HBA — Herzfeld-Berger Analysis

User Manual

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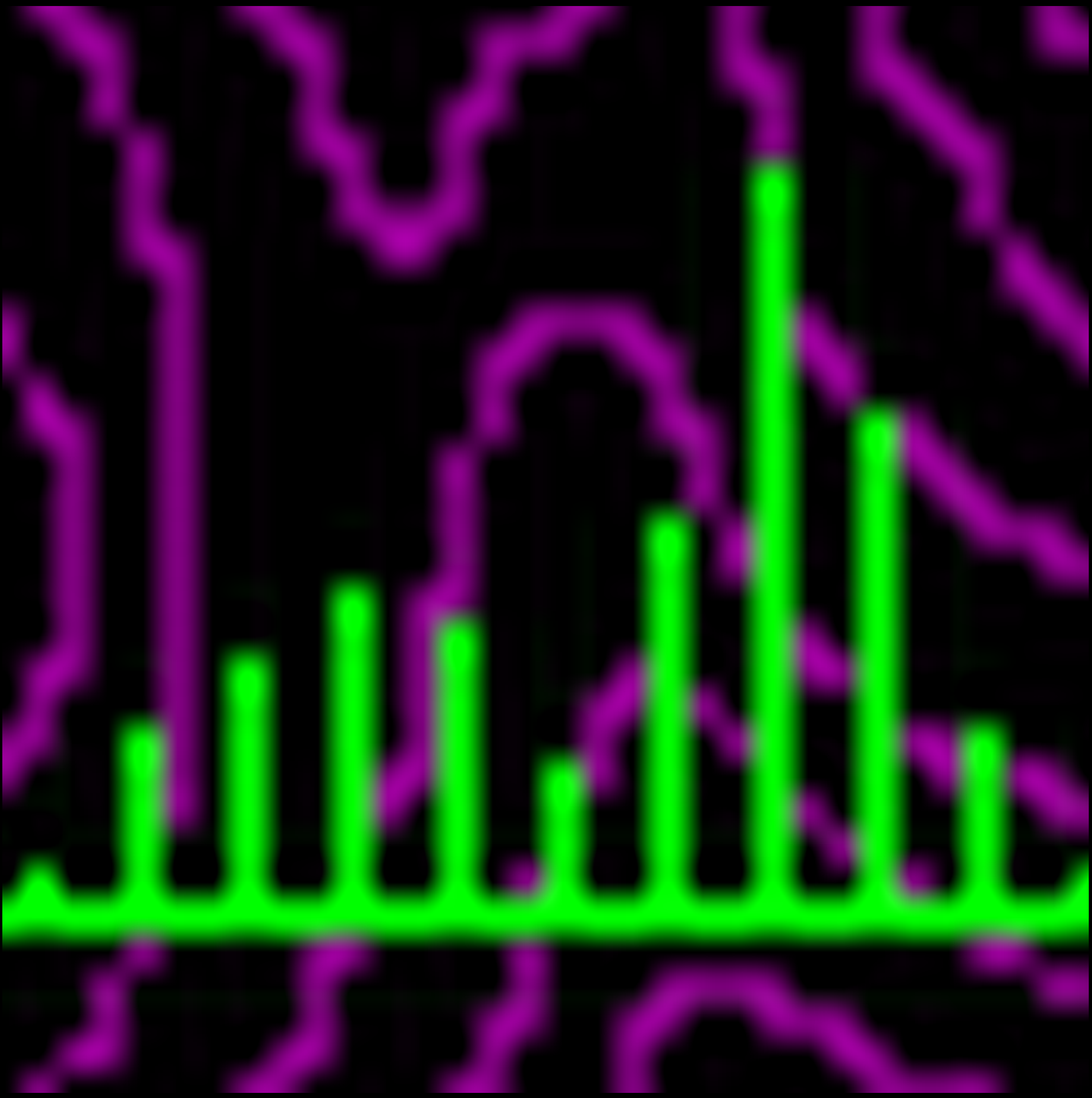

Contents

1 Getting Started

This chapter covers the following topics:

Introduction	An introduction to HBA
Overviews	An overview of some of the common tasks and actions
Revision History	Summary of changes versus previous versions
Acknowledgements	Credits for important contributions etc.

1.1 Introduction

1.1.1 Purpose of the program

HBA derives its name from the first letters of the term **H**erzfeld-**B**erger **A**nalysis [1]. And it simply does just that: it is aimed at assisting the NMR experimentalist in analyzing spinning-sideband intensities in magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra using the Herzfeld-Berger approach to obtain the principal components of nuclear spin interaction tensors. There are already several programs available doing this also, so why another one?

The primary reason why I wrote this program was to gain some experience in iterative data fitting. The Herzfeld-Berger analysis could be considered as one of the simpler problems in iterative fitting, because it requires “only” two parameters to be fitted. However, the nature of the data requires to use non-linear least-squares techniques with the additional problem of boundaries, imposed on the μ parameter by the size of the data tables and on the parameter ρ by the very definition of the skew of a tensor. Also, the iterative procedure is subject to the problem of local and global minima.

The second reason has to do with something that the other programs don’t do. Herzfeld and Berger [1] suggested that their method could be used as a graphical approach to the problem of determining the tensor parameters. During the first few years of my dabbling in solid-state NMR, I used to analyze hundreds of MAS spectra by drawing and tracing contour lines on transparencies and determining the intersections. Certainly tedious, but also quite instructive! With the aid of a computer, this can be done in a much pleasanter way.

HBA is a simulation package developed during my stay at the Department of Chemistry, Dalhousie University, Halifax, Canada. The initial version has been written in C++ using Borland C++ 4.52 and has been developed to run on IBM-compatible personal computers under the MS-Windows environment in the 16-bit subsystem. For the 32-bit version, Borland C++ 5.0 has been used initially. The current version has been produced using Microsoft Visual C++ 2008 Express Edition. HBA is actually a spin-off of a larger package, WSolids, aimed at simulating solid-state NMR spectra for a variety of nuclear spin interactions and experimental conditions.

Figure 1.1: Dalhousie University chemistry department.

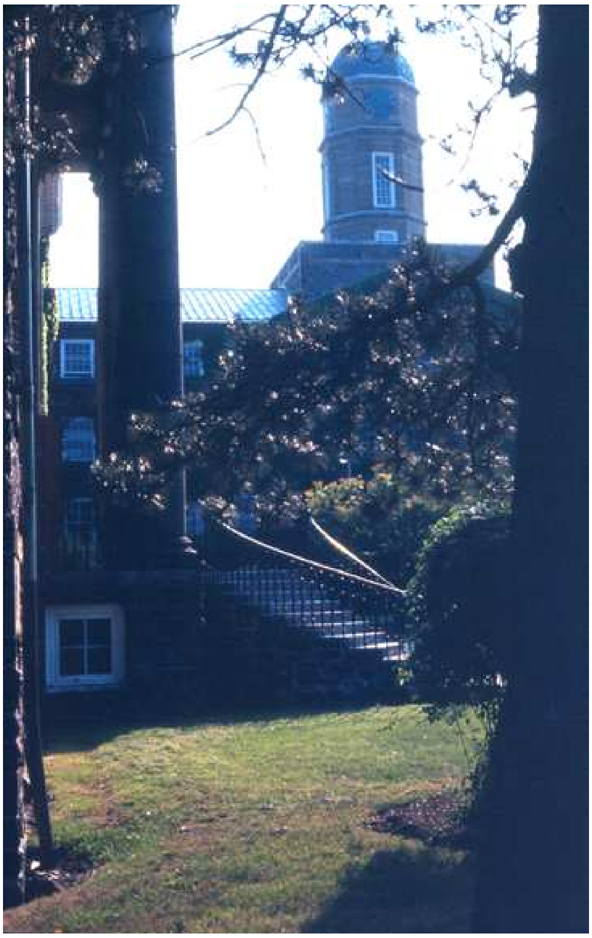

Figure 1.2: Dalhousie University administration building and faculty club (left).

1.1.2 Features

- Extended Herzfeld-Berger tables, allowing spinning sideband orders in the range from -30 to +30, and values of μ in the range $0 \leq \mu \leq 50$ (the original tables have ±5 spinning sidebands and $0 \leq \mu \leq 15$).
- Intensities can be entered manually or parsed from peak-picking or integration files.
- The intensities can be displayed as contour diagrams, giving a very instructive visualization of the quality of the data.
- The initial guess required for the iterative refinement may result from a systematic grid-search or can be entered interactively. This provides different starting positions for the fitting procedure.
- The iterative refinement of the starting guess is achieved via the Marquardt-Levenberg nonlinear least-squares fitting procedure.
- The best fit can be graphically displayed as symbol in the contour plot or by comparison of stick spectra using experimental and calculated intensities.
- The error surface can be displayed as contour diagram and exported as text file for use with spread sheet applications.
- The output also includes the results of a moment analysis of the spinning sideband intensities.
- So far, HBA doesn't read and fit experimental spectra.

1.1.3 License

This program package can be used by any individual or organization without any fee, as detailed in the Copyright statement. If you find this program useful and publish results obtained by using HBA, we would appreciate if you cite this program as:

HBA 1.8.1, K. Eichele, Universität Tübingen, 2021.

1.1.4 Troubleshooting

Although HBA has been tested and used both in-house and by others, it is always possible that errors still 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. As stated in the Disclaimer, we disclaim all warranty. 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 always welcome:

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1.2 Overview

The ordering in this list corresponds to the order of actions taken in a typical session. New users may want to follow each step in sequence.

Action	How to achieve this action
Enter intensities	Before starting the Herzfeld-Berger analysis, input of the spinning sideband intensities is required. Basically, there are three different ways of entering the spinning sideband intensities: • Enter the intensities manually (p. 12) • Read an integration or peak picking file (p. 13) • Read a previous session (p. 23)
Display contours	After the intensities of the spinning sidebands have been entered, one can display the corresponding contour lines: Show contours (p. 26) One can use the Data reader (p. 28) to query the principal components of the chemical shift tensor corresponding to a specific μ,ρ (p. 42) pair or to set an initial guess (p. 29) for the iteration (p. 29).
Simulate interactively	One can simulate the experimental data by using the simulation feature. The Herzfeld-Berger parameters are simply modified via two scroll bars, and the effect is shown in real time as comparison of stick spectra: Simulate (p. 36). This feature sets also an initial guess (p. 29) for the iterative refinement (p. 29).
Enter initial guess	The iteration procedure requires an initial guess (p. 29) on the parameters to be refined. There are three ways to obtain this guess: • the default action, a grid search, is performed automatically if there are no user defined starting values (selection of rms error (p. 27) display also performs a grid search and updates the initial guess, if no iteration of the data has been performed) • one can use the data reader (p. 28) • one can use the interactive simulation (p. 36)
Iterative refinement	Starting from an initial guess, a Marquardt-Levenberg algorithm is employed to find the best fit (p. 29) to the experimental data. The result can be examined by using: • the contour display (p. 26) • the comparison (p. 35) of experimental and calculated intensities • the display of rms errors (p. 27) as contours • the text report (p. 34) file generated by the fitting procedure • the error surface about the best fit can be exported using the error inspector (p. 31)

Output fitting result	Output options for the fitting results: • the report (p. 34) action opens the text file generated by the fitting procedure; • creation of a graphics meta file (*W*indows *M*eta *F*ile format) selected from the file menu, using the Meta file (p. 24) menu item; • export to a file, for later use as spin system file (p. 24) in WSolids; • save the session data to a data file (p. 23) for later retrieval/continuation

1.3 Revision History

This page summarizes the changes made compared to previous versions of HBA. Experienced users may use this information as a quick update on new program features.

New in Version 1.8.1 (20.05.2021):

- New feature: the Herzfeld-Berger tables got recalculated to allow for more spinning sidebands and greater spans: spinning sideband orders in the range from -30 to +30, and values of μ in the range $0 \leq \mu \leq 50$ are now possible (compared to ± 15 ssbs and $\mu \leq 30$)
- New feature: using the Error Inspector (p. 31), the error surface about the best fit can be exported as text file for use with spread sheet applications.
- New feature: an error analysis of the initial guess (p. 29) is also included in the report (p. 34).
- New feature: the output also includes the results of a moment analysis (p. 60) of the spinning sideband intensities.
- New feature: deal with TopSpin 3.x and 4.x peak picking (p. 14) files, and with SpinWorks 4 peak picking lists
- Bug fix: fixed bug in the calculation of $R = marg^2/cond^2$ (thanks to Abil Aliev) and the calculation of the error in δ_{33}
- Neither bug nor feature: determination of the Adobe Acrobat version looks up now a registry key to determine the proper version of the Acrobat DDE server

New in Version 1.7.5 (17.04.2015):

- New feature: the location of the INI file (p. 38) has changed: in the pograms directory for the portable version, or in the user's documents directory.
- New feature: added support for PDF-XChange Editor (by Tracker Software Products, Ltd., `http://www.tracker-software.com`) as PDF viewer to display context sensitive help.
- Bug fix: the relative scaling of experimental and calculated stick spectra did not always work properly.

New in Version 1.7.3 (23.08.2012):

- New feature: when selecting Report (p. 34) the result file is now written in the users documents path.
- New feature: reading of peak picking and integrals files got combined into one function, Read Integrals/Peak Lists (13), HBA itself figures out the file format. Also, TopSpin native peak lists and SpinWorks peaks and integrals can be retrieved.
- New feature: included Olivieri's error treatment in the iteration (p. 29); the normalized intensities of spinning sidebands and center band are now fitted instead of fitting the ratios.
- New feature: added support for other PDF viewers to display context sensitive help: added handling of PDF XChange Viewer (by Tracker Software Products, Ltd., `http://www.tracker-software.com`), **currently my prefered PDF viewer**, and Sumatra PDF Viewer (`http://blog.kowalczyk.info/software/sumatrapdf`), also deal with the new Adobe Reader X.
- Modified: the Background Information (p. 41) section in the documentation got expanded

(caveats, alternatives).

New in Version 1.6.14. (27.05.2010):

- The result of the iteration can now be written as spin system file (p. 24) for later retrieval in WSolids1

New in Version 1.6.12. (02.01.2010):

- Added handling of TopSpin integrals (p. 13) and peak lists (p. 13).
- Added command line parameters (p. 39) to supply information on spectrometer reference frequency, spinning frequency, and isotropic chemical shift

New in Version 1.6.9. (06.01.2009):

- switched to a different development platform: Microsoft Visual C++ 2008 Express Edition; the user interface has thus changed a little
- introduced a level selection tool (p. 28) for the contour display; this allows to select/deselect the levels to be displayed
- the documentation/help is now in Adobe Acrobat PDF format; for context sensitive help from HBA, Acrobat Reader or Acrobat Professional is required. Just for viewing the PDF file, any PDF reader should work.
- abandoned the 16bit line, HBA32 is now hba.exe! (If someone is desperate to use the old file names, everything should work if the hba.exe, hba.ini and hba.pdf are renamed to hba32.*, or any name.*)

New in Version 1.5.8. (07.07.2005):

- bug fix: entering data in the **Enter intensities, Read Peaklist, Read Integrals** dialog boxes did not work (caused by the transition from 16 to 32 bit Windows).

New in Version 1.5.1. (26.01.2005):

- most importantly: **first 32 bit Windows release**
- dealt with enabling/disabling of toolbar buttons in a better way, added tooltips
- introduced command line parameters (p. 39) for reading of sessions, peak picking lists, or integral lists, etc.

New in Version 1.4.4 (29.05.2001):

- started to work on calculation of fit parameter errors, but this is not ready yet
- more important: incorporated new, recalculated Herzfeld-Berger tables (calculations took roughly a week on a Pentium 400 MHz under Windows NT 4, each spectrum required ca. 1200 seconds)
- added writing and reading of session data as ini type file (Read session (p. 23), Write session (p. 23))
- source of intensity data is now documented in the output (p. 34) (if information is available)
- increased the sensitivity of the scroller bar in interactive simulation (Simulate (p. 36))

New in Version 1.3.1 (15.06.1999):

- Upon startup, HBA is automatically in contour display mode (p. 26), using data from the previous session, if available.
- Included a Setup dialog (p. 25), where the user can customize color settings directly instead of editing the INI file (p. 38).
- In contour display mode (p. 26), display of initial guess (p. 29) and iteration result (p. 29) can be toggled individually

New in Version 1.2.12 (10.10.1998):

- In reading peak picking (p. 13) or integral (p. 13) files, the estimation of the isotropic chemical shift is done via analysis of the first moment
- Fixed a few bugs

New in Version 1.2.10 (09.04.1998):

- The result of the iteration can now be written as spin system file (p. 24) for later retrieval in

WSolids 2.0
- The rms errors (p. 27) can be displayed as contour plots. This required that the grid calculation uses a finer step size.
- INI (p. 38) file contains some additional parameters
- The menu got rearranged a little

New in Version 1.2.9 (10.03.1998):

- The default extension for peak picking (p. 13) and integral (p. 13) files is now set to .TXT (as produced by WinNMR)
- The format of the output (p. 34) file changed:
  - The .LOG entry in the first line, forcing Notepad to append date and time, got removed. Date and time are now given in the file header
  - Derived tensor parameters, using different conventions (p. 42), are also listed
- The initial guess (p. 29) is now shown in the contour plot as a small circle.
- The **About** dialog box shows now detailed version and system information.
- The dialog box for input of intensities got changed in layout.
- The help file documents INI file (p. 38) settings.

New in Version 1.2.5 (06.08.1997):

- Added a menu item File | Meta file (p. 24) to create a meta file containing the graphics shown on screen

New in Version 1.2.4 (05.08.1997):

- Added entries to ini file which allow customization of background and control colors (colors for contours were available previously)

New in Version 1.2:

- Added reading of WinNMR 5.0/5.1 integration (p. 13) or peak picking (p. 13) files (ASCII)
- Added a data reader (p. 28) to the contour display; one can set an initial guess for the iteration using this option
- Added interactive simulation of the experimental spectrum; one can also set an initial guess for the iteration using this option

New in Version 1.1:

- Only some minor improvements in the display

1.4 Acknowledgements

This section covers the following topics:

	Credits	Credits for important contributions
	Trademarks	Trademark acknowledgements
	Copyright	The obligatory copyright statement
	Disclaimer	The obligatory disclaimer message

1.4.1 Credits

- **Dr. Alejandro C. Olivieri** kindly provided BASIC programs that
  - taught me how to calculate spinning sidebands in the frequency domain:
    Olivieri, A. C. *Solid State Nucl. Magn. Reson.* **1997**, *10*, 19-24, DOI: 10.1016/S0926-2040(97)00023-4;
    Olivieri, A. C. *Solid State Nucl. Magn. Reson.* **1998**, *11*, 181-187, DOI: 10.1016/S0926-2040(98)00035-6;
    the extended tables used by `HBA` since 2001 are tables that I calculated using a home-made program, based on this knowledge;
  - helped me to figure out how to do an estimation of fitting errors:
    Olivieri, A. C. *J. Magn. Reson., Ser. A* **1996**, *123*, 207-210, DOI: 10.1006/jmra.1996.0237.
- **He Sun** (Washington University in St. Louis) suggested addition of error calculation for the initial guess.
- **Dr. Abil E. Aliev** (University College London) for reporting the bug in R_i (implementation of Eq. 2.5).
- **Prof. Dr. Cecil Dybowski** (University of Delaware) for suggesting a different place for the report.
- **Dr. Michael H. Frey** (Jeol) for suggesting the use of command line parameters and for beta testing.
- **Dr. William P. Power** performed the calculations to extend the original Herzfeld-Berger tables to 15 spinning sidebands and for μ to range up to 30. These extended tables were used by HBA up to 2001.
- **Drs. Judith Herzfeld** and **Alan E. Berger** kindly provided to Dr. William P. Power the code to generate the extended tables. The original reference:
  J. Herzfeld, A. E. Berger, *J. Chem. Phys.* **1980**, *73*, 6021-6030.
- **Dr. A. Kentgens** kindly provided the program `HBLSQFIT`, which we used prior to `HBA`, and which also employed Bill Power's extended tables.
- The contouring algorithm is relatively simple but works sufficiently well. It follows the BASIC subroutine `CONREC` written by **Paul D. Bourke**:
  BYTE **1987**(6), 143-150.
- The algorithms for bicubic spline interpolation and Marquardt-Levenberg non-linear least-squares procedures are adopted and adapted from:
  W. H. Press, S.A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in C*, Cambridge University Press: Cambridge 1992.
- Microsoft for providing `Visual C++ 2008 Express Edition` for free
- Jordan Russell for making `Inno Setup` available (`http://www.jrsoftware.org/`)
- Jochen Kalmbach for demonstrating how to statically link against the Microsoft CRT and thus

get rid of `VCREDIST_X86.EXE` (`http://blog.kalmbach-software.de`)

- "chicks" for demonstrating in his `pdfp` PDF tools how to establish Dynamic Data Exchange (DDE) with Adobe Acrobat (Reader) (`http://www.esnips.com/web/PDFTools`, website not available anymore).
  Here are some "substitute kudos" pages: `http://www.quickpdf.org/forum/printdocument-blank-pages_topic688.html` or `https://www.techrepublic.com/forums/discussions/want-to-print-pdfs-from-access-form/`.
- This manual has been produced using the MiKTEX (`http://www.miktex.org`) distribution of LATEX in combination with the TeXnicCenter editor (`http://www.ToolsCenter.org`).
- `IrfanView` (`http://www.irfanview.com/`) has been used to process bitmapped images, and `Inkscape` (`www.inkscape.org`) for dealing with vector graphics.

1.4.2 Trademarks

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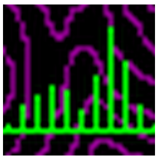
1.4.3 Copyright Information



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2 Reference

This section covers the following topics:

Help on Menu Items	Explains the meaning of specific menu items
Help on Button Bar Items	Explains the actions of specific buttons
INI File Settings	Documents the INI file parameters
Command Line Parameters	Documents the parameters that can be passed to HBA on the command line
Known Problems	Summarizes known problems

2.1 Help on Menu Items

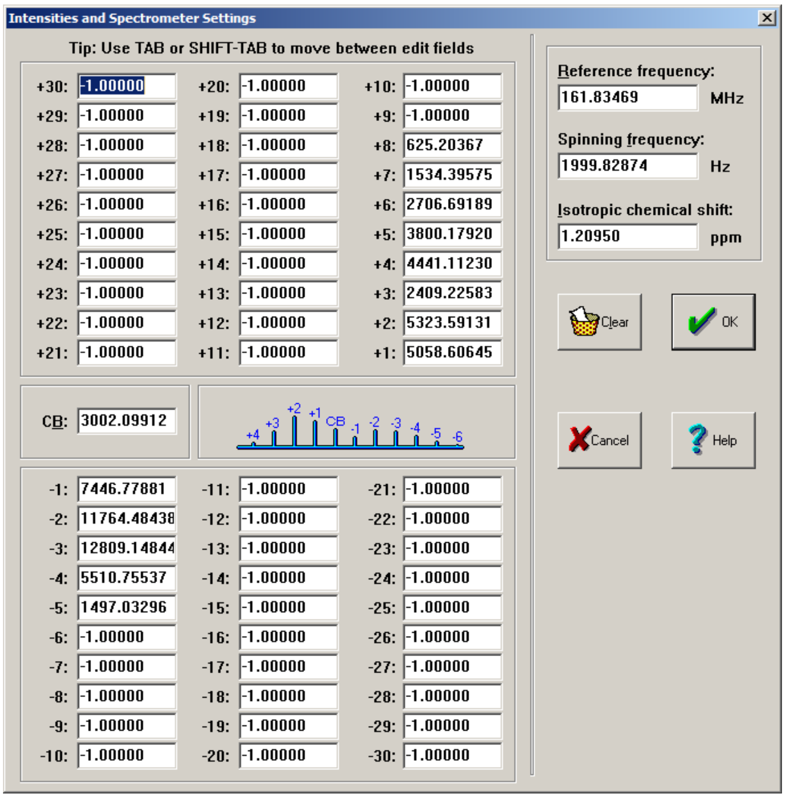
Category	Menu Item	Action
File	Enter intensities (p. 12)	Enter spinning sideband intensities manually
	Read integrals / peak lists... (p. 13)	Read spinning sideband intensities from an integration file or peak picking file
	Read session (p. 23)	Retrieve parameters (intensities, fitting results etc.) from a previous session with HBA
	Write session (p. 23)	Save parameters (intensities, fitting results etc.) to a file for later retrieval
	Write meta file (p. 24)	Creates a graphics file in Windows meta file format
	Write spin system (p. 24)	Writes chemical shift tensor information into a WSolids spin system file
	Setup (p. 25)	Customize color settings
	Exit (p. 25)	Exit HBA
Contours	Show contours (p. 26)	Display contour lines using the Herzfeld-Berger nomograms
	Show rms (p. 27)	Display rms errors as contour levels
	Show fit (p. 28)	Toggle display of iteration result on/off
	Show initial guess (p. 28)	Toggle display of initial guess on/off
	Show level selector (p. 28)	Toggle display of level selector tool on/off
	Data reader (p. 28)	Use the mouse to read data off the Herzfeld-Berger nomograms or to set an initial guess
Fit	Discard initial guess (p. 29)	Discards the user defined starting guess for the iterative refinement

Iterate (p. 29)	Starts the iterative refinement of the Herzfeld-Berger parameters
Report (p. 34)	Show the fitting results by calling Notepad
Compare (p. 35)	Compare the experimental and fitted sideband intensities using stick spectra
Simulate (p. 36)	Simulate the experimental sideband intensities interactively

2.1.1 Enter Intensities

The dialog box **Enter Intensities** is available from:

- the menu via **File | Enter intensities**
- by using the button bar
- by using the keyboard accelerator key **E**.



Tip: Use TAB or SHIFT-TAB to move between edit fields

+30:	-1.00000	+20:	-1.00000	+10:	-1.00000
+29:	-1.00000	+19:	-1.00000	+9:	-1.00000
+28:	-1.00000	+18:	-1.00000	+8:	625.20367
+27:	-1.00000	+17:	-1.00000	+7:	1534.39575
+26:	-1.00000	+16:	-1.00000	+6:	2706.69189
+25:	-1.00000	+15:	-1.00000	+5:	3800.17920
+24:	-1.00000	+14:	-1.00000	+4:	4441.11230
+23:	-1.00000	+13:	-1.00000	+3:	2409.22583
+22:	-1.00000	+12:	-1.00000	+2:	5323.59131
+21:	-1.00000	+11:	-1.00000	+1:	5058.60645

CB: 3002.09912

-1:	7446.77881	-11:	-1.00000	-21:	-1.00000
-2:	11764.48438	-12:	-1.00000	-22:	-1.00000
-3:	12809.14844	-13:	-1.00000	-23:	-1.00000
-4:	5510.75537	-14:	-1.00000	-24:	-1.00000
-5:	1497.03296	-15:	-1.00000	-25:	-1.00000
-6:	-1.00000	-16:	-1.00000	-26:	-1.00000
-7:	-1.00000	-17:	-1.00000	-27:	-1.00000
-8:	-1.00000	-18:	-1.00000	-28:	-1.00000
-9:	-1.00000	-19:	-1.00000	-29:	-1.00000
-10:	-1.00000	-20:	-1.00000	-30:	-1.00000

Reference frequency: 161.83469 MHz

Spinning frequency: 1999.82874 Hz

Isotropic chemical shift: 1.20950 ppm

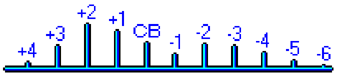
Figure 2.1: Dialog "Enter Intensities"

Purpose

- This dialog box serves to enter the intensities of the spinning sidebands and of the center peak manually. It also contains the parameters defining the spectrum settings, i.e. reference frequency, spinning rate, and isotropic chemical shift.

- One can also use this dialog box to check the result from parsing integration or peak picking (p. 13) files.
- Units for the intensity data are irrelevant because all data will be normalized with respect to the intensity of the center peak.
- The intensities might have been obtained by using a ruler and measuring the peak heights, using a peak picking listing with intensities, or by integrating the experimental spectrum.

Convention



The convention used in the HBA program for numbering the spinning sidebands is indicated by the picture. It follows the direction of the frequency axis, i.e. spinning sidebands to high frequency of the center peak have positive ordinal numbers, spinning sidebands to the low frequency side of the center peak have negative ordinal numbers (note that the Herzfeld-Berger paper uses the opposite convention, because they use a magnetic shielding convention instead of a chemical shift convention). The absolute value of the ordinal number increases with the separation of the spinning sideband from the center peak.

Clear Button

By default, HBA loads the intensities used in the last session from the HBA.INI file. Use the **Clear** button to reset the contents of each field. This action will set the intensities of all spinning sidebands to -1 and the intensity of the center peak to 1.

Neglecting Spinning Sidebands

Use a negative intensity to indicate that a spinning sideband should be neglected in the iterative calculation. This option is not allowed for the center peak. Neglecting sidebands may cause HBA to fall into a false, local minimum. One might be better off guessing the intensity of a sideband than in neglecting it.

2.1.2 Read Integrals/Peak Lists

The option to read an integration file is available from:

- the menu via **File | Read integrals/peak lists**
- by using the keyboard accelerator key **P**.
- the command line (p. 39)

The purpose of this action is to retrieve peak position - intensity data pairs from a specified file. This file may contain integrals or a peak picking list, produced by any of the programs detailed below. In older versions of HBA (pre 1.7), the user had to preselect the kind of file, integrals or peak picking, then specify the file name. Current versions of HBA will try to figure out the kind of file and the software producing the file. Currently, the following file formats are recognized (more details will be provided in the following subsections):

- Bruker **TopSpin** 2.1, 3.6 and 4.0 peak picking (p. 14) and integrals (p. 17) (other TopSpin versions may work as well, but have not been checked)
- Bruker **XWinNMR** 3.5 peak picking and integrals (p. 17)
- Bruker **WinNMR** (5.0, 5.1, or 6) peak picking or integrals files (p. 20) in ASCII format.
- Kirk Marat's (University of Manitoba) **SpinWorks** (3.1 and 4.x) peak picking or integrals (p. 18), `ftp://davinci.chem.umanitoba.ca/pub/marat/SpinWorks`

If your NMR files do not correspond to any of the Bruker formats specified above or originate from a different vendor, consider using SpinWorks to process your data.

A few other points are worth considering:

- If your spectrum contains several sites that need to be analyzed separately, be aware that most of the above processing software packages write their data to a file of constant, fixed name. Hence, analyzing a second site will overwrite the data of the first site. The following subsections on file formats will contain some hints on that.
- Should you use peak picking or integrals? Integrals are more robust with respect to small variations in spinning speed (the spinning sidebands will show a systematic increase in line width with increasing order of the spinning sideband) but require excellent signal to noise ratios and well defined baselines. If spinning is stable, peak picking is not worse than integration, is often done quicker (especially for spectra containing only one spinning sideband family), and with low signal to noise ratios may even give better results than integrals [2].

Once **File|Read Integrals/Peak Lists...** has been selected from the menu, HBA opens a dialog box to retrieve the name of the file containing the integrals or peak-picking results. After parsing the file, HBA prompts for input to define the “reference frequency” (frequency of the chemical shift standard), spinning rate, and isotropic chemical shift, using the dialog box Define Spectrum Settings (p. 23). Using the information contained in the files, HBA attempts to guess these values:

- The reference frequency is determined from the ratio of the frequency/ppm values given for the peak position or integrals, if available. The TopSpin peak picking format has the disadvantage that it does not contain sufficient information to work out the reference frequency. Hence, its default value is set to 1 MHz. HBA will recalculate the spinning frequency if you enter the correct reference frequency and move away the cursor (e.g., hit the Tab key on the keyboard).
- The average distance between peaks or integrals serves as a default for the spinning rate in Hz (if a proper value for the reference frequency has been retrieved) or in ppm (if the reference frequency could not be determined).
- The isotropic peak is determined by an analysis of the first moment.

It is crucial that these values are set properly! You can check or modify the result using Enter Intensities (p. 12).

TopSpin Peak Picking Files

The native file name is `peaklist.xml` (see also XWinNMR Peak Picking Files (p. 17)), but HBA does not care. If your spectrum contains several sites, I recommend the following procedure: perform peak picking for site 1 and save the result, copy `peaklist.xml` to `peaklist1.xml` for site 1, peak pick site 2, copy `peaklist.xml` to `peaklist2.xml` etc. This way you can make the data available to TopSpin again by copying `peaklist2.xml` back to `peaklist.xml`.

Note that the file `peaklist.xml` does not provide sufficient information to determine the reference frequency (default value: 1 MHz). If you keep the peak lists in their native subdirectory, `pdata/<procno>/.`, HBA will try to retrieve the reference frequency from the file `procs` in the same directory (parameter SF).

TopSpin peak picking files are recognized by these features:

- an XML tag at the beginning: `<?xml`
- the following root element in the second line: `<PeakList`
- data are contained in attributes such as: `<Peak1D F1="..." intensity="..."`

An example of a TopSpin 2.1 file is shown in Figure 2.2 and in Figure 2.3 for TopSpin 3.5-4.0. Note that you can highlight and copy the content of the figure box, paste it into the Windows Editor, save the file, and read it into HBA. The reference frequency will default to 1 MHz; enter 161.978043 and move the cursor away. This should update the spinning frequency from 24.70341 (in ppm) to 4001.41089 (in Hz). Change the spinning frequency to 4000 Hz.

```
<?xml version="1.0" encoding="UTF-8"?>
<PeakList>
  <PeakList1D>
    <PeakList1DHeader expNo="1" name="cpniphms" procNo="1" source="D:\u">
      <PeakPickDetails>F1=146.992ppm, F2=-707.941ppm, MI=0.37cm, MAXI=16.00cm, PC=4.000
      </PeakPickDetails>
    </PeakList1DHeader>
    <Peak1D F1="54.2179" intensity="1.31" type="0"/>
    <Peak1D F1="29.4939" intensity="3.35" type="0"/>
    <Peak1D F1="4.7639" intensity="6.69" type="0"/>
    <Peak1D F1="-19.8985" intensity="10.54" type="0"/>
    <Peak1D F1="-44.5997" intensity="12.34" type="0"/>
    <Peak1D F1="-69.3021" intensity="12.72" type="0"/>
    <Peak1D F1="-94.0019" intensity="14.8" type="0"/>
    <Peak1D F1="-118.7134" intensity="15.0" type="0"/>
    <Peak1D F1="-143.4123" intensity="13.95" type="0"/>
    <Peak1D F1="-168.0808" intensity="12.13" type="0"/>
    <Peak1D F1="-192.8133" intensity="9.09" type="0"/>
    <Peak1D F1="-217.5482" intensity="7.62" type="0"/>
    <Peak1D F1="-242.2048" intensity="7.88" type="0"/>
    <Peak1D F1="-266.908" intensity="8.88" type="0"/>
    <Peak1D F1="-291.6273" intensity="7.68" type="0"/>
    <Peak1D F1="-316.3145" intensity="5.84" type="0"/>
    <Peak1D F1="-341.0205" intensity="7.15" type="0"/>
    <Peak1D F1="-365.7328" intensity="6.92" type="0"/>
    <Peak1D F1="-390.4183" intensity="5.28" type="0"/>
    <Peak1D F1="-415.1213" intensity="5.86" type="0"/>
    <Peak1D F1="-439.8502" intensity="6.3" type="0"/>
    <Peak1D F1="-464.5187" intensity="5.59" type="0"/>
    <Peak1D F1="-489.2395" intensity="4.31" type="0"/>
    <Peak1D F1="-513.937" intensity="4.21" type="0"/>
    <Peak1D F1="-538.6281" intensity="5.25" type="0"/>
    <Peak1D F1="-563.3579" intensity="5.9" type="0"/>
    <Peak1D F1="-588.0827" intensity="4.96" type="0"/>
    <Peak1D F1="-612.7285" intensity="3.47" type="0"/>
    <Peak1D F1="-637.4625" intensity="2.06" type="0"/>
    <Peak1D F1="-662.1812" intensity="1.02" type="0"/>
  </PeakList1D>
</PeakList>
```

Figure 2.2: A TopSpin 2.1 peak picking file (`peaklist.xml`)

```
<?xml version="1.0" encoding="UTF-8"?>
<PeakList modified="2021-03-23T21:47:07">
  <PeakList1D>
    <PeakList1DHeader creator="Klaus" date="2021-03-23T21:47:07" expNo="1"
    name="cpniphms" owner="" procNo="1" source="e:\u\data\nmrguest\nmr">
      <PeakPickDetails>F1=188.440704ppm, F2=-876.398804ppm, MI=0.26cm,
      MAXI=16.29cm, PC=1.000
      </PeakPickDetails>
    </PeakList1DHeader>
    <Peak1D F1="79.052513" intensity="0.3991254" type="0"/>
    <Peak1D F1="54.349491" intensity="1.302032" type="0"/>
    <Peak1D F1="29.633114" intensity="3.295171" type="0"/>
    <Peak1D F1="4.912099" intensity="6.706567" type="0"/>
    <Peak1D F1="-19.7831" intensity="10.65635" type="0"/>
    <Peak1D F1="-44.466148" intensity="12.27146" type="0"/>
    <Peak1D F1="-69.160736" intensity="12.99304" type="0"/>
    <Peak1D F1="-93.888519" intensity="15.0" type="0"/>
    <Peak1D F1="-118.583298" intensity="14.91271" type="0"/>
    <Peak1D F1="-143.271515" intensity="14.26254" type="0"/>
    <Peak1D F1="-167.965805" intensity="12.15398" type="0"/>
    <Peak1D F1="-192.687103" intensity="9.091316" type="0"/>
    <Peak1D F1="-217.40564" intensity="7.734756" type="0"/>
    <Peak1D F1="-242.093796" intensity="7.955214" type="0"/>
    <Peak1D F1="-266.776489" intensity="8.852458" type="0"/>
    <Peak1D F1="-291.489471" intensity="7.813173" type="0"/>
    <Peak1D F1="-316.202148" intensity="5.92612" type="0"/>
    <Peak1D F1="-340.879791" intensity="7.177431" type="0"/>
    <Peak1D F1="-365.589569" intensity="7.097795" type="0"/>
    <Peak1D F1="-390.299042" intensity="5.296233" type="0"/>
    <Peak1D F1="-414.983887" intensity="5.840922" type="0"/>
    <Peak1D F1="-439.7099" intensity="6.374835" type="0"/>
    <Peak1D F1="-464.408539" intensity="5.621387" type="0"/>
    <Peak1D F1="-489.123138" intensity="4.306616" type="0"/>
    <Peak1D F1="-513.801086" intensity="4.298375" type="0"/>
    <Peak1D F1="-538.525635" intensity="5.336715" type="0"/>
    <Peak1D F1="-563.232056" intensity="5.823566" type="0"/>
    <Peak1D F1="-587.94043" intensity="5.007322" type="0"/>
    <Peak1D F1="-612.623962" intensity="3.494107" type="0"/>
    <Peak1D F1="-637.336914" intensity="2.036194" type="0"/>
    <Peak1D F1="-662.069824" intensity="1.012799" type="0"/>
    <Peak1D F1="-686.739868" intensity="0.4251609" type="0"/>
  </PeakList1D>
</PeakList>
```

Figure 2.3: A TopSpin 3.5-4.0 peak picking file (`peaklist.xml`)

```
Current data set:
NAME =        KOOPH2BU       EXPNO =       5       PROCNO = 1
USER =        klaus       DU    =       D:/u

Number   Integrated Region     Integral
  1    129.324    119.220        0.99161
  2    113.495    104.402        3.25990
  3     99.014     86.889       14.97713
  4     82.848     70.387       44.46394
  5     69.377     54.558       81.38064
  6     53.885     37.719       68.14137
  7     34.352     23.238       40.19295
  8     18.860      6.736       14.68601
  9      4.041     -8.083       25.05822
 10    -11.451    -24.585       31.95773
 11    -29.637    -38.056       20.61244
 12    -44.118    -54.895       16.28154
 13    -60.957    -69.714       23.33287
 14    -76.449    -88.237       11.32771
 15    -91.941   -103.055       20.89910
 16   -107.096   -118.884       21.40571
 17   -123.262   -134.712       17.52124
 18   -139.090   -149.531       10.06131
 19   -155.929   -164.686        4.95554
 20   -172.432   -180.851        1.79446
 21   -186.913   -196.006        0.81569
```

Figure 2.4: A TopSpin / XWinNMR integration file (`integrals.txt`)

TopSpin / XWinNMR Integrals Files

The native file name is `integrals.txt`, but HBA does not care. If your spectrum contains several sites, I recommend the following procedure: perform integration for site 1 and save the result, copy `integrals.txt` to `integrals1.txt` for site 1, integrate site 2, copy `integrals.txt` to `integrals2.txt` etc. This way you can make the data available to TopSpin again by copying `integrals2.txt` back to `integrals.txt`.

Note that the file `integrals.txt` does not provide sufficient information to determine the reference frequency (default value: 1 MHz). If you keep the integrals file in their native subdirectory, `pdata/<procno>/.`, HBA will try to retrieve the reference frequency from the file `procs` in the same directory (parameter SF).

TopSpin / XWinNMR integrals files are recognized by these features:

- at the beginning: `Current data set:`
- in the second line: `NAME =`

An example of a file is shown in Figure 2.4. Note that you can highlight and copy the content of the figure box, paste it into the Windows Editor, save the file, and read it into HBA. The reference frequency will default to 1 MHz; enter 81.023559363091 and move the cursor away. This should update the spinning frequency from 15.78658 (in ppm) to 1279.08447 (in Hz). Change the spinning frequency to 1277 Hz.

XWinNMR Peak Picking Files

The native file name is `peak.txt`, but HBA does not care. Note that TopSpin can export its peak picking into XWinNMR format (however, from this file you cannot go back to TopSpin format). If your spectrum contains several sites, I recommend the following procedure (only works in TopSpin): perform peak picking for site 1 and save the result, copy `peak.txt` to `peak1.txt` for site 1, peak pick site 2, copy `peak.txt` to `peak2.txt` etc. With XWinNMR, it is not possible to perform peak picking manually, hence, with several sites, you should use integrals.

```
DU=D:\u, USER=klaus, NAME=KOOPH2BU, EXPNO=5, PROCNO=1
F1=515.705ppm, F2=-512.803ppm, MI=0.20cm, MAXI=10000.00cm, PC=1.000
     #     ADDRESS            FREQUENCY          INTENSITY
                            [Hz]        [PPM]
     1      1623.1      8752.227     108.0208         0.68
     2      1686.3      7466.867      92.1567         2.10
     3      1749.6      6177.484      76.2431         6.44
     4      1812.4      4901.389      60.4934        12.00
     5      1874.8      3630.764      44.8112        10.76
     6      1937.5      2355.498      29.0718         6.36
     7      2000.3      1078.195      13.3072         1.80
     8      2063.9      -216.748      -2.6751         3.60
     9      2126.1     -1481.216     -18.2813         5.13
    10      2189.0     -2760.907     -34.0754         3.35
    11      2252.8     -4058.491     -50.0903         2.42
    12      2314.8     -5320.644     -65.6679         3.68
    13      2378.0     -6605.740     -81.5286         1.40
    14      2440.9     -7887.141     -97.3438         3.06
    15      2504.2     -9174.000    -113.2263         3.16
    16      2567.1    -10453.771    -129.0214         2.72
    17      2630.0    -11733.727    -144.8187         1.64
    18      2692.9    -13012.852    -160.6058         0.86
    19      2755.7    -14290.209    -176.3710         0.39
```

Figure 2.5: A XWinNMR (TopSpin) peak list (`peak.txt`)

Note that the file `peak.txt` contains sufficient information to determine the reference frequency. Therefore, you can keep the file in any location you like, separate from the rest of the spectrum.

XWinNMR peak picking files are recognized by these features:

- at the beginning: `DU=` and `USER=`

An example of a file is shown in Figure 2.5. Note that you can highlight and copy the content of the figure box, paste it into the Windows Editor, save the file, and read it into HBA. Change the spinning frequency to 1277 Hz.

SpinWorks Peak Picking or Integrals Files

The native file name in SpinWorks 3.x is `peaks.txt`, no matter whether it contains integrals or a peak picking list. In SpinWorks 4.x and the Java version, peak lists are in `peaks.txt` and integrals in `integ.txt`. HBA does not care about the actual file name. If your spectrum contains several sites, I recommend the following procedure: perform peak picking or integration for site 1 and save the result, copy `peaks.txt` to `peaks1.txt` for site 1, peak pick or integrate site 2, copy `peak.txt` to `peak2.txt` etc. This way you can make the data available to SpinWorks again by copying `peaks2.txt` back to `peaks.txt`.

Manual peak picking is easy in SpinWorks:

- place the mouse cursor on the desired peak and hit the right mouse button; a peak label will appear on the screen;
- select **Peak Pick | List** to confirm that your peaks ended up in the file `peaks.txt`

Note that in the case of a peak picking list, the file `peaks.txt` contains sufficient information to determine the reference frequency. Therefore, you can keep the file in any location you like, separate from the rest of the spectrum. If the peak picking list contains a mix of automatically and manually picked peaks, the positions may not be in sequence; this screws up HBAs method to guess the spinning rate. Make sure to enter the proper value.

In the case of integrals, the file `peaks.txt` does not provide sufficient information to determine the reference frequency (default value: 1 MHz). If your spectrum is a TopSpin data set and you keep the integrals file in the location natural to SpinWorks (the subdirectory where the fid is located),

```
SpinWorks peak list for:    E:\wsolids\TopSpin\cpniphms\1\
peak #   freq. (Hz)    freq. (ppm)  intensity  intensity(Absolute)
0001   12835.858    79.2444     0.0261      69151
0002   8838.911    54.5686     0.0863      228852
0003   4835.805    29.8547     0.2278      604416
0004   831.592    5.1340     0.4555      1208377
0005   -3163.533    -19.5306     0.7031      1865232
0006   -7162.284    -44.2176     0.8495      2253664
0007   -11163.056    -68.9171     0.8651      2295016
0008   -15163.274    -93.6131     0.9931      2634531
0009   -19163.879    -118.3116    1.0311      2735493
0010   -23164.447    -143.0098    0.9557      2535396
0011   -27159.128    -167.6717    0.8196      2174433
0012   -31163.564    -192.3938    0.6308      1673497
0013   -35169.052    -217.1223    0.5281      1401075
0014   -39162.846    -241.7787    0.5306      1407680
0015   -43161.960    -266.4680    0.6137      1628051
0016   -47166.051    -291.1879    0.5308      1408305
0017   -51163.796    -315.8687    0.3954      1049017
0018   -55163.414    -340.5611    0.4976      1320201
0019   -59166.330    -365.2738    0.4795      1272095
0020   -63163.477    -389.9509    0.3529      936114
0021   -67162.918    -414.6421    0.4038      1071376
0022   -71168.260    -439.3698    0.4337      1150522
0023   -75163.613    -464.0358    0.3727      988660
0024   -79165.947    -488.7449    0.2965      786614
0025   -83166.840    -513.4451    0.2902      769786
0026   -87165.281    -538.1302    0.3489      925547
0027   -91167.412    -562.8381    0.3997      1060454
0028   -95170.999    -587.5549    0.3405      903275
0029   -99167.878    -612.2304    0.2239      594128
0030   -103167.578    -636.9232     0.1384      367095
0031   -107172.653    -661.6493     0.0690      183144
0032   -111165.095    -686.2973     0.0267      70949
```

Figure 2.6: A SpinWorks peak picking file (`peaks.txt`)

```
SpinWorks integral list for:    E:\wsolids\TopSpin\cpniphms\1\

peak #   start (ppm)   end (ppm)  intensity  intensity(Absolute)

001    88.393  71.284  1.0000  182
002    62.279  46.071  5.3956  984
003    39.767  17.256  15.5858  2843
004    12.753  -4.356  33.2712  6069
005    -9.759  -28.669  54.0414  9858
006    -35.872  -53.882  63.9669  11668
007    -57.484  -79.095  69.1362  12611
008    -81.797  -105.209  81.0864  14791
009    -108.811  -131.323  78.8533  14384
010    -133.124  -154.735  74.2664  13547
011    -156.536  -178.147  63.9885  11672
012    -183.550  -203.361  48.4859  8844
013    -206.062  -226.773  41.7548  7617
014    -231.275  -251.986  42.5950  7770
015    -258.290  -277.200  46.8464  8545
016    -282.602  -300.612  41.5667  7582
017    -306.015  -326.726  32.3039  5893
018    -331.228  -350.138  37.6363  6865
019    -356.441  -374.451  36.5269  6663
020    -382.555  -398.764  27.6157  5037
021    -405.067  -423.977  29.5102  5383
022    -429.380  -450.091  32.2221  5878
023    -455.494  -473.503  28.3826  5177
024    -480.707  -498.716  22.2018  4050
025    -505.920  -522.129  21.5916  3939
026    -530.233  -547.342  26.3894  4814
027    -554.546  -572.555  28.4303  5186
028    -579.759  -596.868  24.2943  4432
029    -604.972  -622.081  16.9160  3086
030    -631.987  -644.593  8.9432  1631
031    -656.299  -668.906  4.2139  769
032    -678.811  -690.518  1.0642  194
```

Figure 2.7: A SpinWorks integrals file (`peaks.txt`)

HBA will try to retrieve the reference frequency (parameter SF) from the file `procs` in the `pdata/1/` subdirectory.

SpinWorks peak picking or integrals files are recognized by these features:

- at the beginning: `SpinWorks integral` or `SpinWorks peak` (for SpinWorks 3.x) or `SpinWorks 4 peak` (for SpinWorks 4.x)

An example of a peak picking file is shown in Figure 2.6 and an integrals file in Figure 2.7.

WinNMR Peak Picking or Integrals Files

To generate a peak picking or integrals file with WinNMR, perform peak picking or integration for all spinning sidebands belonging to one spinning sideband manifold. Display the results using the **Report** button and save the result as an ASCII file using a name and location at your convenience.

Note that in both cases, peak picking list or integrals, the file contains sufficient information to determine the reference frequency. Therefore, you can keep the file in any location you like, separate from the rest of the spectrum.

WinNMR peak picking or integrals files are recognized by these features:

- at the beginning: `Peak List` or `Integral List`

An example of a peak picking file is shown in Figure 2.9 and a integrals file in Figure 2.8.

If you don't have WinNMR but want to use peak lists, it is relatively straightforward to create such

```
Integral List                                Date: 25.04.2007    Time: 18:31


File Name                         : D:\nmr\aa\KOOPH2BU\002001.1R
Integration regions saved in File : D:\NMR\AA\KOOPH2BU\002001.TXT

Start(ppm)  Start(Hz)   End(ppm)    End(Hz)  Integral(norm)  Integral(abs)

 154.6224    12528.06   144.3273   11693.91            1.00  6.079783E+004
 118.9661     9639.06   104.9045    8499.74            5.23  3.181884E+005
  84.3143     6831.44    66.7372    5407.29           26.96  1.639402E+006
  46.3981     3759.34    27.0634    2192.77           49.30  2.997328E+006
   6.7242      544.82    -9.8484    -797.95           22.55  1.370712E+006
 -32.4474    -2629.01   -47.0113   -3809.02            6.71  4.078642E+005
 -69.1081    -5599.39   -86.9362   -7043.88           22.75  1.382878E+006
-107.7776    -8732.52  -123.5969  -10014.26           10.13  6.160914E+005
-146.4470   -11865.66  -158.7510  -12862.57            4.91  2.983119E+005
-184.8654   -14978.45  -196.1649  -15893.98            1.04  6.309909E+004
```

Figure 2.8: A WinNMR integration file

an ASCII file, because HBA does not care about the prosa. All it wants for each spinning sideband is a row containing two integers, specifying the peak number and data point, followed by four floating point numbers specifying the frequency in Hertz, chemical shift in ppm, intensity, and relative intensity in per cent. HBA actually uses frequency, ppm, and intensity.

If you want to use integrals, HBA requires `Integral List` as the first line, otherwise it wants for each spinning sideband a row containing five floating point numbers specifying the beginning, in ppm and Hertz, and ending, in ppm and Hertz, of the integration range, followed by the actual value of the integral. In “short hand” notation: ppm1, nu1, ppm2, nu2, Int.

```
Peak List
---------

File Name                  : f:\nmr\kooph2bu\005001.1R
Peak Results saved in File : F:\NMR\KOOPH2BU\005001.PP
Nucleus                    : 31P
SF                         : 81.023559 MHz
OFFSET                     : 515.7048 ppm
SW_p                       : 83333.33 Hz
SI                         : 4096

Peak Picking Parameter
----------------------
Peak constant PC =       1.00
Noise            =       2236
Sens. level      =       8944

Peak Picking region
-------------------
  Start(ppm/Hz)        End(ppm/Hz)       MI(%)        MAXI(%)
----------------------------------------------------------------
 515.70/41784.2    -512.80/-41549.1       -0.97        100.00
----------------------------------------------------------------

Peak Picking results
--------------------
 Peak Nr. Data Point   Frequency       PPM     Intensity   %Int.
----------------------------------------------------------------
   1       1560.5       10034.81    123.8505       10618     1.3
   2       1623.1        8762.29    108.1450       45345     5.6
   3       1686.3        7477.14     92.2835      142188    17.5
   4       1749.6        6188.38     76.3775      438379    53.9
   5       1812.3        4912.09     60.6255      813997   100.0
   6       1874.8        3641.48     44.9435      717164    88.1
   7       1937.5        2365.97     29.2011      436170    53.6
   8       2000.3        1088.10     13.4295      122305    15.0
   9       2063.9        -205.77     -2.5397      243424    29.9
  10       2126.1       -1470.45    -18.1485      340400    41.8
  11       2189.0       -2750.08    -33.9418      223965    27.5
  12       2252.7       -4046.86    -49.9467      164764    20.2
  13       2314.7       -5309.27    -65.5275      247248    30.4
  14       2377.9       -6594.69    -81.3923       96832    11.9
  15       2440.9       -7875.35    -97.1983      208677    25.6
  16       2504.1       -9161.80   -113.0757      214262    26.3
  17       2567.0      -10441.46   -128.8694      183193    22.5
  18       2629.9      -11721.46   -144.6673      109480    13.4
  19       2692.8      -13000.25   -160.4502       56732     7.0
  20       2755.5      -14277.38   -176.2127       24902     3.1
----------------------------------------------------------------
```

Figure 2.9: A WinNMR peak list

2.1.3 Read Session

The option to read data from a previous session is available from:

- the menu via **File | Read session**

This action retrieves parameters (intensities, fitting results etc.) from a previous session with HBA. Note that HBA can read session files via the command line (p. 39).

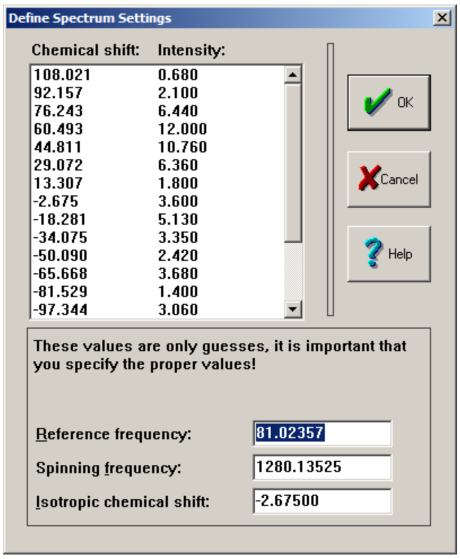
2.1.4 Write Session

The option to write session data to a file is available from:

- the menu via **File | Write session**

This action writes the current session parameters (intensities, fitting results etc.) to a file.

2.1.5 Define Spectrum Settings



Chemical shift:	Intensity:
108.021	0.680
92.157	2.100
76.243	6.440
60.493	12.000
44.811	10.760
29.072	6.360
13.307	1.800
-2.675	3.600
-18.281	5.130
-34.075	3.350
-50.090	2.420
-65.668	3.680
-81.529	1.400
-97.344	3.060

These values are only guesses, it is important that you specify the proper values!

Reference frequency: 81.02357
Spinning frequency: 1280.13525
Isotropic chemical shift: -2.67500

Figure 2.10: Dialog "Read Integrals"

After using File | Read integrals (p. 13) to retrieve the spinning sideband intensities from a file, it is necessary to define the spectrum settings:

- reference frequency (the frequency of the chemical shift reference)
- spinning rate
- isotropic chemical shift

HBA attempts to guess these values. Usually, the guesses for the reference frequency and the spinning rate could be acceptable; however, the isotropic chemical shift might be off because it is determined by an analysis of the first moment. This analysis relies on the assumption that all spinning sidebands of significant intensity are available. Enter the correct value or double-click with the left mouse button in the list box on the peak representing the center peak.

2.1.6 Write Meta File

The option to create a graphics file in Windows meta file format is available from:

- the menu via **File | Write meta file**

Selection of this menu item allows to write the graphics content of the client area to a file, using the Windows meta file format (WMF). This format can be read by a variety of graphics programs, and further processed there. The user will be asked to specify a file name. It is recommended to use the *.WMF extension.

Possibly, the labels of the ρ axis are missing and the font size for the μ axis labels will be too small.

2.1.7 Write Spin System

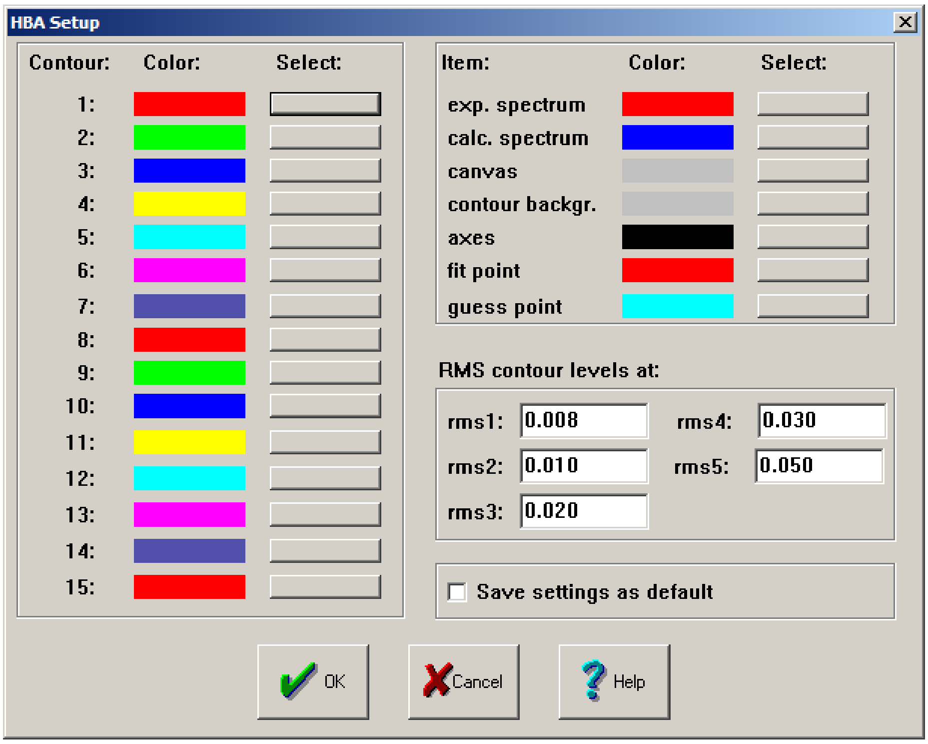
The option to write chemical shift tensor information as WSolids spin system file is available from:

- the menu via **File | Write spin system**

After an iteration, the chemical shift tensor information can be written in XML format to a WSolids compatible spin system file for later display of simulated spectra. In order to use this file in WSolids1, follow this procedure:

1. In HBA, save the fitting results as WSolids spin system file.
2. In WSolids1, read the created spin system file: File | Open | WSolids Document...
3. If the spectrum consists of several sites, read additional spin system files, and tell WSolids1 to add to the spin system (press the No button on the corresponding dialog box)
4. After all spin systems have been read, read an experimental spectrum (if available), File | Open | Spectrum..., or create a spectrum window, File | New window.
5. So far, HBA does not provide information on the observed nucleus; fix this before performing a calculation: Simulation | Default parameters...
6. Perform a calculation. If necessary, change the convolution parameters.

2.1.8 Setup



RMS contour levels at:

rms1: 0.008
rms2: 0.010
rms3: 0.020
rms4: 0.030
rms5: 0.050

☐ Save settings as default

Figure 2.11: Dialog "Setup"

The option to customize colors and set a few parameters is available from:

- the menu via **File | Setup**

The dialog box allows to customize the colors of the contour lines and several other data items used by HBA. Also, the levels for the display of RMS errors can be set. If the option **Save settings as default** is enabled, the selected settings are stored in the ini file of HBA. Otherwise, they only affect the current session.

2.1.9 Exit

To exit HBA, simply use:

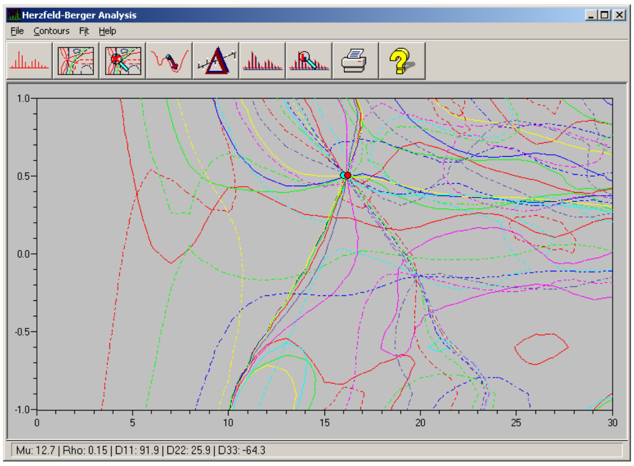
- the menu item **File | Exit**
- the keyboard keys **ALT-F4**

This action exits HBA.

2.1.10 Show Contours

The contour lines can be displayed as an overlay of Herzfeld-Berger nomograms by using the:

- menu item **Contours | Show contours**
- button bar
- keyboard accelerator key **S**



Mu: 12.7 | Rho: 0.15 | D11: 91.9 | D22: 25.9 | D33: -64.3

Figure 2.12: Display of contour lines

Ideally, the contour lines for all spinning sidebands should intersect in one unique point. This unique point would correspond to the correct μ, ρ parameters for this particular chemical shift tensor. In less ideal cases, the intersection of all contours might not be as clear. The spread of contours and their intersections gives a good visual indication of the quality of the data. It may also indicate if this particular case is more likely to have problems in determining the skew of the tensor or the span.

Spinning sidebands of positive and negative ordinal number are represented by solid and dashed lines, respectively.

The horizontal axis corresponds to the μ parameter, and the vertical axis to the ρ parameter of the Herzfeld-Berger analysis [1]. μ corresponds approximately to the number of visible spinning sidebands (and is therefore spinning-rate and field-dependent), while ρ corresponds to the skew (axiality) of the tensor and is field- and spinning-rate independent.

2.1.11 Show RMS

The contour lines of the rms errors can be displayed by using the:

- menu item **Contours | Show rms**
- button bar
- keyboard accelerator key **M**

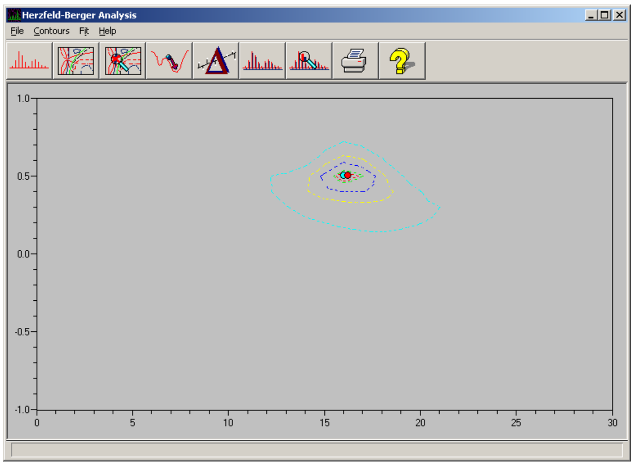


Figure 2.13: Display of RMS error contour lines

The display of rms errors as contours provides a great opportunity to visually assess the accuracy and uniqueness of a fit. This requires that the rms error at each grid point of the Herzfeld-Berger tables is calculated, on slow computers a quite lengthy process. If an iteration (p. 29) after a grid search has been performed already, the rms errors are available for display immediately. Otherwise, with no iteration done yet, a grid search is initiated (which updates the initial guess (p. 29) for an iteration also). The rms errors used for the display are actually s_{fit} errors, see iteration (p. 29) for details.

The levels for the contours are stored in the ini file (p. 38), and the colors correspond to those of spinning sideband orders 1 to 5. They can be manipulated via the Setup (p. 25) item of the File menu.

2.1.12 Show Fit | Show Initial Guess

While displaying contour lines, one can toggle the display of initial guess and fit by the:

- menu item **Contours | Show initial guess**
- menu item **Contours | Show fit**

While viewing the contour lines, one can toggle the display of the position corresponding to the data of the initial guess or the fit on and off. The colors of the points can be customized using the File | Setup (p. 25) dialog box.

2.1.13 Show Level Selector Tool

While displaying contour lines, using this tool, one can customize the amount of information displayed. The Hide All button is useful to quickly erase the list.

2.1.14 Data Reader

The mouse data reader can be activated by using the:

- menu item **Contours | Data reader**
- button bar

While displaying the spinning sideband intensities as contour lines, one can select the mouse cursor as a data reader. For any point within the range of the Herzfeld-Berger tables, the status bar will display the values of μ,ρ for the current mouse cursor position. Also, using the parameters describing the spectrum settings (p. 23), the values of the principal components of the chemical shift tensor will be calculated.

One can use this data reader to set an initial guess (p. 29) for the iterative refinement (p. 29), by pressing the left mouse button at the desired position over the contour plot.

2.1.15 Discard Initial Guess

The option to discard the initial guess is available from:

- the menu via **Fit | Discard initial guess**

The iterative refinement (p. 29) requires an initial guess as starting values. This starting position may determine whether the iteration falls into a local minimum or finds the global minimum. So far, three different routes are available to obtain a starting guess:

1. the default action, if there is no user specified starting guess, is to perform a grid search (a grid search can also be initiated by the display of rms errors (p. 27)).
2. a starting point can be provided by the user via the data reader (p. 28)
3. a starting point can be provided by the user via the interactive simulation (p. 36)

In the two last cases, a flag is set to indicate that initial values are provided by the user, and no grid search is performed then. Also, the menu option to discard this starting guess is enabled.

2.1.16 Iterative Refinement

The iterative determination of the principal components is activated by:

- the menu item **Fit | Iterate**
- the button bar
- the keyboard accelerator key **I**

The Iteration Procedure

The iterative refinement as implemented here requires an initial guess. This is common to all iteration algorithms. Only the way this starting guess (or guesses, in the case of a SIMPLEX algorithm) is obtained will vary from one problem to the other. If there is no user defined starting guess, HBA performs a grid search automatically. For this purpose, it scans through the Herzfeld-Berger tables using fixed increments and calculates the s_{fit} error at each grid point:

$$s_{\text{fit}} = \left\{ \sum_{k=1}^{N} \frac{[I_k(\text{calc}) - I_k(\text{exp})]^2}{(N - p)} \right\}^{1/2} \tag{2.1}$$

I : intensity of spinning sideband or isotropic peak

N : number of experimental points

p : number of refined parameters

This procedure should help HBA to find the global minimum rather than getting stuck in a local minimum. During this stage, HBA needs to calculate several hundred spectra. Therefore, this is the most time consuming step. However, on a Pentium processor the price paid for this safety measure seems to be inconsequential. Alternatively, the user can specify a starting guess (p. 29) interactively, thereby greatly reducing the time required for the iteration.

Having obtained a starting guess, HBA calls a Marquardt-Levenberg routine to iteratively refine the required parameters using gradient methods and least-squares fitting techniques [3]. After finishing successfully, the results (p. 42) are written to a scratch file. Using the Report (p. 34) option, the results can be inspected and sent to a printer, or they can be displayed on the screen either on the contour map (p. 26) or as a comparison of stick spectra (p. 35).

Once a fitting result has been obtained, HBA explores the topography about the fit parameters in order to obtain error estimates. The procedure follows the rigorous statistical analysis of errors documented by Olivieri [4]. However, while his approach uses the chemical shift anisotropy $\Delta\sigma$ and asymmetry parameter η to describe the chemical shift tensor and that are used as fit parameters, HBA employs the Herzfeld-Berger parameter μ instead of $\Delta\sigma$ and κ instead of η, see conventions (p. 42). The results should be comparable.

The matrix **B**:

$$B_{ij} \;=\; \sum \left[\frac{\partial I_k(\text{calc})}{\partial p_i}\right]\left[\frac{\partial I_k(\text{calc})}{\partial p_j}\right] \tag{2.2}$$

is evaluated numerically. The summation involves all sidebands observed experimentally, $p_{i,j}$ are the parameters μ and κ. The partial derivatives $\partial I_k(\text{calc})/\partial p_i$ are estimated as quotients $\delta I_k(\text{calc})/\delta p_i$, where $\delta I_k(\text{calc})$ is the change in calculated intensity when p_i is changed by a small amount from its refined value. Currently, μ is changed by ± 0.2 and κ by ± 0.05.

The diagonal elements of **B** are used to calculate the conditional standard deviation for p_i:

$$s_{\text{COND}}(p_i) \;=\; s_{\text{fit}} \;\times\; (B_{ii})^{-1/2} \tag{2.3}$$

while the diagonal elements of the inverse of the matrix **B** give the marginal standard deviation of the refined p_i values:

$$s_{\text{MARG}}(p_i) \;=\; s_{\text{fit}} \;\times\; [(B^{-1})_{ii}]^{1/2} \tag{2.4}$$

Also given in the report is the ratio

$$R_i \;=\; s^2_{\text{MARG}}(p_i)/s^2_{\text{COND}}(p_i) \tag{2.5}$$

the value of which is close to 1 if the parameters are reasonably well defined by the experimental data. Note that $s_{\text{MARG}}(p_i)$ takes into account

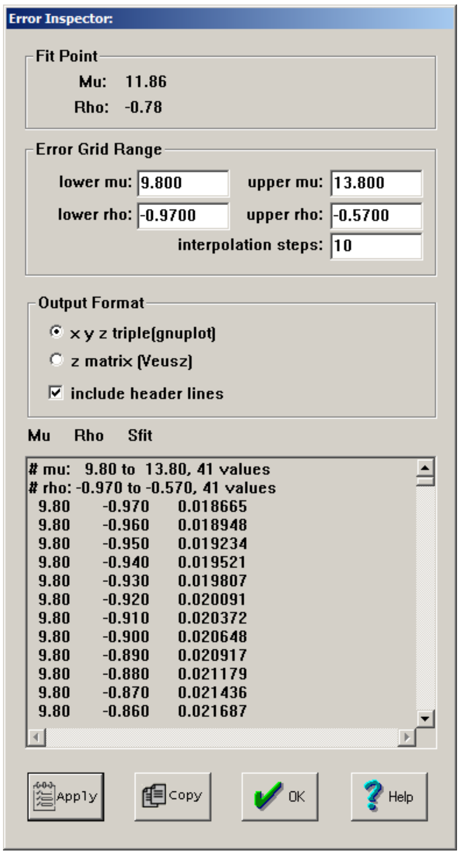
- the presence of random errors (contained in s_{fit})
- the sensitivity of s_{fit} toward small changes in p_i
- the interdependency with other refined parameters.

Note that realistic errors could be greater than the reported standard deviations. My estimation is that likely errors are on the order of 1-2 ppm or up to 5% of the span, whichever number is greater. Newer versions of HBA will also carry out and report an analysis of first to third moments (p. 60) to provide an alternative way of analysis and and independent way to obtain the principal components.

2.1.17 Error Inspector

The error inspector may be launched by using:

- the menu item **Fit | Error Inspector**



Fit Point
Mu: 11.86
Rho: -0.78

Error Grid Range
lower mu: 9.800
upper mu: 13.800
lower rho: -0.9700
upper rho: -0.5700
interpolation steps: 10

Output Format
● x y z triple(gnuplot)
○ z matrix (Veusz)
☑ include header lines

```
Mu    Rho    Sfit
# mu:   9.80 to  13.80, 41 values
# rho: -0.970 to -0.570, 41 values
 9.80     -0.970     0.018665
 9.80     -0.960     0.018948
 9.80     -0.950     0.019234
 9.80     -0.940     0.019521
 9.80     -0.930     0.019807
 9.80     -0.920     0.020091
 9.80     -0.910     0.020372
 9.80     -0.900     0.020648
 9.80     -0.890     0.020917
 9.80     -0.880     0.021179
 9.80     -0.870     0.021436
 9.80     -0.860     0.021687
```

At the end of the iteration (p. 29) procedure, the fitting error s_{fit} surface around the optimized solution can be mapped out for the purpose of illustrating the error using fancy external software. In order to facilitate the specification of the grid, HBA reports the fitted μ and ρ parameters as fit point.

Error Grid Range: Around that fit point, the user needs to specify the lower and upper limits on μ and ρ as well as the number of interpolation steps. Usually, HBA will suggest (in my opinion) sensible default values, about ± 1 unit around μ and ± 0.2 units about ρ. Note that the Herzfeld-Berger tables are stored in intervals of 1 for μ and of 0.1 for ρ. Hence an interpolation step value of 10 will map out the surface in steps of $1/10$ for μ and $0.1/10$ for ρ.

With these settings, activation of the **Apply** button performs the calculation of the spectra and the associated s_{fit} errors (in the example, 40×41 spectra!) and sends the results to the read-only edit box in the center.

The **output format** can be x y z triples (consisting of $\mu, \rho, s_{\mathrm{fit}}$), that can be used with GnuPlot (see below), or as a matrix of z values (i.e. s_{fit}), that can be used with Veusz or similar.

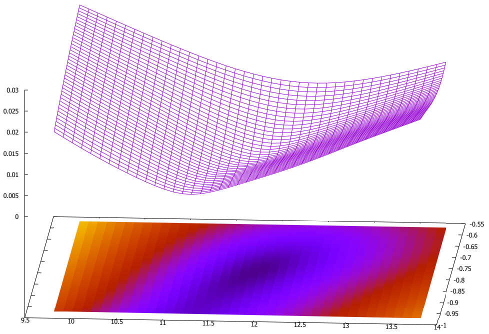
If the check box **include header lines** is checked, HBA will prepend the output with two comment lines stating the limits. Some programs have problems dealing with header lines, hence the option to skip the headers.

The content of the edit box can be copied to the clipboard with the **Copy** button.

The following subsections might serve as a gallery of possibilities in the use of the output of the error inspector.

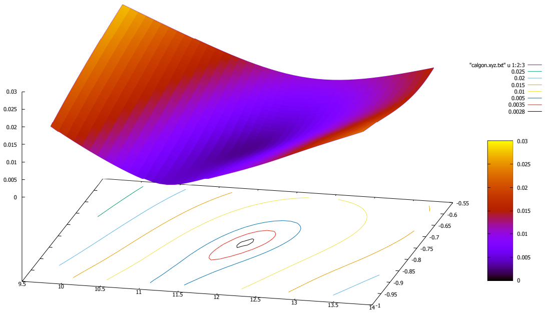
X,Y,Z Triples

This outout format is geared at programs such as gnuplot, that offers a variety of different cool renderings of the data. Some examples are shown in Figs. 2.14-2.16, together with the scripts used to render them. Gnuplot can deal with the header lines, if present.



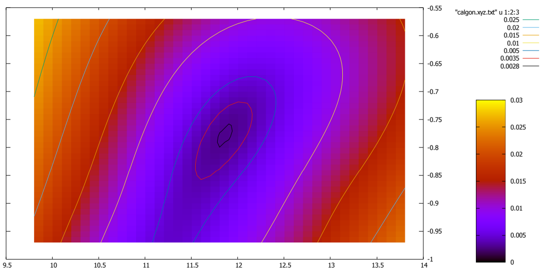
```
set dgrid3d 41,41
set hidden3d
set pm3d at b
set ticslevel 0.8
set isosample 40,40
set view 66,4,1,1
splot "calgon.xyz.txt" u 1:2:3 with lines
```

Figure 2.14: A gnuplot rendering of the error surface s_{fit} using the script shown on the right.



```
set dgrid3d 41,41
set hidden3d
set pm3d
set ticslevel 0.8
set isosample 40,40
set contour base
set cntrparam levels discrete 0.0028,0.0035,
   0.005,0.01,0.015,0.02,0.025
set view 61,13,1,1
splot "calgon.xyz.txt" u 1:2:3 with lines
```

Figure 2.15: A gnuplot rendering of the error surface s_{fit} using the script shown on the right.

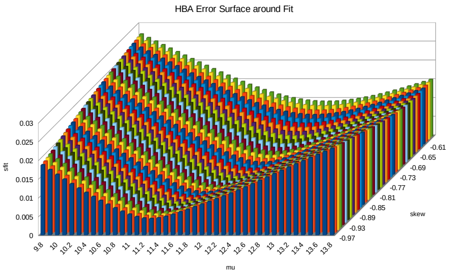


```
set dgrid3d 41,41
set hidden3d
set pm3d at b
set ticslevel 0.8
set isosample 40,40
set contour base
set nosurface
set cntrparam levels discrete 0.0028,
   0.0035,0.005,0.01,0.015,0.02,0.025
set view 0,0
splot "calgon.xyz.txt" u 1:2:3 with lines
```

Figure 2.16: A gnuplot rendering of the error surface s_{fit} using the script shown on the right.

Z Matrix

The z matrix output format is for programs that prefer to have column and row headers.



Among the typical non-Excel spread sheet applications is LibreOffice Calc. It cannot produce 3D surface charts, but emulate something similar. The example was produced using the x,y,z triples and selecting **chart type: column**, Deep, 3D Look; **data ranges:** data series in rows, first row as label, first column as label.

Another kind of software is Veusz, two renderings using Veusz are shown in Figs. 2.17-2.18.

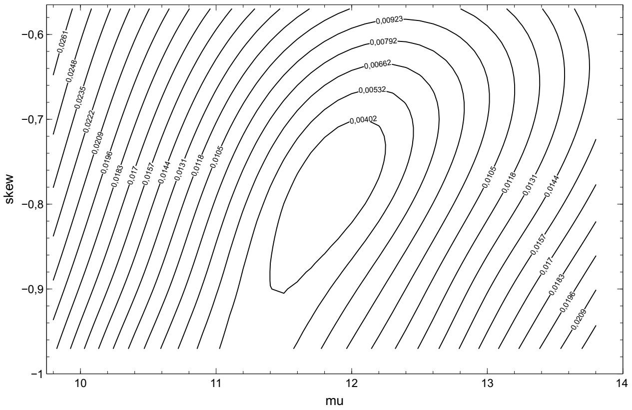


Figure 2.17: A rendering of the error surface s_{fit} as contour diagram with Veusz

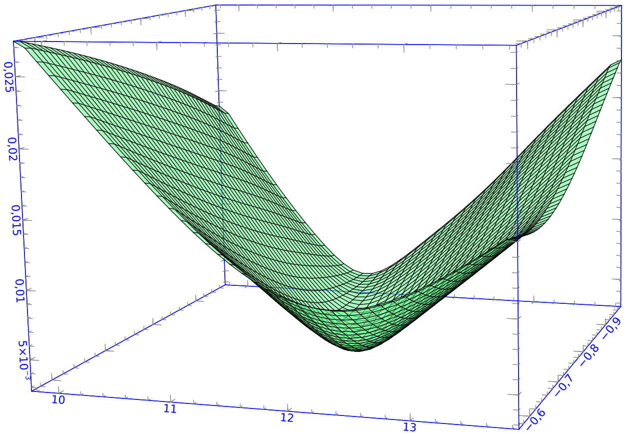


Figure 2.18: A rendering of the error surface s_{fit} as mesh plot diagram with Veusz

Links to the software mentioned:

- LibreOffice Calc: `https://www.libreoffice.org/`
- gnuplot: `http://www.gnuplot.info/`
- Veusz: `https://veusz.github.io/`

2.1.18 Report

The output of the fitting results can be inspected by using:

- the menu item **Fit | Report**
- the button bar
- the keyboard accelerator key **R**

At the end of the iteration (p. 29) procedure, the results (p. 42) are written to a scratch file. From version 1.7.3 on, the file is named `hba_iterate.txt` and is located in the users `My Documents` path under subdirectory `WSolids`. Right now, the Report option just calls Notepad with the output file. From Notepad, one can modify the output file to include a descriptive title or save the results under a different file name or print the results.

The experimental sideband intensities are also saved in the `HBA.INI` file to serve as defaults for the next session. If one is interested in keeping the data, one could copy the ini file to a different file name or write it to a session file (p. 23)-

2.1.19 Compare Results

The display of stick spectra representing experimental and calculated intensities is activated by:

- the menu item **Fit | Compare**
- the button bar
- the keyboard accelerator key **C**

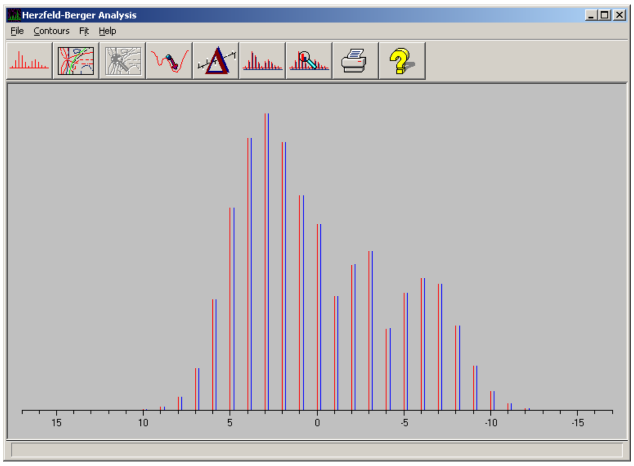


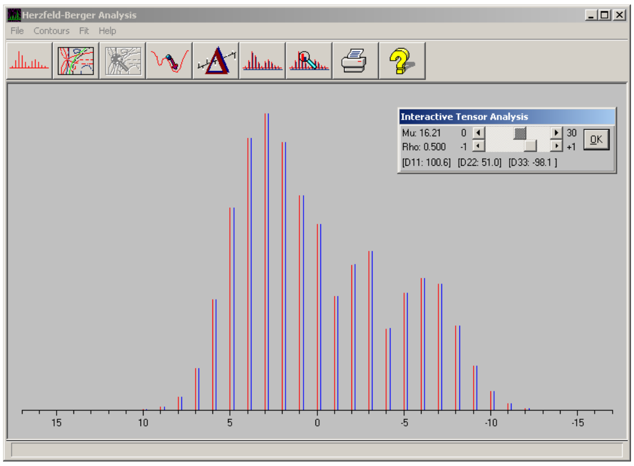
Figure 2.19: Display of experimental and theoretical stick spectra.

The direct, visual comparison of calculated and experimental spinning sideband intensities allows for a better assessment of the quality of the fit. In earlier versions of HBA, both spectra were normalized to have the same center peak intensity. Now, the total sum of sidebands and centerband are normalized, and experimental and calculated spectra are plotted with a slight horizontal offset to avoid overlap.

2.1.20 Simulate Interactively

The display of stick spectra representing experimental and calculated intensities is activated by:

- the menu item **Fit | Simulate**
- the button bar
- the keyboard accelerator key **M**



Mu: 16.21

Rho: 0.500

[D11: 100.6] [D22: 51.0] [D33: -98.1]

Figure 2.20: Simulate the experimental stick spectrum manually.

Using this feature, one can easily vary the Herzfeld-Berger parameters μ and ρ via scroll bars and directly observe the effect on the calculated spectrum. In earlier versions of HBA, both spectra were normalized to have the same center peak intensity. Now, the total sum of sidebands and centerband are normalized, and experimental and calculated spectra are plotted with a slight horizontal offset to avoid overlap.

This action automatically sets the current values of μ and ρ as initial guess for the iterative refinement. To disable this initial guess, select Discard initial guess (p. 29).

2.2 Help on Button Bar Items

Button	Menu Item	Action
	Enter Intensities (p. 12)	Enter intensities of spinning sidebands and center peak; all following actions are based on these data
	Show Contours (p. 26)	Display the contour lines in the Herzfeld-Berger tables using the normalized intensities
	Data Reader (p. 28)	Use the mouse cursor to read data off the contour diagrams or to set an initial guess for the iteration
	Iterate (p. 29)	Starts the iterative determination of the chemical shift tensor parameters
	Show rms (p. 27)	Show the rms error as contour levels
	Compare (p. 35)	Based on the results from the iterative determination, experimental and calculated stick spectra are compared
	Report (p. 34)	Report the results of the iterative determination of chemical shift tensor parameters
	Simulate (p. 36)	Simulate the experimental data interactively
	Help (p. iii)	Opens the HBA help file with the Contents page

2.3 INI File Settings

Several of the items of the INI file can be modified via the Setup (p. 25) item of the **File** menu. The HBA.INI file contains the following sections:

[INTENSITIES]

This section contains the spinning sideband and centerband intensities used in the last session with HBA. The letter *p* represents high-frequency (positive) sidebands, the letter *m* stands for the low-frequency (negative, “minus”) sidebands.

[SETTINGS]

This section contains entries characterizing the experimental spectrum:

SF	spectrometer frequency (actually, the frequency of the chemical shift reference)
Rot	spinning frequency
Shift	isotropic chemical shift
Mu, Rho	the Herzfeld-Berger parameters of the last fit
rms0...rms4	rms error contour levels (the colors used correspond to those of spinning sideband orders 1 to 5)

[COLORS]

All color entries specify the values for red, green, and blue (RGB triple) constituting the color. Such values can be determined, for example, by using Windows’ color selection box.

S1-S15	This section contains color entries for the spinning sidebands of different order, S1 to S15 (contours for sidebands of negative order have the same color as the sideband of positive order, but the lines are broken).
EXP	The color of the experimental stick spectrum
CALC	The color of the calculated stick spectrum
CANVAS	The color of the client window (background color)
CONTBG	The color of the background rectangle for displaying contours
AXES	The color of the axes

2.4 Command Line Parameters

Using command line parameters, HBA can read, on start-up, session files, peak lists, or integration files, followed by iterative fitting, output to a report file, and quit. Such options can be useful for batch processing or for integrating HBA in other applications.

Usage:

```
hba -switch [parameter] [-switch [parameter]...]
```

where:

-switch:		
	-s	for session files, a file name as parameter is mandatory
	-i	for integration files, a file name as parameter is mandatory
	-p	for peak lists, a file name as parameter is mandatory
	-sf	for reference frequency, followed by the value in MHz as parameter
	-nur	for spinning frequency, followed by the value in Hz as parameter
	-diso	for isotropic chemical shift, followed by the value in ppm as parameter
	-f	do iterative fitting, no further parameter required
	-r	create a report file, if no file name is given, output will be written to ITERATE.TXT
	-q	quit HBA
parameter:	**filename**: a fully qualified file name (full path including drive) specifying the session, integration, or peak list file. If the file name or path contain blanks, filename should be put between double quotes. **value**: a floating point value.	

Note: Parameters will be processed in the order given on the command line.

In newer versions of HBA, you can use the switch `-i` or `-p` followed by the file name independent of the actual content of the file, peak picking or integration, because HBA will check the content anyway. I.e. the options `-i` and `-p` are now equivalent.

Examples

- Start HBA with a peak picking file:

```
"d:\program files\winsolids\hba.exe" -p "c:\documents and settings
\klaus\my files\hba data\triphenylphosphine.pp"
```

- Start HBA with a session file, iterate, write report to a file and quit:

```
hba.exe -s e:\nmr\projects\phosphate.ini -f -r "f:\my results\
phosphate_fit.txt" -q
```

2.5 Known Problems

- Some programs are not happy with the metafiles produced by HBA.

3 Background Information

Background information might be available some day on the following topics:
(depending on whether someone is actually going to read this)

Chemical Shift Anisotropy (CSA):

- What is CSA?
- Conventions (p. 42)
- What is sample rotation?
- What are spinning sidebands?

Herzfeld-Berger Analysis:

- What are the Herzfeld-Berger parameters?
- How does the Herzfeld-Berger method work?
- What are possible caveats in working with the Herzfeld-Berger Method (p. 45)
- What are the alternatives (p. 56)?

3.1 Conventions

Unfortunately, there are many different conventions for labeling the principal components of chemical shift tensors around in the literature. 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.

3.1.1 Shifts and Shieldings

It is recommended that the IUPAC conventions [5, 6] are obeyed:

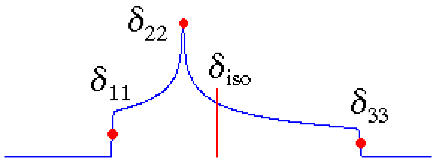
- The **absolute magnetic shielding**, σ, in ppm is the difference in shielding between the frequency of the bare nucleus, ν_{nucl}, and the frequency of the same nucleus in the species under investigation, ν_{s}:
  σ / ppm = 1e06 * (ν_{nucl} - ν_{s}) / ν_{nucl}
- The **chemical shift**, δ, is the difference in shielding between the nucleus in the species under investigation, σs, and the shielding of the same nucleus in a reference compound, σ_{ref}:
  δ / ppm = (σ_{ref} - σ_{s}) / (1 - σ_{ref})

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 magnetic shielding scale is not a trivial task and requires both careful theoretical calculations and experimental measurements. Some examples of established shielding scales are available for carbon [7, 8]; oxygen [9]; silicon [10]; phosphorus [11]; and tin [12].

Comments

The symbol σ 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.

3.1.2 Standard Convention

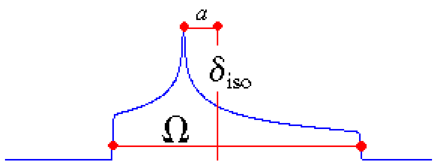


Principal Components	$\delta_{11} \geq \delta_{22} \geq \delta_{33}$
	$\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$
Isotropic Value	$\delta_{\mathrm{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$
	$\sigma_{\mathrm{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$

In what we shall call the standard convention, the principal components of the chemical shift tensor, δ_{11}, δ_{22}, and δ_{33}, are labeled according to the IUPAC rules [13]. They follow the high frequency-positive order. Thus, δ_{11} corresponds to the direction of least shielding, σ_{11}, with the highest frequency, while δ_{33} corresponds to the direction of highest shielding, σ_{33}, with the lowest frequency. The isotropic values, δ_{iso} or σ_{iso}, are the average values of the principal components, and correspond to the center of gravity of the line shape.

3.1.3 Herzfeld-Berger Convention

In the Herzfeld-Berger notation [1], 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.



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

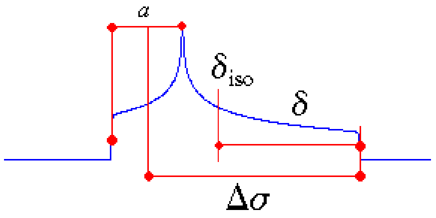
The **skew** of the tensor is a measure of the amount and orientation of the asymmetry of the tensor. As indicated, κ is given by $3a$ / Ω. Depending on the position of δ_{22} with respect to δ_{iso}, the sign is either positive or negative. If δ_{22} equals δ_{iso}, a and the skew are zero. In the case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

The parameter μ used with the Herzfeld-Berger tables is related to the span of a tensor by:
$\mu = \Omega$ * SF / spinning rate

The parameter ρ used with the Herzfeld-Berger tables corresponds to the skew of a tensor described here. For "historical" reasons we used ρ throughout this manual, but generally we prefer κ [13].

The Herzfeld-Berger convention is related to the Standard convention via:
$\delta_{22} = \delta_{\text{iso}} + (\kappa\, \Omega\ /\ 3)$
$\delta_{33} = (\ 3\ \delta_{\text{iso}} - \delta_{22} - \Omega\ )\ /\ 2$
$\delta_{11} = 3\ \delta_{\text{iso}} - \delta_{22} - \delta_{33}$

3.1.4 Haeberlen Convention



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

The Haeberlen-Mehring [14, 15] 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 δ 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. $\delta_{zz} = \delta_{33}$)
$\delta_{11} = \delta_{iso} + \delta$	$\delta_{33} = \delta_{iso} + \delta$
$\delta_{22} = \delta_{iso} - \delta(1-\eta)/2$	$\delta_{22} = \delta_{iso} - \delta(1-\eta)/2$
$\delta_{33} = \delta_{iso} - \delta(1+\eta)/2$	$\delta_{11} = \delta_{iso} - \delta(1+\eta)/2$

3.2 Possible Caveats

Some of the pathological situations, and their potential cure, are listed below (additions or comments welcome):

3.2.1 Fictitious Data

The major problem is that the Herzfeld-Berger method (and the moment method, sect. 3.3) will always give a result, no matter how bad or fictitious the input parameters (sideband intensities) are, an issue discussed by Clayden *et al.* [16].

Consider a hypothetical MAS spectrum obtained at 80.96 MHz at a spinning rate of 1 kHz and consisting of the center peak at $\delta_{\mathrm{iso}} = 0$ ppm and first order spinning sidebands, all three peaks having equal intensities (cf. the red spectra in Fig. 3.2). **N.B., there will be no chemical shift tensor that, under any experimental conditions, will produce exactly such a spectrum!**

As stated by Clayden [16], a moment analysis (Sect. 3.3) will yield principal components of $\delta_{11} = 19.5$, $\delta_{22} = 0.0$, $\delta_{33} = -19.5$ ppm. However, a simulation using these parameters (cf. Fig. 4b in Ref. [16]) will yield a spectrum that contains more than three peaks and, more importantly, the first order spinning sidebands have intensities much lower than that of the isotropic peak (you can reproduce this spectrum using HBA by using in File | Enter intensities (p. 12) the experimental settings stated above, then Fit | Simulate (p. 36); adjust μ to 3.16 and ρ to 0.0).

In contrast to the single solution of the moment method, any of the intersections of the I_1/I_0 and I_{-1}/I_0 contour lines represent solutions where the center peak and first order spinning sidebands will have equal intensities; three example spectra corresponding to the indicated intersections in Fig. 3.1 are shown in Fig. 3.2. In each case, the center peak and the first order spinning sidebands have equal intensities. However, comparison of "experimental" and calculated spectra reveals that the calculated spectra are increasingly poor representations of the experimental data because they contain more spinning sidebands than required.

You can reproduce the three cases by

- entering under File | Enter intensities (p. 12) the experimental settings mentioned above and setting the intensities of the +1, CB, and -1 peaks to 1.0, while the intensities of all other peaks are set to -1 (this neglects these spinning sidebands during the iteration);
- setting the initial guess at, or close to, the desired intersection using the Contours | Data Reader (p. 28); and
- performing an iteration.

Have a look at the errors reported by HBA, Fit | Report (p. 34). Because only three peaks have been considered in the iteration, the agreement between experimental and calculated spectra is perfect and the errors zero in all three examples (spinning sidebands present in the calculation but not in the experiment have been neglected, because their intensities have been set to -1)! To indicate such potential problems, the display of stick spectra under Fit | Compare (p. 35), and the intensities listed in the Report (p. 34), utilize normalized intensities of the total spectra, hence the visual agreement gets increasingly worse for the examples shown in Fig. 3.2. (Note that the simulations shown by Clayden *et al.* in Fig. 4c,d of their paper are crude: the three peaks of sideband orders +1,0,-1 should have equal intensities; also, the intensities of sidebands should be symmetric about the isotropic peak.)

Actually, the proper procedure to obtain a fit for this hypothetical example is to set the intensities of all spinning sidebands not observed experimentally to zero explicitly. In this case, the fit will be the best compromise, $\delta_{11} = 29.5 \pm 2.0$, $\delta_{22} = -0.0 \pm 1.1$, $\delta_{33} = -29.5 \pm 1.7$, to a non-existant solution.

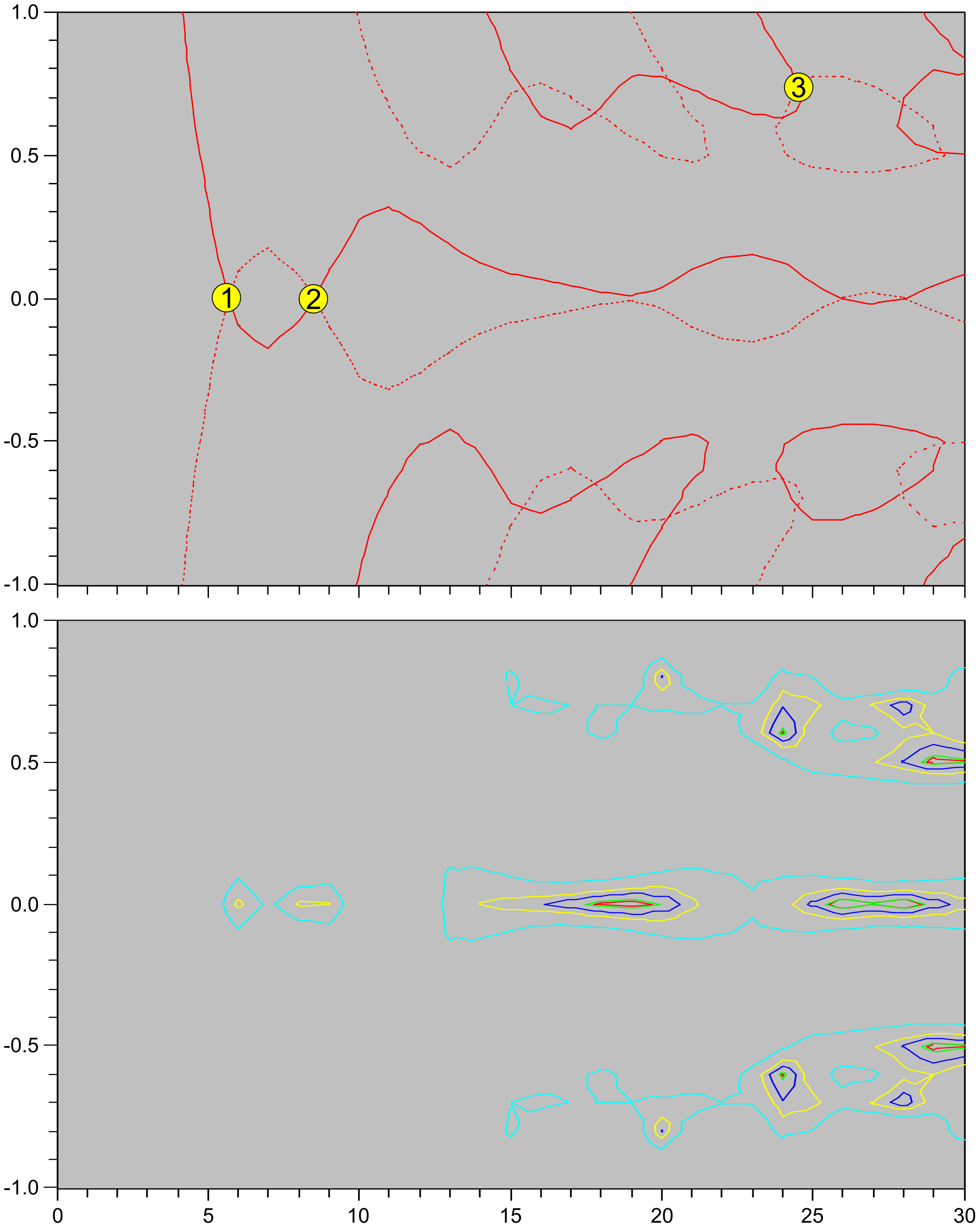


Figure 3.1: Contour lines (top) and error levels (bottom) for a hypothetical three-line MAS spectrum consisting of spinning sidebands of orders +1, 0, -1 and of equal intensities. Spectra corresponding to the three intersections representing possible solutions are shown in Fig. 3.2

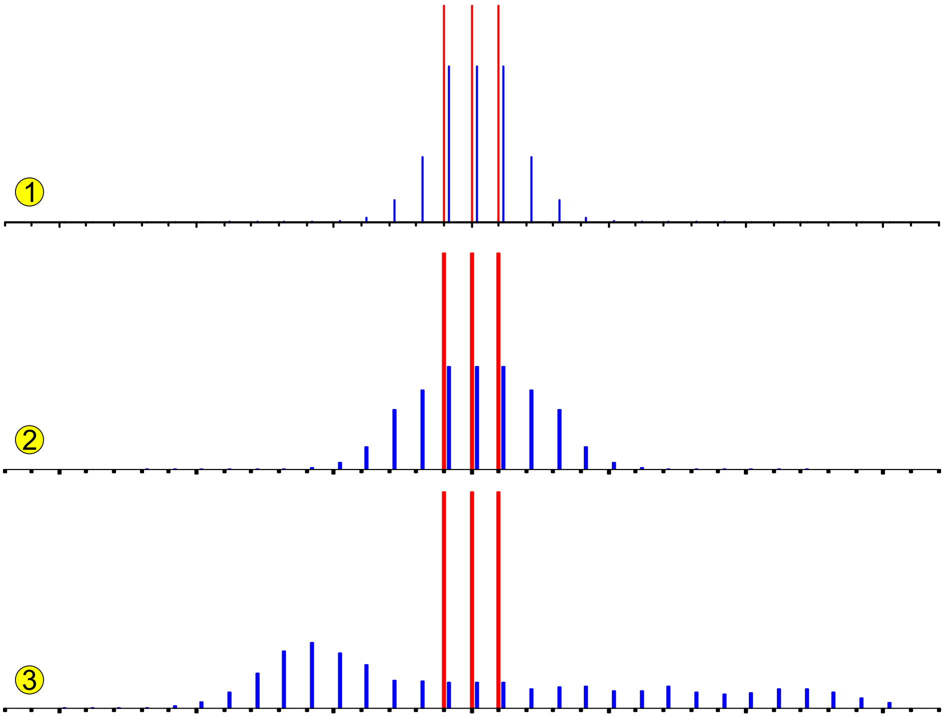


Figure 3.2: Spectra corresponding to the three intersections of contour lines shown in Fig. 3.1. For SF = 80.96 MHz, $\nu_\mathrm{r} = 1.0$ kHz, the spectra correspond to principal components of:
① $\delta_{11} = 35.0$, $\delta_{22} = 0.0$, $\delta_{33} = -35.0$ ppm;
② $\delta_{11} = 52.5$, $\delta_{22} = 0.0$, $\delta_{33} = -52.5$ ppm;
③ $\delta_{11} = 114.3$, $\delta_{22} = 74.7$, $\delta_{33} = -189.0$ ppm

To protect yourself yourself from the above pitfalls:

- Don't trust the reported errors blindly. Look at and compare the experimental spectrum to the calculated spectrum. If there is some systematic deviation, such as significant spinning sidebands that have not been observed (Fig. 3.2), try to figure out the reason.

3.2.2 Inappropriate Data

The Herzfeld-Berger method is based on the assumption that the chemical shift interaction is the only interaction affecting the intensitites of the spinning sidebands. Problems may arise if the dipolar or quadrupolar interaction contribute to the line shape. Actually, some papers state that magic angle spinning removes the dipolar interaction and therefore the spinning sidebands can be used to extract information on the chemical shift tensor. However, this is a misconception. MAS usually removes the effect of dipolar interactions on the line shape of the isotropic peak (unless coupling to a quadrupolar nucleus is involved), but it does not remove their effect on the intensities of the spinning sidebands. If, on top of that, also indirect spin spin coupling is involved that separates the subspectra associated with different spin states of the coupled nucleus into discrete spinning sideband manifolds, one can actually analyze the subspectra to obtain information on the chemical shift tensor **and** the dipolar interaction as well as their relative orientations. The theory involved has been outlined by Harris and coworkers [17].

In contrast, if the presence of a dipolar interaction is not taken into account properly, the resulting principal components of the chemical shift tensor may have large errors. One example is the carbon of a cyano group; here, the spinning sideband intensities in the ^{13}C MAS spectrum are also affected by the dipolar interaction with the directly attached ^{14}N nucleus. It has been noted that a Herzfeld-Berger analysis of the spinning sideband intensities results in relatively large errors in the principal

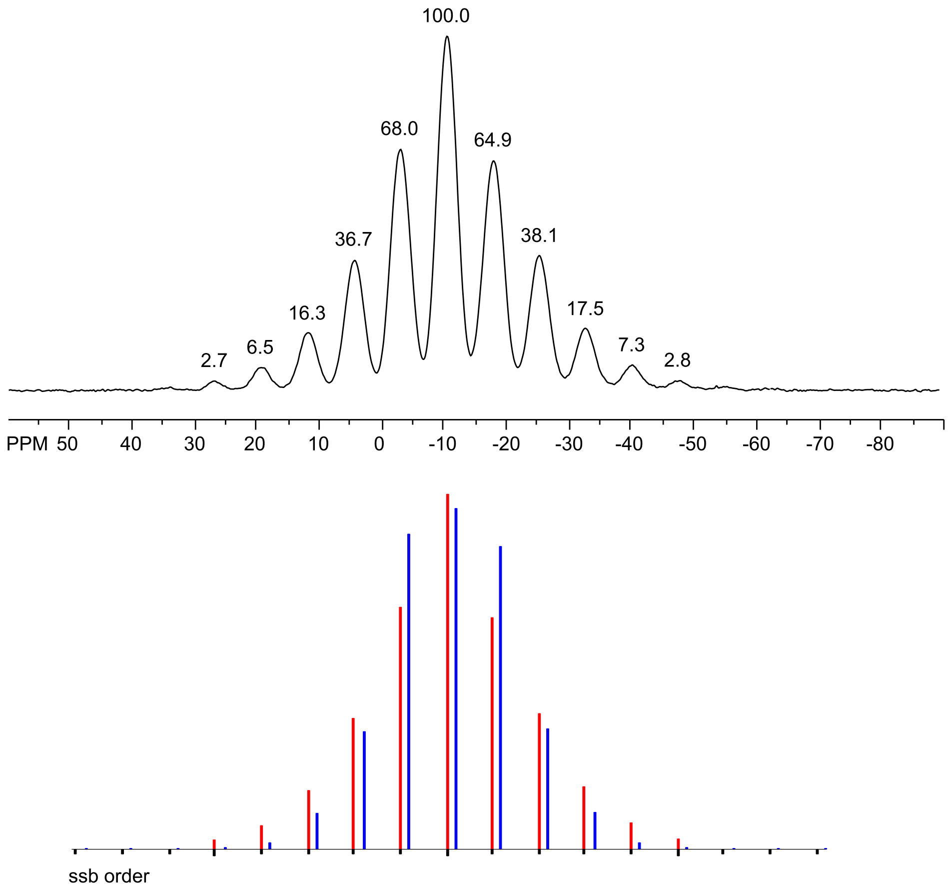


Figure 3.3: Experimental ^{31}P MAS NMR spectrum of β-VOPO$_4$ obtained at 161.974 MHz and a spinning speed of 1200 Hz, $\delta_{\text{iso}} = -10.4$ ppm [21]. Intensities obtained from peak picking are indicated. Bottom: comparison of experimental intensities and best fit corresponding to the fit indicated in Fig. 3.4.

components, up to 22 ppm, compared to those of other carbons, up to 4 ppm [18]. Proper analysis of such spectra requires requires that the dipolar (and ^{14}N quadrupolar) interaction are included in the simulation [19, 20].

Another example is the ^{31}P MAS NMR Spectrum of β-VOPO$_4$ [21], shown in Fig. 3.3, and the corresponding HBA analysis shown in Fig. 3.4. The MAS spectrum looks normal, but the systematic spread of intersections of the contour lines (Fig. 3.4) and the systematic deviations of calculated spinning sideband intensities from experimental data (Fig. 3.3 bottom) indicate that there could be a problem. The results in [21] demonstrate that the "anisotropy" in the ^{31}P spectra is mainly the result of heteronuclear ^{51}V-^{31}P dipolar interactions. The strongest indicator is the observation that the apparent principal components of the chemical shift tensor show a pronounced field dependence [21].

A more heineous case is the ^{31}P MAS NMR spectrum of ammonium dihydrogen phosphate, ADP [22] (Fig. 3.5). Evidence has been brought forward that the ^{31}P chemical shift tensor is not axially symmetric [23, 24]. The HBA analysis shown in Fig. 3.6 confirms that the shift tensor clearly **appears** nonaxially symmetric: the intersection of contour lines is well defined, and the error surface indicates that this non-zero value of ρ is unambiguous. Accordingly, the simulation of spinning sidebands shows excellent agreement with the experimental data (Fig. 3.5 bottom). However, experiments and simulations on ADP in [22] demonstrate that homonuclear dipolar interactions to neighbouring phosphate groups play an important role in the ^{31}P NMR spectra and cause this apparent deviation from an axially symmetric case. The crystal symmetry at the phosphorus site dictates an axially symmetric chemical shift tensor, and this has been confirmed by a ^{31}P single crystal NMR study of ADP [22]. Olivieri and coworkers have subsequently shown that the inclusion of the effects of dipolar

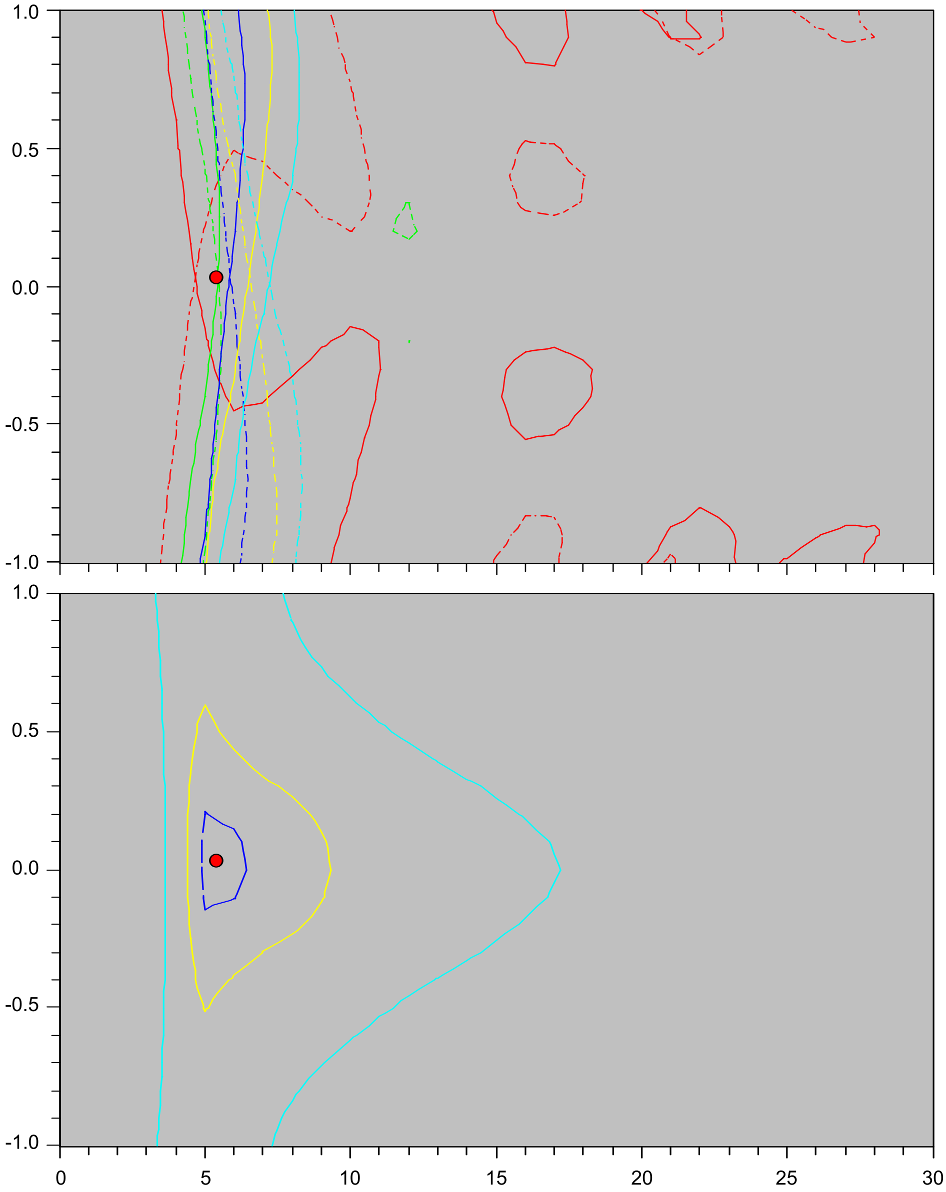


Figure 3.4: Contour lines (top) and error levels (bottom) for the spectrum and fit for the ^{31}P MAS NMR spectrum of β-VOPO$_4$ shown in Fig. 3.3. The best fit is obtained with $\mu = 5.393$ and $\rho = 0.024$, corresponding to $\delta_{11} = 9.4(0.8)$, $\delta_{22} = -10.1(0.4)$, $\delta_{33} = -30.5(0.7)$ ppm.

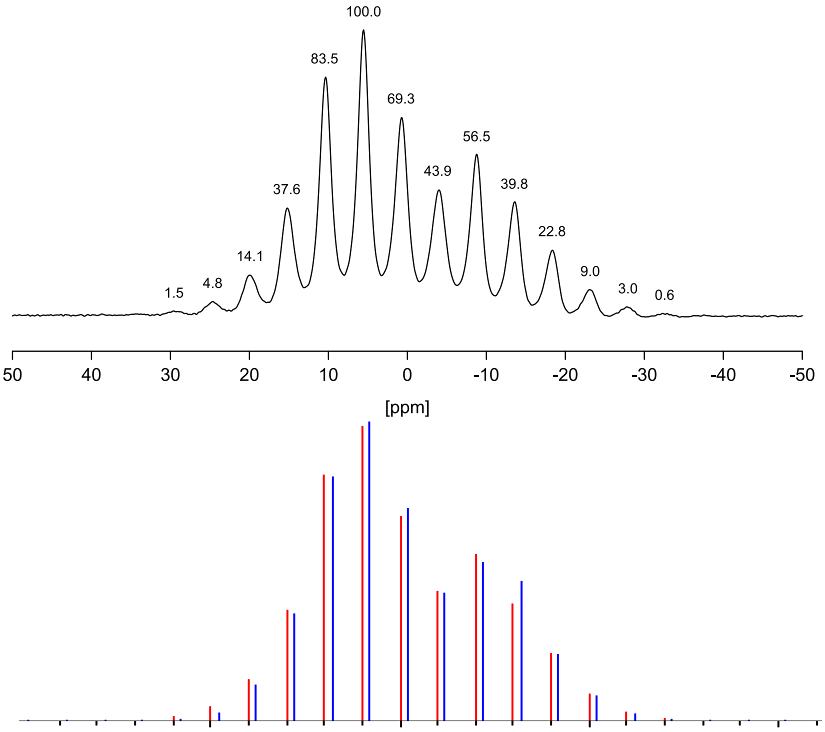


Figure 3.5: Experimental ^{31}P MAS NMR spectrum of $NH_4H_2PO_4$ obtained at 81.033 MHz and a spinning speed of 383 Hz, $\delta_{\text{iso}} = 0.81$ ppm [22]. Intensities obtained from peak picking are indicated. Bottom: comparison of experimental intensities and best fit corresponding to the fit indicated in Fig. 3.6.

interactions in the spinning sideband analysis allows to extract chemical shift tensor information [25].

In my opinion, you should be able to recognize that there is something not right in the case of the analysis of the ^{31}P MAS spectrum of $\beta-$VOPO$_4$. However, the only indication that something is wrong in the case of the ^{31}P MAS spectrum of ADP is the discrepancy between expectations based on the X-ray structure and the non-axial symmetry determined in the analysis. Note that the absolute errors in the principal components may not be good indicators that something is wrong, they are less than 1 ppm in both cases. In the case of $\beta-$VOPO$_4$, the error ratio $R_{\text{MARG/COND}}$ (Eq. 2.5) determined for μ and ρ, 3.59, might be a better indication (the ratios are 1.37 for ADP). Here, I need more experience in assessing these parameters.

The conclusions of this section are quoted from Olivieri's paper [25]:

> »It should be noted that all anisotropic interactions affecting the nucleus of interest will exert an effect on the intensities of the side-band manifold. The most ubiquitous is the dipolar coupling (both direct and anisotropic indirect). In principle, therefore, the study of the side-band intensities will give useful results when all anisotropic interactions other than that arising from the chemical-shift tensor have been removed or are negligible in comparison with the latter.«

To protect yourself yourself from the above pitfalls:

- Check the contours, they may give an indication of how bad or inappropriate the input data are.
- Generate stick spectra to visually inspect the agreement. Are there systematic deviations?
- The best test: if dipolar interactions play a role, the results should show a systematic field-dependence.

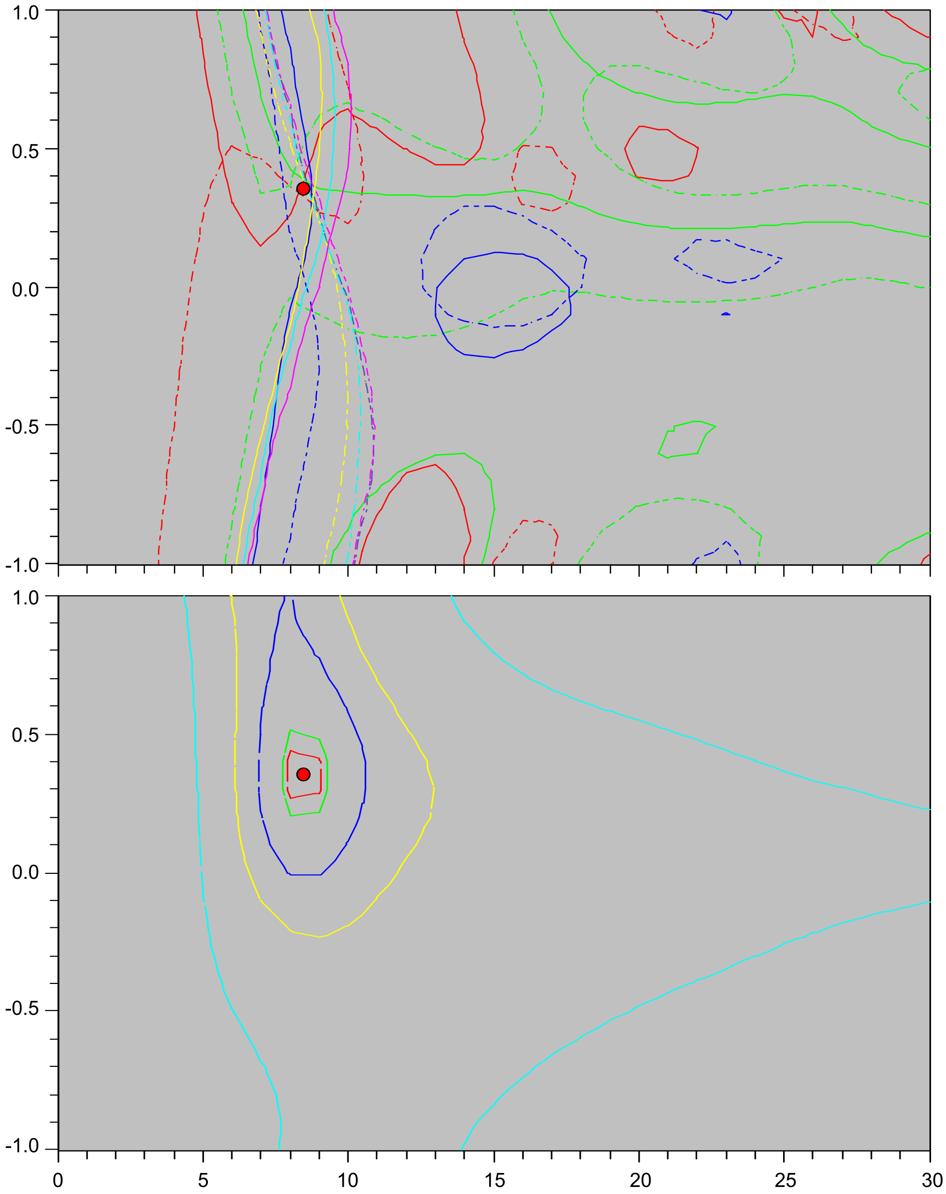


Figure 3.6: Contour lines (top) and error levels (bottom) for the spectrum and fit for the ^{31}P MAS NMR spectrum of $NH_4H_2PO_4$ shown in Fig. 3.5. The best fit is obtained with $\mu = 8.456$ and $\rho = 0.346$, corresponding to $\delta_{11} = 18.5(0.2)$, $\delta_{22} = 5.4(0.1)$, $\delta_{33} = -21.5(0.2)$ ppm.

3.2.3 Distorted Data

For a variety of reasons, the experimental intensities can be inaccurate or distorted, for example:

- A low signal-to-noise ratio will render the determination of intensities difficult; it could be preferable to use peak heights from peak picking rather than integrals [2]; the errors, however, should be statistical
- If MAS spectra have been obtained after cross polarization (CP), the sideband intensities may suffer CP efficiency artifacts because the Hartmann-Hahn matching condition is violated for large frequency offsets from the true Hartmann-Hahn match; a simple empirical correction function has been suggested [26]; alternatively, application of variable-amplitude CP [27, 28] will also reduce such problems [29]. The intensity distortions should show systematic deviations.
- There is a fundamental problem with the graphical approach to Herzfeld-Berger fitting and the approach used by HBA prior to version 1.7: it assumes that the intensity of the center peak is error and distortion free. This is certainly not justified. Using intensity ratios I_N / I_0 for the spinning sidebands will "contaminate" all data if the intensity of the isotropic peak is in error, e.g., due to the presence of impurities. Grimmer *et al.* suggested to use intensity ratios not involving the center band in such cases [30]. Otherwise, one advantage of the Herzfeld-Berger method is that "distorted" peaks can be excluded from the analysis [31], in contrast to methods that use all sideband intensities, e.g., the method proposed by Fenzke *et al.* [32] or the method of moments (p. 56).
- Another source of distortions are radial sidebands, outlined in the following section.

To protect yourself yourself from the above pitfalls:

- Check the contours, is the scatter of intersections systematic or statistical?
- Generate stick spectra; are the differences in spinning sideband intensities systematic or statistical?

3.2.4 Radial Sidebands

While analyzing MAS spectra by hand using the graphical method of Herzfeld-Berger, I frequently noticed that the contour line of one of the first-order spinning sidebands seemed to behave strangely and not in line with the other sidebands, i.e., there was a clear intersection of most contour lines except for the +1 spinning sideband. Examples are also available in the literature: in Fig. 3 of Clayden's paper [16] and in Fig. 6 of the Herzfeld-Berger paper [1], the $N = -1$ contour does not pass through the intersection of the other contour lines (the presence of a saddle point could also be part of the problem).

Fortunately, Tekely [33] was also observant and actually had the math and physics to unveil the cause of this phenomenon. This intensity aberration is caused by radial radio frequency components at the edge of the coil and may especially affect the +1 spinning sideband. Interestingly, the intensity distortion is independent of the spinning frequency and this provides a test as to the origin. Also, TOSS (total suppression of spinning sidebands) is not able to suppress this effect and its intensity aberration survives this sequence. (Note that Tekely and the two examples quoted above use a shielding convention to label the spinning sidebands, i.e., their -1 spinning sideband is to the high-frequency side of the isotropic peak.)

To protect yourself yourself from the above pitfalls:

- Check the contours, is the +1 contour line off the intersection of the other contours?
- Note that you can exclude the bad sideband intensity from fitting by setting its intensity to -1.
- The radial sidebands are caused by sample molecules at the edge of the coil; restricting the sample to the center of the coil should remove radial sidebands.

3.2.5 Exceeding the Limits

The experimental data can be inappropriate for use with the Herzfeld-Berger tables. For example, sample spinning might be so slow that the parameter μ exceeds the limits of the precalculated tables.

To protect yourself yourself from the above pitfalls:

- This situation might be encountered if spinning sidebands of order higher than 15 are visible.
- Quite likely, the parameter μ will bounce against the borders of the Herzfeld-Berger tables, i.e., will have a value of 30.
- Generate stick spectra to visually inspect the agreement.
- If your experimental data exceed the limits of the precalculated Herzfeld-Berger tables, the method of moments (p. 56) might be used, or a direct simulation using other software.

3.2.6 Axially Symmetric or Not?

In the literature, there is a certain fascination with "proving" that a certain chemical shift tensor is axially symmetric. In my opinion, such proof is impossible. Principal components might be degenerate or nearly so by chance; it could be just a matter of going to a magnetic field strength sufficiently high to lift the degeneracy that will never be exact, unless required by the symmetry about the nucleus of interest.

As stated by Clayden [16], part of the problem arises from the fact that the contour lines have similar curvatures for values of ρ close to ± 1 (see Fig. 3.7a), hence run almost parallel to each other and a unique convergence is hard to establish, at least with experimental data that are subject to noise and other sources of error. Therefore, it is not surprising that often μ is better defined than ρ (see the error contours in Fig. 3.7a on the right hand side, they are elongated in the ρ direction).

This problem is not limited to axially symmetric chemical shift tensors (see Fig. 3.7c). In this example, the situation is comparable to Fig. 3.7a. To deal with such situations, one should think of the spinning speed as some sort of resolution power, i.e., if the spinning speed is much higher than the difference between two principal components in Hz, then HBA will have problems to discriminate between them. On the other hand, if the spinning speed is sufficiently slow so that not only vertical contours are available, but also horizontal lines, then the situation improves (cf. Figs. 3.7a and 3.7b, and 3.7c and 3.7d). In the slow spinning cases, Figs. 3.7b and 3.7d, the intersection is defined much better. These examples with $\mu > 20$ also illustrate why it has been worth-while to extend the original Herzfeld-Berger tables to values of μ up to 30 and to correct the tables (in version 1.4.4 (p. 6)). Hodgkinson et al [34] stated that for values of the asymmetry parameter smaller than 0.3 the reliability of the determination is a monotonically decaying function of the spinning speed and that static spectra always provide a more reliable determination of the asymmetry parameter than spinning spectra. More recently, a similar conclusion was reached in a thorough investigation of the ^{119}Sn chemical shift tensor of SnO_2 by Aliev at al. [35].

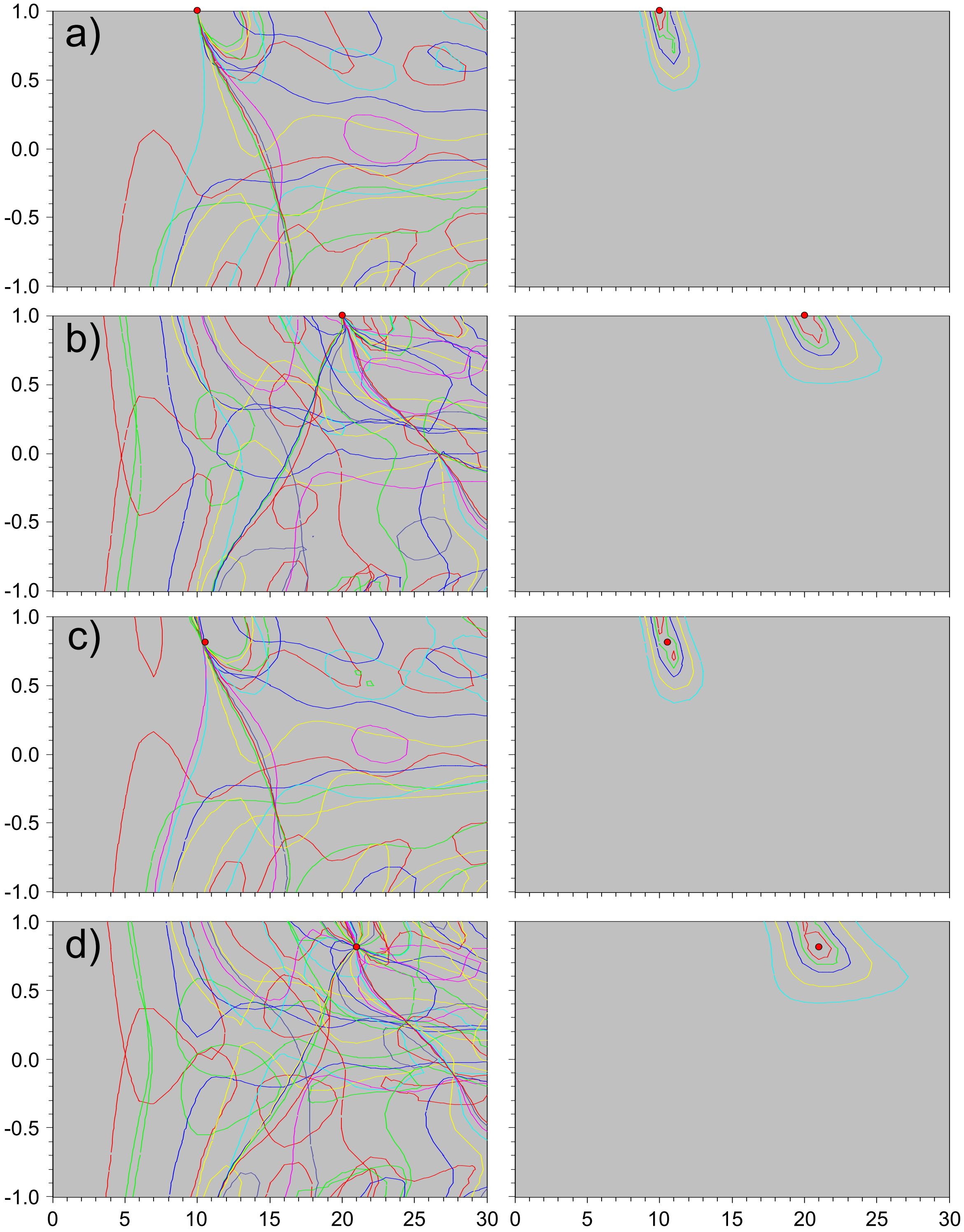


Figure 3.7: Contour lines (left) and error levels (right) for spectra obtained at 100 MHz and at spinning rates of 2000 Hz [a) and c)] or 1000 Hz [b) and d)] corresponding to an axially symmetric chemical shift tensor [a),b)], $\delta_{11} = \delta_{22} = 100$, $\delta_{33} = -100$ ppm, or non-axially symmetric chemical shift tensor [c),d)], $\delta_{11} = 110$, $\delta_{22} = 90$, $\delta_{33} = -100$ ppm, $\rho = 0.81$.

3.2.7 Malicious Software

Another pitfall could be malicious software. The program might not work properly. Although tested and found working fine, there might be some extreme situation where the program fails. Never trust anything! All warranty is disclaimed!

One problem that we became aware of has been associated with the extended Herzfeld-Berger tables themselves; for relatively large values of μ (> 10), some of the outer spinning sidebands did not have the proper intensity. This gets particularly bad for $\mu = 30$.

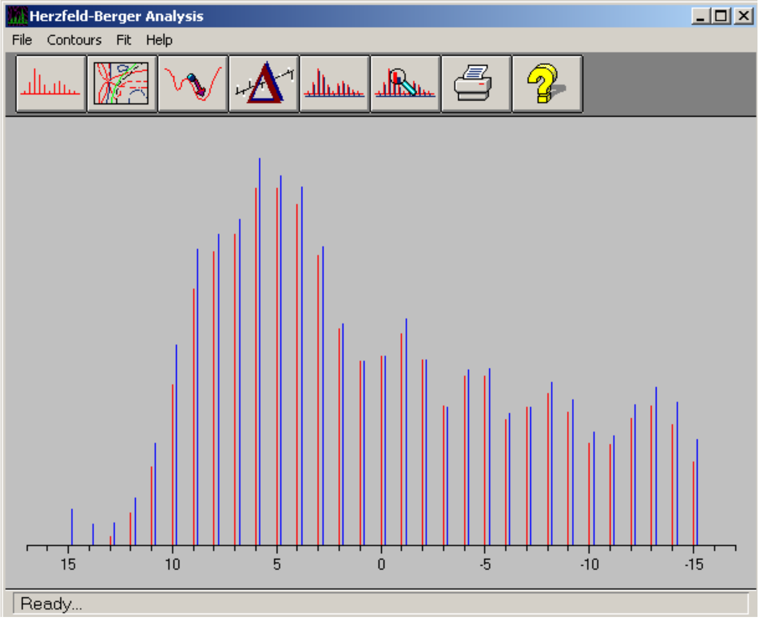


Figure 3.8: Problem with the extended Herzfeld-Berger tables: aliasing in the calculations causes an increase in intensity for spinning sideband orders greater than 12; the spinning sidebands on the left hand side are too high.

This issue was fixed in version 1.4.4 (p. 6). Some programs by other people may also show this problem.

To protect yourself yourself from the above pitfalls:

- Test the software that you are using. Try to reproduce literature data.

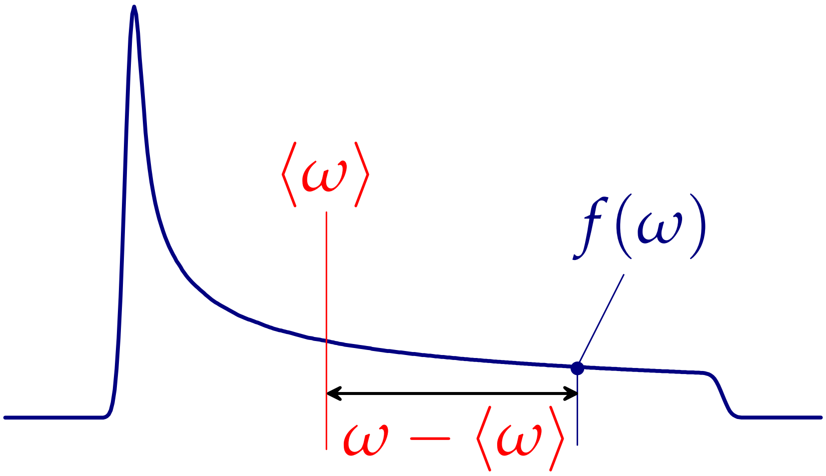


Figure 3.9: Definition of the moment of a line shape illustrated for the line shape of a static chemical shift powder pattern. The mean angular frequency $\langle\omega\rangle$ corresponds to the isotropic chemical shift, the value of $f(\omega)$ corresponds to the intensity of the line shape at ω.

3.3 Method of Moments

3.3.1 Theory

Although the theory necessary to calculate MAS spectra of nuclei under the influence of chemical shift anisotropy is well known, Maricq and Waugh stated that a calculation of this type requires approximately 15 minutes on a state of the art computer in 1979 [36]. Because only two parameters, the span and skew of the chemical shift tensor, should be extracted from line shape, one has the task of constructing a theory of two independent moments of this line shape. The jth moment, M_j, for a line shape $f(\omega)$ is defined in angular frequency units as (Fig. 3.9):

$$M_j = \frac{\int_{-\infty}^{\infty} (\omega - \langle\omega\rangle)^j f(\omega) \mathrm{d}\omega}{\int_{-\infty}^{\infty} f(\omega) \mathrm{d}\omega} \tag{3.1}$$

where the denominator is a normalizing factor and $\langle\omega\rangle$ is the mean angular frequency of the band:

$$\langle\omega\rangle = \frac{\int_{-\infty}^{\infty} \omega f(\omega) \mathrm{d}\omega}{\int_{-\infty}^{\infty} f(\omega) \mathrm{d}\omega} \tag{3.2}$$

Under MAS, the theoretical second and third moments of the spectrum remain unaffected by sample spinning, and one needs to only consider the intensities of the spinning sidebands and neglect the intensity of the baseline. Because of the discreteness of the spinning sidebands, the k−th moment of a magic−angle spinning spectrum (in different units) is given as:

$$M_k\,[\mathrm{rad}^\mathrm{k}\mathrm{s}^{-\mathrm{k}}] = (\,2\pi\nu_\mathrm{r}\,[\mathrm{Hz}]\,)^k \sum_{i\,=\,-M}^{N} i^k * I_i \tag{3.3}$$

$$M_k\,[\mathrm{Hz}^\mathrm{k}] = (\,\nu_\mathrm{r}\,[\mathrm{Hz}]\,)^k \sum_{i\,=\,-M}^{N} i^k * I_i \tag{3.4}$$

$$M_k\,[\mathrm{ppm}^\mathrm{k}] = \left(\frac{\nu_\mathrm{r}\,[\mathrm{Hz}]}{\nu_0\,[\mathrm{MHz}]}\right)^k \sum_{i\,=\,-M}^{N} i^k * I_i \tag{3.5}$$

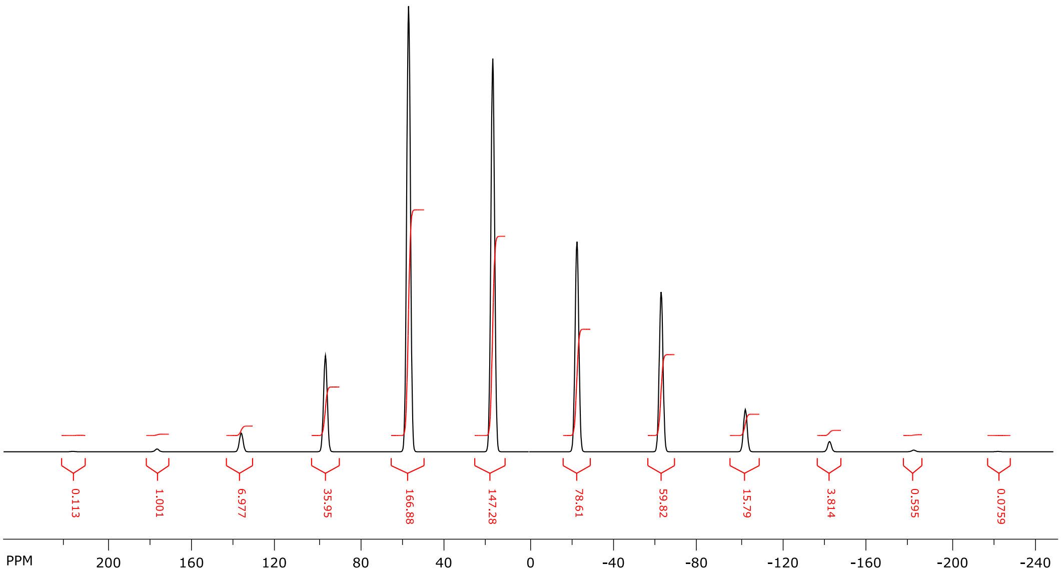


Figure 3.10: Theoretical MAS NMR spectrum calculated for a chemical shift tensor of $\delta_{11} = 100$, $\delta_{22} = 50$, $\delta_{33} = -100$ ppm at an observation frequency of 100 MHz and a spinning frequency of 4000 Hz.

where ν_r is the spinning frequency in Hz, ν_0 the frequency of the chemical shift standard, and the sideband order i runs from the spinning sideband at lowest frequency of order -M to the spinning sideband at highest frequency of order N and its intensity I_i is normalized such that

$$\sum_{i\,=\,-M}^{N} I_i \;=\; 1 \tag{3.6}$$

For the first few moments, Maricq and Waugh have shown [36]:

$$M_0 = 1 \qquad \text{(total intensity normalized to unity)} \tag{3.7}$$

$$M_1 = 0 \qquad \text{(the first moment about the isotropic shift is zero)} \tag{3.8}$$

$$M_2 = (\delta^2/15)(3+\eta^2) \tag{3.9}$$

$$M_3 = (2\delta^3/35)(1-\eta^2) \tag{3.10}$$

where δ is the reduced anisotropy and η the asymmetry parameter defined according to the Haeberlen convention (see 3.1.4).

3.3.2 Application

In Fig. 3.10 we show a calculated MAS spectrum that shall be used to illustrate the application of the method of moments to

- determine the isotropic peak via analysis of the first moment,
- determine the principal components of the chemical shift tensor via analysis of second and third moments.

Starting from the high-frequency end of the spectrum, our first task will be to note the frequency and intensity of each significant peak, as shown in Table 3.5. In the following, we shall use the intensities I obtained from peak picking, but the integrals could be used as well. In the table, we normalize the intensities of the peaks such that their sum gives 1, obtaining I(norm).

peak	order	frequency	I	integral	I(norm)	integral(norm)	M_1 [Hz]
1	5	21679.678	0.0007	0.1132	0.000228938	0.000218942	-20000.52329
2	4	17675.780	0.0060	1.0002	0.001962323	0.001934502	-16000.15396
3	3	13671.875	0.0413	6.9778	0.013507326	0.013495866	-12000.52329
4	2	9667.969	0.2127	35.9616	0.069564364	0.069553862	-8000.523286
5	1	5712.891	0.9870	166.9209	0.322802198	0.322844178	-4000.523286
6	0	1708.984	0.8710	147.3136	0.284863946	0.284921409	-0.523286238
7	-1	-2294.922	0.4650	78.6330	0.152080063	0.152085246	3999.476714
8	-2	-6298.828	0.3538	59.8367	0.115711669	0.115731045	7999.476714
9	-3	-10302.735	0.0934	15.7900	0.030546834	0.030539672	11999.47671
10	-4	-14306.641	0.0226	3.8147	0.007391418	0.007378068	15999.47671
11	-5	-18310.545	0.0036	0.5952	0.001177394	0.001151185	19999.47671
12	-6	-22314.445	0.0005	0.0755	0.000163527	0.000146026	23999.47671
$\sum$			3.0576	517.0324	1.000000000	1.000000000	

Table 3.5: Frequencies and intensities or integrals of spinning sidebands and centerband in the spectrum shown in Fig. 3.10. The M_1 is calculated according to Eq. 3.11 with respect to the peak in that row as center band.

Determination of Isotropic Peak

Then we start the trial by assigning one of the peaks as center band and calculating the first moment about that peak according to the following equation:

$$M_1[\mathrm{Hz}] = \sum_{i\,=\,-M}^{N} i \times \nu_\mathrm{r} \times I_i \tag{3.11}$$

where the sideband order i runs from the spinning sideband at lowest frequency of order -M to the spinning sideband at highest frequency of order N. Sum up all the products of order i times intensity I_i of that peak to obtain M_1 about that trial center peak. Now take the next peak at higher or lower frequency to this trial peak and calculate the first moment for that new trial assignment. If the absolute value of that new first moment is smaller than the old value, then you should keep going into that direction until the magnitude of the first moment starts to increase again. Now you have located the position of the isotropic peak. The solution for the example shown in Fig. 3.10 is already indicated in Tab. 3.5: for each peak, the last column gives the value of M_1 calculated for the spectrum about that peak. If peak 6 is taken to be the center band, the first moment has the smallest magnitude. It is not exactly zero because we have neglected some smaller peaks (*vide infra*).

The value of M_1 given in Tab. 3.5 may indicate by how many spinning sideband orders the current test peak is off from being the center peak. This result might be fortuitous, nor have I seen anyone mentioning this in the literature, nor do I have any mathematical proof. I should do some more tests!!

Determination of Higher Moments

In the next step, we calculate the second and third moments about the isotropic peak. The contribution of each spinning sideband to the second and third moments is listed in Tab. 3.6. It is obvious that high-order spinning sidebands still make large contributions to the second and third moments, albeit their low normalized intensity. We have noted above the effect of missing some high-order spinning sidebands to cause a non-zero value of the first moment. This is an issue that generally makes the

N	I	I(norm)	M_1 [ppm]	M_2 [ppm^2]	M_3 [ppm^3]
5	0.0007	0.000228938	0.045787546	9.157509158	1831.501832
4	0.0060	0.001962323	0.313971743	50.23547881	8037.676609
3	0.0413	0.013507326	1.620879121	194.5054945	23340.65934
2	0.2127	0.069564364	5.565149137	445.2119309	35616.95447
1	0.9870	0.322802198	12.91208791	516.4835165	20659.34066
0	0.8710	0.284863946	0	0	0
-1	0.4650	0.152080063	−6.083202512	243.3281005	−9733.124019
-2	0.3538	0.115711669	−9.256933543	740.5546834	−59244.37467
-3	0.0934	0.030546834	−3.665620094	439.8744113	−52784.92936
-4	0.0226	0.007391418	−1.182626897	189.2203035	−30275.24856
-5	0.0036	0.001177394	−0.235478807	47.09576138	−9419.152276
-6	0.0005	0.000163527	−0.039246468	9.419152276	−2260.596546
Sum	3.0576	1.000000	−0.005232862	2885.086342	−74231.29252

Table 3.6: Contribution of each spinning sideband and the center band in the spectrum shown in Fig. 3.10 to the first, second and third moments.

Herzfeld-Berger approach more robust, because only some of the spinning sidebands are required rather than the complete lineshape as in the case of the moment analysis. The last row of the table lists the second and third moments for the total lineshape, the values of which are used in combination with the isotropic chemical shift to obtain the three principal components of the chemical shift tensor.

Solving the Cubic Equation

Given the second and third moments, we need to solve for the reduced anisotropy the reduced cubic equations created by the combination of eqs. [3.9] & [3.10] under elimination of the asymmetry of the chemical shift tensor:

$$\delta^3 + a\,\delta + b = 0 \tag{3.12}$$

with

$$a = -\frac{15}{4} M_2 \tag{3.13}$$

$$b = -\frac{35}{8} M_3 \tag{3.14}$$

Using a trigonometric solution, we compute the value of the angle ϕ in the expression

$$\cos\phi = -\frac{\frac{b}{2}}{\sqrt{-\frac{a^3}{27}}} \tag{3.15}$$

	solution 1	solution 2	solution 3
δ	83.145	-116.63	33.489
η	1.806	0.4260	5.9655
δ_{iso}	16.67	16.67	16.67
δ_{11}	99.82	99.83	99.82
δ_{22}	50.16	50.14	50.16
δ_{33}	-99.96	-99.96	-99.96

Table 3.7: The three equivalent solutions, Eqs. 3.16-3.18, for the principal components of the chemical shift tensor from the spectrum shown in Fig. 3.10.

and use the angle to solve one of the three equations for δ:

$$\delta(1) = 2\sqrt{-\frac{a}{3}}\cos\frac{\phi}{3} \tag{3.16}$$

$$\delta(2) = 2\sqrt{-\frac{a}{3}}\cos\left(\frac{\phi}{3} + 120^\circ\right) \tag{3.17}$$

$$\delta(3) = 2\sqrt{-\frac{a}{3}}\cos\left(\frac{\phi}{3} + 240^\circ\right) \tag{3.18}$$

With one of the values for δ, we solve eq. [3.9] for η:

$$\eta = \sqrt{\frac{15\,M_2}{\delta^2} - 3} \tag{3.19}$$

Although this procedure generally results in three different sets of values for δ and η, they end up in equivalent solutions (see Sec. 3.1.4) for the three principal elements of the chemical shift tensor, Tab. 3.7.

Moment Analysis of Experimental Intensities

The report file (p. 34) of the iterative refinement will also include the results of a moment analysis of the experimental spinning sideband intensities. An evaluation of the first moment has already been used in identifying candidates for the isotropic peak (p. 58) after reading peak picking or integration files (see Define Spectrum Settings (p. 23)). The second and third moment (p. 58) are calculated also and the cubic equations (p. 59) are solved to obtain the principal components of the chemical shift tensor. In the literature, there is no real discussion on options for an error analysis (probably not trivial, anyway) in the moment analysis. However, my estimate is that the residual value reported for the first moment, M_1 in ppm, could be a good starting point.

Obviously, and as mentioned under Determination of Higher Moments (p. 58), this analysis is only meaningful if all significant sidebands have been included in the analysis.

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