to low frequency, and are only accessible via theoretical calculations. The establishment of a correspondence between a chemical shift scale and a chemical shielding scale is not a trivial task and requires both careful theoretical calculations and experimental measurements [2].

The nuclear magnetic shielding (absolute shielding) is **the** molecular electronic property. The chemical shift is a quantity that we experimentalists have defined and use because of our inability to directly measure the absolute magnetic shielding. This inability results from our inability to know the magnitude of the magnetic field to an accuracy on the order of parts per billion, independent of the resonance experiment [3].

**Comments**

The symbol  $\sigma$  should only be used for absolute shieldings. Often, however, authors use a “pseudo” shielding scale, where the “shielding” is obtained by simply reversing the sign of the chemical shift. In our opinion, this adds only to the confusion without providing any additional insight.

Note that the exact formulation of the [span \(p. 70\)](#),  $\Omega$ , contains the factor  $(1 - \sigma_{\text{ref}})$  [3]:

$$\Omega = (\delta_{11} - \delta_{33}) (1 - \sigma_{\text{ref}})$$

**References**

[1] *Pure Appl. Chem.* **1972**, 29, 627; **1976**, 45, 217.

[2] Some examples for established shielding scales:

*Carbon:*

A. K. Jameson, C. J. Jameson, *Chem. Phys. Lett.* **1987**, 134, 461.

W. T. Raynes, R. McVay, S. J. Wright, *J. Chem. Soc., Faraday Trans. 2* **1989**, 85, 759.

*Silicon:*

C. J. Jameson, A. K. Jameson, *Chem. Phys. Lett.* **1988**, 149, 300.

*Phosphorus:*

C. J. Jameson, A. De Dios, A. K. Jameson, *Chem. Phys. Lett.* **1990**, 167, 575.

*Tin:*

A. Laaksonen, R. E. Wasylshen, *J. Am. Chem. Soc.* **1995**, 117, 392.

[3] C. J. Jameson, *Solid State Nucl. Magn. Reson.* **1998**, 11, 265.

**3.12.8 Coupled To**

In some models, the observed nucleus is coupled to another nucleus via indirect spin-spin or direct dipole-dipole coupling. The coupled nucleus can be selected from a list of available isotopes. In some cases, this also updates an entry with the [natural abundance \(p. 73\)](#) of the selected isotope as well as the spin of this nucleus.

**3.12.9 Natural Abundance**

By default, this parameter is set to the natural abundance of an isotope, in percent. This parameter can, however, be changed to reflect isotopic enrichment.

**3.12.10 Dipolar Coupling Constant D**

The direct dipole-dipole coupling is the through-space interaction between the magnetic moments of nuclei. The magnitude of this interaction is characterized by the **Dipolar Coupling Constant**, given in Hz. It depends on the inverse cube of the distance between the interacting nuclei, besides some natural and nuclear constants:

$$D = \frac{\mu_0}{4\pi} \frac{\gamma_I \gamma_S \hbar}{2\pi} \langle r_{IS}^{-3} \rangle$$

In contrast, the [indirect spin-spin coupling \(p. 73\)](#) between nuclear magnetic moments is mediated by intervening electrons.

**3.12.11 Indirect Spin-Spin Coupling J**

The **indirect spin-spin coupling** between the magnetic moments of nuclei is mediated by intervening electrons. In contrast to the [direct dipole-dipole coupling \(p. 73\)](#), there is no simple relationship between its magnitude and geometry. In solution NMR studies, the magnitude of this interaction

is simply called the spin-spin coupling constant,  $J$ , reported in Hz. In solid-state NMR, it is more adequately referred to as **isotropic spin-spin coupling constant**, as it is, in principle, **anisotropic** (p. 74) in nature.

### 3.12.12 Anisotropy in Indirect Spin-Spin Coupling Delta-J

The **indirect spin-spin coupling** between the magnetic moments of nuclei is mediated by intervening electrons. This interaction is, in principle, anisotropic in nature. Assuming axial symmetry, the anisotropy of the indirect spin-spin coupling is defined as the difference between the unique component and the perpendicular components:

$$\Delta J = J_{\parallel} - J_{\perp}$$

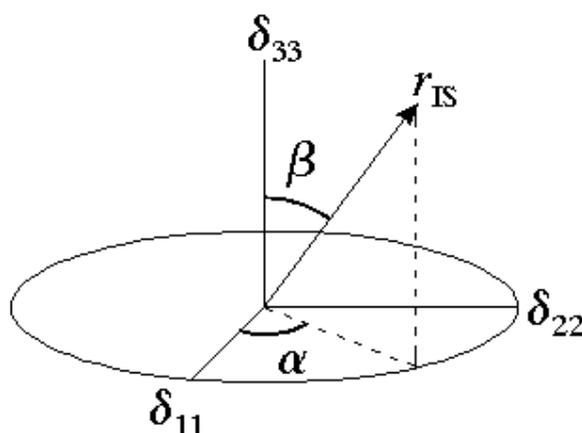
In solution NMR spectra, the anisotropy of the indirect spin-spin coupling does not lead to splittings, although it could provide a mechanism for relaxation. Physically, the anisotropy of the indirect spin spin coupling behaves exactly the same way as the direct dipole-dipole coupling. Therefore, one cannot determine both interactions separately in an experiment, only an effective dipolar coupling constant:

$$D_{eff} = \kappa \left[ D - \frac{\Delta J}{3} \right]$$

However, one could calculate the **dipolar coupling constant** (p. 73) from known internuclear separations (cf. **Calculate Dipolar Coupling Constant** (p. 34)). For an AX spin system, the prefactor  $\kappa$  of the equation above equals one,  $\kappa = 1$ , while for a pair of magnetically equivalent spins this factor corresponds to 3/2,  $\kappa = 1.5$

**Note:** For an A2 spin system, the isotropic part of the **indirect spin-spin coupling** (p. 73) does not contribute to the spectrum, but the anisotropy of the indirect spin-spin coupling **does!**

### 3.12.13 Polar Angles

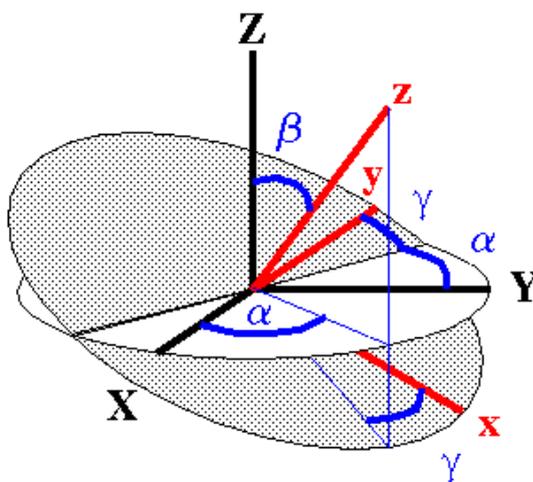


Polar angles are used to define the orientation of a vector in a three-dimensional Cartesian coordinate system,  $x,y,z$ , as shown in this figure describing the orientation of the internuclear vector  $r$  in the principal axis system of the chemical shift tensor. The azimuthal angle  $\alpha$  is the angle between the  $x$  axis (=  $d_{11}$ ) and the projection of the vector into the  $x,y$  plane (=  $d_{11}$ ,  $d_{22}$ , "equatorial plane"). The polar angle  $\beta$  is the angle between the vector and the  $z$  axis (=  $d_{33}$ , "pole"). The polar angles are closely related to the type of **Euler angles** (p. 75) used by WSolids1. Because the dipolar interaction is

axially symmetric, the two polar angles are sufficient to describe the relative orientations of chemical shift and dipolar interaction. For more general cases, the set of three Euler angles is required.

### 3.12.14 Euler Angles

The triplet of Euler angles  $(\alpha, \beta, \gamma)$  is useful to describe rotations or relative orientations of orthogonal coordinate systems. Unfortunately, their definition is not unique and in the literature there are as many different conventions as authors. The convention employed here is one of the more common ones. All rotations are in a counter-clockwise fashion (right-handed, mathematically positive sense).



The Euler angles  $(\alpha, \beta, \gamma)$  relate two orthogonal coordinate systems having a common origin. The transition from one coordinate system to the other is achieved by a series of two-dimensional rotations. The rotations are performed about coordinate system axes generated by the previous rotation step (the **step-by-step procedure** is illustrated in the topic [Rotation Matrices](#) (p. 75), and a more humorous account is given in topic [The Swivel Chair](#) (p. 78)). The convention used here is that  $\alpha$  is a rotation about the Z axis of the initial coordinate system. About the  $y'$  axis of this newly generated coordinate system a rotation by  $\beta$  is performed, followed by a rotation by  $\gamma$  about the new z axis.

Given the Euler angles, the step-by-step procedure illustrates how to move from one coordinate system to the other. However, given the two coordinate systems, how can one determine the Euler angles relating them? This is described in topic [Determining Euler Angles](#) (p. 79).

The usual ranges for **Alpha**, **Beta**, and **Gamma** are:

$$0 \leq \text{Alpha} \leq 360$$

$$0 \leq \text{Beta} \leq 180$$

$$0 \leq \text{Gamma} \leq 360$$

#### References

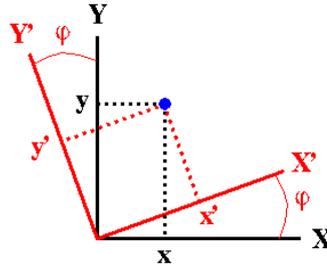
- (1) G. Arfken, *Mathematical Methods for Physicists*, 3rd. ed., Academic Press: New York 1985.
- (2) M. E. Rose, *Elementary Theory of Angular Momentum*, Wiley: New York 1957.
- (3) K. Schmidt-Rohr and H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, Academic Press: London 1994.

### 3.12.15 Rotation Matrices

Rotations or transformations from one coordinate system into another are conveniently described by the triplet of [Euler angles](#) (p. 75)  $(\alpha, \beta, \gamma)$ . Using the Euler angles, this three-dimensional problem can

be dissected into a sequence of two-dimensional rotations, whereby in each rotation one axis remains invariant. Here, all rotations are counter clockwise (right-handed, mathematically positive sense).

In order to simplify the problem, let us start with a two-dimensional rotation:



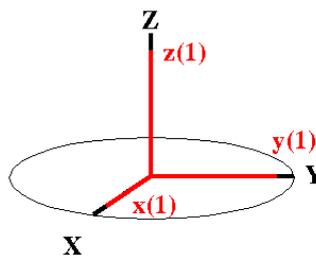
Suppose the coordinates,  $(x,y)$ , of a point in the two-dimensional  $XY$  system are known, but we are actually interested in knowing the coordinates of this point in another coordinate system,  $X'Y'$ , which is related to the  $XY$  system by a counter-clockwise rotation by an angle  $\varphi$ .

As the figure indicates, the coordinates of the given point in the new coordinate system will be:

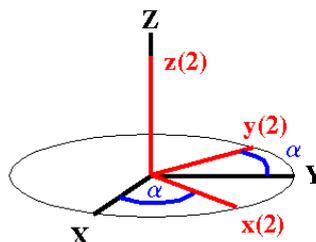
$$\begin{aligned} x' &= x\cos\varphi + y\sin\varphi \\ y' &= -x\sin\varphi + y\cos\varphi \end{aligned} \tag{3.1}$$

or, in matrix notation:

$$R(\varphi) = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix}$$

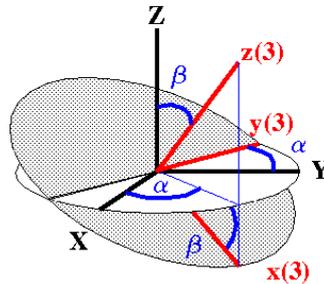


Now, transferred to a three-dimensional problem, the goal will be to describe the coordinates in a final rotated system  $(x,y,z)$  which is related to some initial coordinate system  $(X,Y,Z)$  by the Euler angles. The final system is developed in three steps, each step involving a rotation described by one Euler angle. At the start, both coordinate systems,  $(X,Y,Z)$  and  $(x(1), y(1), z(1))$ , shall be coincident.



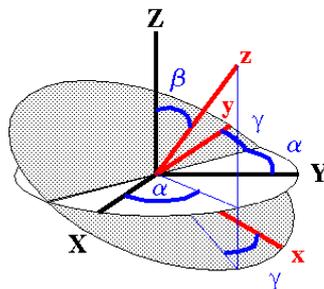
The first rotation involves the Euler angle  $\alpha$ . The  $x(1), y(1), z(1)$  axis system is rotated about the Z axis through an angle  $\alpha$  counterclockwise relative to X,Y,Z to give the new system  $x(2), y(2), z(2)$ . It is clear from the figure that this rotation mixes the coordinates along X and Y, completely analogous to the two-dimensional rotation described above, while the coordinate along Z remains unaffected. The rotation matrix to describe this operation is given by:

$$R_z(\alpha) = \begin{pmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



The second rotation involves the Euler angle  $\beta$ . The  $x(2), y(2), z(2)$  axis system is rotated about the  $y(2)$  axis through an angle  $\beta$  counterclockwise to generate the new coordinate system  $x(3), y(3), z(3)$ . Analogously to the first Euler rotation, this mixes the coordinates along  $x(2)$  and  $z(2)$ , while the coordinate along  $y(2)$  remains unaffected. This operation also generates a line of nodes parallel to the direction of  $y(2)$ . The rotation matrix to describe this operation is given by:

$$R_y(\beta) = \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix}$$



The last rotation involves the Euler angle  $\gamma$ . The  $x(3), y(3), z(3)$  axis system is rotated about the  $z(3)$  axis through an angle  $\gamma$  counterclockwise to generate the final coordinate system  $x, y, z$ . Analogously to the first Euler rotation, this mixes the coordinates along  $x(3)$  and  $y(3)$ , while the coordinate along  $z(3)$  remains unaffected. The rotation matrix to describe this operation is given by:

$$R_z(\gamma) = \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The combined effect of these three rotations is given by this transformation matrix:

$$R_z(\gamma) R_y(\beta) R_z(\alpha) = \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix}$$

Note: This type of rotation about sequentially newly generated axes produces the same result as rotations by the same angles about the fixed original axes (cf. Mehring's book, appendix).

### 3.12.16 The Swivel Chair

The following humorous explanation of how to transform from one coordinate system to the other by using Euler angles has been posted to the newsgroup comp.graphics.algorithms by John Aspinall, jga@harlequin.co.uk, Subject: Rotation matrix – > angles... [an aside], on 16 Feb 1996 21:21:04 GMT [some editing was made here to make the explanation conform to the convention used here].

Many people seem to assume that the three "fixed axis" rotations have to be one each around X, Y, and Z. Not true. I find that a much more intuitive set of Euler angles is produced by using the Z,Y,Z choice of axes. (Z,X,Z is very similar.)

Let me illustrate: Most of you are reading this sitting in a chair at a desk. Let's assemble a completely general rotation allowing you to point at any place on the floor, walls, or ceiling (2 degrees of freedom) with any tilt to your head (1 degree of freedom).

Global coordinate system: Z is up, X is front-to-back (pointing towards you), Y is left-to-right. This system will stay attached to your desk as you move.

#### Rotation 1:

About the Z axis. Turn your chair so that the chosen point is ahead of you. It may still be up on the ceiling, or down on the floor, but it should be in the plane of symmetry of your body. (A swivel chair is great to have here!)

First intermediate coordinate system: Z is still up (because we rotated around Z). X is your new front-to-back (you left the global X attached to the desk). Y is your new left-to-right, attached to the arms of your chair.

#### Rotation 2:

About the Y axis. Tilt forward or backward until your head is pointing at the chosen point. Ignore the strange looks from your office mates.

Second intermediate coordinate system: Z comes out of the top of your head. Y is the same as it was in the previous (first intermediate) coordinate system because we rotated around Y. X is no longer horizontal w.r.t. the room.

#### Rotation 3:

About the Z axis. Turn your head. (Try not to fall out of your chair.)

Final coordinate system: Z (coming out of the top of your head) points at any desired point. The final rotation has allowed you to point your nose (X) in any direction perpendicular to Z.

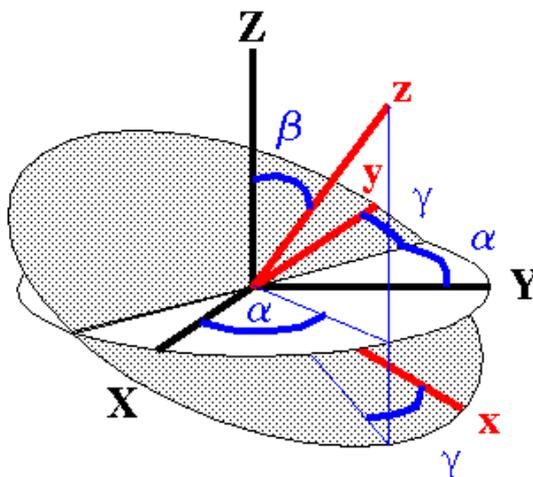
You can think of the three angles as "azimuth, altitude, tilt", or "longitude, latitude, tilt", or whatever.

An additional advantage of the Z,Y,Z formulation is that its inverse is also in the same Z,Y,Z formulation.

### 3.12.17 Determining Euler Angles

Given the relative orientations of two coordinate systems, how does one go about determining the Euler angles relating them?

First, one needs to decide which coordinate system to take as the **reference coordinate system**,  $X,Y,Z$ , and which one as **derived coordinate system**,  $x,y,z$ . Because the Euler transformations allow to switch between coordinate systems easily, it does not matter which one is selected.



The angle  $\beta$  is simply the angle between the  $z$  axes of both coordinate systems. The angle  $\alpha$  is the angle between the  $X$  axis of the reference coordinate system and the projection of  $z$  into the  $X,Y$  plane. Finally,  $\gamma$  is the angle between the  $y$  axis and the line of nodes.

### 3.12.18 Electric Field Gradient Tensor

A quadrupolar nucleus  $S$ , with nuclear spin  $S > 1/2$ , is subject to an interaction of the nuclear quadrupole moment,  $eQ$ , with the component of the electric field gradient (EFG) along a particular direction,  $V_{ii} = eq_{ii}$ . The Laplace equation requires that the trace of the EFG tensor is zero. In addition, the EFG tensor is symmetric, hence consists only of 5 independent components. In its principal axis system (PAS),  $XYZ$ , the EFG tensor is diagonal and can be characterized by the three principal components  $V_{XX}$ ,  $V_{YY}$ ,  $V_{ZZ}$ . In nuclear quadrupole resonance (NQR), the principal components are labelled according to this convention:

$$|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$$

Because of the trace of zero, only two independent parameters are required to characterize the magnitudes of the principal components, and these are usually chosen to be  $V_{ZZ}$  and the dimensionless asymmetry parameter  $\eta$ . The product of  $V_{ZZ}$  and the nuclear quadrupole moment is known as the quadrupolar coupling constant,  $\chi$ :

$$\chi = \frac{eV_{ZZ}Q}{h} = \frac{e^2q_{ZZ}Q}{h}$$

$$\eta = (V_{XX} - V_{YY}) / V_{ZZ}$$

Thus,  $\eta$  is constrained to values between 0 and 1. The quadrupolar coupling constant should not be mixed up with the quadrupolar frequency, observed in NQR experiments.

### 3.12.19 Central Transition (CT) and Satellite Transitions (ST)

For a quadrupolar nucleus, with a nuclear spin greater than  $1/2$ , as observed nucleus, one can select calculation of the central transition,  $1/2 \leftrightarrow -1/2$ , spectrum only (CT), of the satellite transition,  $m \leftrightarrow m - 1$  with  $m \neq 1/2$ , spectrum only (ST), or of all transitions.

CT	ST	Action
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Calculates the total spectrum consistin of central transition and satellite transitions.
<input checked="" type="checkbox"/>	<input type="checkbox"/>	Calculates spectrum only including the central transition. Note that quadrupolar nuclei of integral spin don't have a central transition!
<input type="checkbox"/>	<input checked="" type="checkbox"/>	Calculates spectrum only including the satellite transitions.
<input type="checkbox"/>	<input type="checkbox"/>	This wouldn't calculate anything, therefore the default action is to calculate the central transition.

### 3.12.20 Spinning Frequency

The spinning frequency is required in Hz. Although the sense of rotation does not affect the spectrum, valid values are limited to postivie numbers. WSolids11 allows to have different spinning frequencies for different sites, although this doesn't make sense physically. This design flaw has been remedied in WSolids2.

### 3.12.21 Speedy Calculation

Some calculations are quite time consuming. In such cases, it is possible to select **Speedy calculation**, in which case only  $1/16$  of the orientations will be included. This is usually sufficient to reproduce the gross features of the line shape, but this gain in speed is bought at the expense of accuracy. In any case, a final calculation with Speedy Calculation disabled should be performed to verify the parameters.

## 4 Acknowledgements



### Contents

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4.1 Credits	81
4.2 Trademark Acknowledgements	82
4.3 Copyright Information	82
4.4 Disclaimer of Warranty	82

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### 4.1 Credits

- Some of the early FORTRAN modules were written by:  
**William P. Power** (dipolar-chemical shift NMR, quadrupolar powder patterns QUADPOW and SECQUAD)  
**Gang Wu** (dipolar-chemical shift NMR of homonuclear spin pairs)
- This program contains for space-tiling and interpolation purposes the POWDER routine. We are grateful to **D. W. Alderman** for a copy of the routine in FORTRAN.  
D. W. Alderman; M. S. Solum; D. M. Grant; *J. Chem. Phys.* **1986**, *84*, 3717.
- We learned a lot from **A. C. Olivieri**'s BASIC program ANYCHI to calculate the MAS spectrum of a spin-1/2 nucleus coupled to a spin-3/2 nucleus:  
S. H. Alarcon; A. C. Olivieri; R. K. Harris; *Solid State Nucl. Magn. Reson.* **1993**, *2*, 325.  
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- “chicks” for demonstrating in his [pdfp](http://www.esnips.com/web/PDFTools) PDF tools how to establish Dynamic Data Exchange (DDE) with Adobe Acrobat (Reader) (<http://www.esnips.com/web/PDFTools>)
- This manual has been produced using the MiKTeX (<http://www.miktex.org>) distribution of L<sup>A</sup>T<sub>E</sub>X in combination with the TeXnicCenter editor (<http://www.ToolsCenter.org>).

## 4.2 Trademark Acknowledgements

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# Index

- A2, [55](#)
- AB, [56](#)
- absolute shielding, [59](#)
- absolute value, [36](#)
- absorption, [29](#)
- abundance, [60](#)
- accelerators, [14](#)
- acknowledgements, [69](#)
- alpha, [61](#)
- anisotropy in indirect coupling, [61](#)
- apodization, [27, 28](#)
- AX, [55](#)
  
- beginner, [5](#)
- beta, [61](#)
- Bruker, [19, 20](#)
- bugs, [39](#)
  
- calculation, [24, 32](#)
- central transition, [67](#)
- changes, [10](#)
- Chemagnetics, [21](#)
- chemical shift, [59](#)
- chemical shift anisotropy, [41, 42, 44, 46, 48](#)
- chi, [66](#)
- convention, [57, 59](#)
- convolution, [26–28, 35](#)
- copyright, [70](#)
- coupling, [60, 61](#)
- credits, [69](#)
- cycle, [32](#)
  
- D, [34, 60](#)
- derivative, [29](#)
- dipolar, [42, 44](#)
- dipolar coupling, [60](#)
- dipolar coupling constant, [34](#)
- disclaimer, [70](#)
  
- edit site, [32](#)
- electric field gradient, [66](#)
- elements, [35](#)
- eta, [66](#)
- Euler angles, [62, 65, 66](#)
  
- F1, [26](#)
- F2, [26](#)
- features, [6](#)
- files, [18–22](#)
  
- gamma, [34](#)
- Gaussian, [28](#)
  
- Haeberlen, [57](#)
- help, [38](#)
- Herzfeld-Berger, [48, 57](#)
- heteronuclear, [42, 46, 49, 50, 52, 54, 55](#)
- history, [10](#)
- homonuclear, [42, 44, 46, 55, 56](#)
- Hz, [25](#)
  
- indirect coupling, [60, 61](#)
- intensity, [57](#)
- introduction, [6, 9](#)
- isotopic labelling, [60](#)
  
- J, [60, 61](#)
- JCAMP-DX, [21](#)
  
- keyboard, [14](#)
  
- Larmor frequency, [25](#)
- license, [6](#)
- line broadening, [27, 28](#)
- Lorentzian, [28](#)
  
- MAS, [48–50, 52, 54, 67](#)
- MDI, [12](#)
- menus, [15](#)
- model, [31](#)
- multiple documents, [12](#)
- multiple spectra, [12](#)
  
- natural abundance, [34, 60](#)
- nuclear properties, [34](#)
- nuclei, [35](#)
- nucleus, [25](#)
  
- offset, [36](#)
- overview, [9](#)
  
- periodic system, [35](#)
- polar angles, [61](#)
- ppm, [25](#)
- problems, [39](#)
- program version, [38](#)
  
- Q, [34](#)
- quadrupolar, [46, 49, 50, 52, 54](#)
  
- R, [34](#)

reverse spectrum, [36](#)  
revision, [10](#)  
rotations, [62](#), [65](#), [66](#)

satellite transition, [67](#)  
scaling, [35](#)  
SF, [25](#)  
shielding, [59](#)  
shift, [59](#)  
SI, [25](#)  
Simpson, [22](#)  
simulation, [24](#)  
site, [30–32](#)  
SOLIDS, [21](#)  
spectrometer frequency, [25](#)  
spectrum, [18](#), [22](#), [24](#), [26](#), [35](#), [36](#)  
spectrum size, [25](#)  
spin, [34](#)  
spin pair, [42](#), [44](#), [46](#), [49](#), [50](#), [52](#), [54–56](#)  
spin system, [30](#), [31](#)  
spinning, [67](#)  
SpinSight, [21](#)  
standard, [57](#)

tie, [57](#)  
tools, [34](#)  
TopSpin, [19](#)  
trademarks, [69](#)  
trouble, [6](#)

Varian, [22](#)  
VAS, [55](#), [56](#)

warranty, [70](#)  
window, [37](#)  
WinNMR, [20](#), [22](#)

XWINNMR, [20](#)  
XWinNMR, [19](#)