# MossWinn 4.0i

# Manual

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# 1. Introduction

Thank you for choosing the latest version of the MossWinn program, and Congratulations! Today's most accomplished software for Mössbauer spectrum analysis is ready to serve you in your scientific work. Following the release of the first version in 1996, the unique and user-friendly features of MossWinn still remain unrivaled. Building on the strengths of MossWinn 3.0i xp, the 4.0 series takes several further steps ahead to serve scientists worldwide in the field of Mössbauer spectrum analysis, among others by offering the power of 32 bit computing on MS Windows XP, Vista, 7, 8, 10 and 11. Precision, productivity, versatility, and ease of the scientific work in the field of Mössbauer spectrum analysis have been further extended and improved in the MossWinn 4.0 series, while the uniquely effective, proven design of the software has been preserved.

Your questions and comments concerning MossWinn are welcomed at the e-mail address:

**Z.KLENCSAR@MOSSWINN.HU**

It is recommended to check the site of MossWinn on the web from time to time to get informed about the latest developments in connection with the program. The web site of MossWinn can be accessed via:

**HTTP://WWW.MOSSWINN.COM** and **HTTP://WWW.MOSSWINN.HU**

The MossWinn program is created and tested carefully in order to exclude program errors. Nevertheless, the author has to state the following disclaimer:

***The author of the MossWinn program cannot take the responsibility for any consequential, incidental, or other special damages related to the usage of the MossWinn program.***

**Please, do not tolerate any error or malfunction of the MossWinn program.** If you find that the program does not perform as it should, please, contact the author.

Finally, let me wish you a fruitful work by using the MossWinn program,

With best regards,

Dr. Zoltán Klencsár
author

# 2. Contacts

| | |
|---|---|
| **E-mail (preferred contact)** | Z.KLENCSAR@MOSSWINN.HU |
| **Web** | http://www.mosswinn.hu<br>http://www.mosswinn.com |
| **Mail address** | Pitvar 11., Budapest 1141, Hungary |

# 3. Software licensing

**Each site licence of MossWinn is accompanied by one USB licence hardware key.** A single licence of the MossWinn Software entitles the licensee to use the licensed software for its intended purpose on a single computer at a time, by having the associated licence hardware key attached to the computer in question. Without having connected this USB licence key to the computer, the program runs only in demo mode. Unless explicitly noted otherwise, the MossWinn Software licence is non-exclusive, non-transferable and perpetual.

If the licence hardware key gets damaged then it can be replaced. In this case, please, send the damaged hardware key back to the author. If guarantee doesn't apply then the cost of the replacement is **100 EUR** and **150 EUR** with delivery to a country inside and outside of the EU, respectively.

# 4. Hardware / software requirements

The MossWinn program was compiled to run on Intel compatible processors, on PC systems. Among the usual PC components and peripherals, to run MossWinn 4.0*i* the PC system should contain a 32 bit capable Intel compatible processor of ~ 1 GHz or higher core frequency, a hard disk with at least ~ 60 MB free space, at least ~ 256 MB free RAM, a keyboard and a mouse with two buttons, a video card and color monitor with at least VGA resolution, and a parallel or an USB port depending on the type of the used licence hardware key. Thus, the hardware of most of today's PC systems will easily satisfy the minimum hardware needs of MossWinn. In addition, a preferably broad-band internet connection is required to access the *MossWinn Services* including the MossWinn Internet Database (MIDB).

Although MossWinn will start on a PC having no more power than the minimum requirement stated above, to facilitate efficient work a more powerful system is recommended. Due to the demanding mathematical procedures included in MossWinn, the performance of the program improves considerably with increasing processor speeds. Several procedures of MossWinn can furthermore take advantage of multi-core processor architectures, therefore it is recommended to run the program on a system with a multi-core processor.

Operating systems recommended for **MossWinn 4.0*i*** include 32 bit / 64 bit MS Windows **XP**, **Vista**, **7**, **8**, **10** and **11**. The latest version of the Rainbow Sentinel System Driver has to be installed before the licensed version of MossWinn can be started. (Installation of the driver is not required for the Sentinel HL driverless — solid green or purple — licence keys.)

# 5. Installation

In order to install the software, please, contact the author (via z.klencsar@mosswinn.hu ) who will assist you in the installation process.

# 6. Abbreviations

**LMC** = Left Mouse Click / Click with the Left Mouse button on . . .

**RMC** = Right Mouse Click / Click with the Right Mouse button on . . .

**ZVC, ZCh** = Zero Velocity Channel (The real-valued channel number that — in theory — belongs to the zero velocity value on the X axis. It is used to describe linear velocity axes of folded spectra.)

**CAF, CF** = CAlibration Factor (The velocity difference between two neighboring channels in a folded spectrum having a linearly calibrated velocity axis.)

**DOF** = Degree of Freedom

**DN** = Data Number

**ZDN** = Zero Data Number (Number of data with a value of zero)

**TSA** = Total Spectrum Area **[TSA / Base Line]** (calculated on the basis of the fitting curve)

**SO** = Source nuclide

**PAS** = Principal Axis System

**MSD** = Mean Square Displacement Tensor

**GKE** = Goldanskii-Karyagin Effect

**MSCe** = $\frac{\mu_N g_e c}{E_\gamma}$ (on fit reports): multiply this value by a hyperfine magnetic field value (measured in Tesla) in order to obtain the corresponding hyperfine magnetic splitting of the excited state sublevels in mm/s units.

**MSCg** = $\frac{\mu_N g_g c}{E_\gamma}$ (on fit reports): multiply this value by a hyperfine magnetic field value (measured in Tesla) in order to obtain the corresponding hyperfine magnetic splitting of the ground state sublevels in mm/s units.

**QSCe** = $\frac{Q_e c}{(E_\gamma / \mathrm{keV})} \times 10^{21}$ (on fit reports): multiply this value by $V_{zz}$ / ($10^{21}$ V/m$^2$) in order to obtain $eQ_eV_{zz}$ in mm/s units.

**QSCg** = $\frac{Q_g c}{(E_\gamma / \mathrm{keV})} \times 10^{21}$ (on fit reports): multiply this value by $V_{zz}$ / ($10^{21}$ V/m$^2$) in order to obtain $eQ_gV_{zz}$ in mm/s units.

# 7. Directories used by MossWinn

After the first run of MossWinn the following directories will be present inside the directory
**X:\MOSSWINN**

| **DIRECTORIES AND THEIR FUNCTION** |
|---|
| **..\MOSSWINN 4.0**<br><br>This directory collects the files and folders MossWinn works with. |
| **..\MOSSWINN 4.0\DLLS**<br><br>This directory contains the dynamic link libraries available to MossWinn. The subspectrum model function libraries should have a name corresponding to the file mask **SUB*.DLL**, whereas the functional dependence library should have the name **DEP_DLL1.DLL**. They can be programmed/altered by the user in order to extend the fitting capabilities of MossWinn by adding new theories and functional dependencies not in the program by default. (See also page 108.) |
| **..\MOSSWINN 4.0\EXES**<br><br>This directory contains executables of tools belonging to the MossWinn program system. |
| **..\MOSSWINN 4.0\HELP**<br><br>This directory contains the html help system of MossWinn.<br><br>**..\MOSSWINN 4.0\MIDB**<br><br>This directory contains files associated with the MossWinn Internet Database.<br><br>**..\MOSSWINN 4.0\USERS\PUBLIC**<br><br>This directory contains the configuration and data files associated with MossWinn. |
| **..\MOSSWINN 4.0\USERS\PUBLIC\ABSORBER**<br><br>This directory contains custom calibration-absorber definitions. |
| **..\MOSSWINN 4.0\USERS\PUBLIC\MODELS**<br><br>This directory contains the subspectrum and spectrum fit models which can be defined and saved in the FIT menu of MossWinn via SAVE / SUBSPECTRUM and SAVE / MODEL AS, respectively. |
| **..\MOSSWINN 4.0\USERS\PUBLIC\PRINT**<br><br>This directory contains the printer and clipboard configuration files. |
| **..\MOSSWINN 4.0\USERS\PUBLIC\PROJECTS**<br><br>This directory contains information on the project structure of MossWinn. |

**..\MOSSWINN 4.0\USERS\PUBLIC\READONLY**

When an attempt is made to load a read-only file, then MossWinn creates a non-read-only copy of the file in question. This copy is placed in a DATE SUBDIRECTORY inside this directory. After that MossWinn will work with this copy instead of working with the original read-only file.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS**

This directory contains the configuration files of MossWinn. Turn to the **SET** menu in order to edit these files manually.

**..\MOSSWINN 4.0\USERS\PUBLIC\TMATRIX**

This directory can host the version 2.0i style transformation matrices. (See section 31.)

**..\MOSSWINN 4.0\USERS\PUBLIC\XLS**

MossWinn saves XLS output files into this folder. The name of the files includes the creation time of the file.

**..\MOSSWINN 4.0\USERS\PUBLIC\TEMP**

MossWinn stores temporary files in this directory. By 90 days after their creation, temporary files are moved to the trash directory of MossWinn without notice. Data windows associated with temporary files are denoted by a lightgray - rather than blue - frame in MossWinn.

**..\MOSSWINN 4.0\USERS\PUBLIC\TRASH**

This is the trash directory of MossWinn where it places files scheduled for deletion. MossWinn displays a notification when trashed files take up more space than 10 MB.

# 8. Configuration files

There are several configuration files that can be used to customize MossWinn. Most of the parameters in these files can be set in the MossWinn program itself. The **SET** menu can be used to edit the content of these files manually.

### Configuration files and their function

**..\MOSSWINN 4.0\USERS\PUBLIC\MOSSWINN.CFG**

Main configurations file of the MossWinn program. It includes the following sections.

```
[ User ]

User title: Dr.
User name: Zoltán Klencsár
User contact: z.klencsar@mosswinn.hu
```

User-specific information that is used in connection with the MossWinn Internet Database (MIDB) service.

```
[ Internet ]

Enable MossWinn Internet Database (MIDB) access: YES
Automatically detect and download updates of the MossWinn manual: YES
Automatically detect and download updates of help files: YES
Automatically detect and download updates of exe files: YES
Next attempt to detect executable update: on startup
Last downloaded help file version: 2010/03/23
```

Information concerning MossWinn's internet- and update-related options.

```
[ Startup ]

Last maintenance: Sunday
Start up project group:
Desk loaded on start up:
```

Information concerning the startup of the MossWinn program. Last maintenance indicates the day when MossWinn last performed maintenance operations on project, fit-model, temporary and trashed files. Maintenance is performed maximum once a day when MossWinn is started. *Start up project group* and *Desk loaded on start up* refer to the project group and the project invoked on startup.

```
[ Appearance ]

Fullscreen mode: NO
Maximized mode: NO
Application window client width (pixels): 1280
Application window client height (pixels): 700
Horizontal position of the application's upper left corner (pixels): 315
Vertical position of the application's upper left corner (pixels): 298
GUI resolution: 800 x 450
Windowed GUI resolution: 800 x 450
Full screen GUI resolution: 960 x 540
Set optimum GUI resolution when entering full screen mode: YES
Color scheme: Default color scheme
Error bar color: Lighter gray
```

Settings influencing the appearance of the MossWinn program.

```
[ Window attributes ]

Window Ratio (200..1000): 540
Headline contains full path: NO
Headline contains history: NO
Headline contains spectrum headline: NO
Headline contains extremum values: NO
Headline contains temperature: YES
```

Settings influencing the appearance of the data windows displayed by the MossWinn program. Window Ratio defines the preferred aspect ratio of the spectrum windows, which can influence the way the windows are arranged on the screen when the ARR menu option is selected. (For example, compared to 540 the value of 200 will prefer arrangement in more rows in a single column, while the value of 1000 will prefer more columns in a single row. The actual effect will depend on the number of windows present on the project desk.)

```
[ Graphics output ]

Default graphics font: Cambria
Resolution of spectrum images in HTML FitLogs: LOW/MEDIUM/HIGH
Default HTML-formatted X-title of calibrated data files: <i>v</i>, mm/s
```

Settings influencing the appearance of the graphics displayed, saved, printed or copied (to the clipboard) by the MossWinn program. Other settings of this kind are printer specific and can therefore be found in the configuration files inside the folder **..\MOSSWINN 4.0\USERS\PUBLIC\PRINT**

```
[ Printing options ]

Default printer to be used: PDF
Default printing orientation: LANDSCAPE
An LMC on the Print box in the FIT menu should: print fit results as text
```

Default printing options. They can be altered in the SET menu.

```
[ Calibration options ]

Default source matrix: Rhodium
Default calibration absorber: Alpha Iron
Default isomer shift reference material: Alpha Iron
```

Default calibration options. They can be altered in the SET menu.

```
[ Fit attributes ]

Standard fitting mode (Area/Amplitude): AREA
Amplitudes must not be negative: YES
Line Widths must be positive: YES
Absolute maximum of parameters: 1.0E+20
Fractional Fit Precision: 1.0E-7
Default number of Monte Carlo iterations: 200
Standard StD calculation is based on derivatives (1st/2nd): 1st
```

Default options related to mathematical details of spectrum fitting and fit parameter StD calculations. They can mostly be altered inside the FIT menu by pressing on the SET box. Parameter values higher than the Absolute maximum of parameters will be set to the value given here, which may help avoiding numeric overflows during the fitting procedure. Fits will be considered to be convergent if the relative change of fit parameters, between two iteration steps, is less than the value given here as *Fractional Fit Precision*. The default StD calculation mode (see page 92) can be set in the CONFIGURATION SETTINGS... submenu of the SET menu of the MAIN menu.

```
[ Sequential fit attributes ]

Perform Global fit when doing sequential fit: NO
Enable Monte Carlo Error Estimation when doing sequential fit: NO
Enable linking of fits when doing sequential fit: YES
Ascending ordering when doing sequential fit: YES
Accept fit results only if chisquare is improved: NO
When doing sequential fit order spectra with respect to: PH
Lower limit of the order parameter:
Upper limit of the order parameter:
```

Default options related to automatic sequential fitting of spectra. They can be set on the panel invoked by the SFT menu.

```
[ Data I/O ]

On FLD save file with extension: FLD
On REV save file with extension: DAT
Copies of original data files if created should have an extension of: MOS
Maximum number of windows stored in the TRASH: 9
Enable automatic FitLog creation on Accept: YES
Time interval between automatic fit status save events [min] ( 0 = disabled ): 5
```

Default options related to data input and output. They can be altered in the SET menu. When a window is removed from a project desk via the DEL menu, then it is placed on a TRASH desk where it can be reloaded from. (Press on the DEL menu box with the right mouse button in order to achieve this.) Maximum number of windows stored in the TRASH determines the maximum number of windows stored on such TRASH project desks. Each project group has its own TRASH desk. When the number of deleted windows placed on this desk exceeds the maximum value given here, then the oldest one will be removed. Deleting a window from a project desk does not alter/influence the associated physical file. When the fit menu is abandoned unexpectedly due to, e.g., a power cut, the automatically saved fit status can be reloaded when next time MossWinn is started.

```
[ Database ]

Search rethink on change: YES
Include related database links into FitLogs: YES
```

Options related to the MossWinn Internet Database. Database links are included in HTML FitLogs only when the MIDB database is accessible.

```
[ Performance ]

Number of available processor cores: 6
Enable parallel computing on multiple cores: YES
```

Options related to the performance of MossWinn.

```
[ Form status ]
```

Various parameters of forms as set by the user.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\SPECFRMT.CFG**

Contains definitions of special ASCII data formats that make MossWinn able to load ASCII data with a wide range of formats. See section 9.2 for details.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\SPECPRM.CFG**

Contains the names of built in and user defined special parameters that can be used to characterize the handled data. They can be manipulated in the SET menu. Their value for a given data window can be given in the EDT menu.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\EXECUTE.CFG**

Contains the path and name information of executable files that can be started from the EXE menu of MossWinn.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\EDITPROG.CFG**

Contains the path and name of the text editor program that is executed, e.g., when the key ‘E’ is pressed while in the main menu of MossWinn.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\MASKS.CFG**

Contains the file masks that can be selected when the mask edit box is pressed with the right mouse button, e.g., in the Load menu.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS*.MSK**

Files with arbitrary name having the extension msk can be used to store the masks for “very special data formats” as described in section 9.2.

**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\NUCLEAR.CFG**

Optional configuration file that can be used to override the default nuclear constants built into MossWinn. See section 42 for details.

# 9. I/O operations

Original data files encountered by MossWinn at the first time will be copied first: instead of the original, only the copy will be handled by MossWinn. Normally the copy is placed in the host directory of the original file, unless this turns out to be impossible (e.g. because the file is loaded from a read-only storage medium), in which case the copy is placed in a storage directory inside the host directory of MossWinn. The copy will be given the file extension as set in the configuration file **MOSSWINN.CFG**.

## *9.1. Data formats that can be loaded with MossWinn*

MossWinn can be made to understand automatically most of the ASCII data formats used in practice. There are, however, several basic formats that don't need to be defined. The program automatically identifies the following three formats:

(Separators can be commas and spaces as well.)

| **Data in column** | **Data in rows** | **Numbered data in rows** |
|---|---|---|
| HEADLINE | 65987 , 66848 , 68762 . . . | 1 , 65987 , 66848 . . . |
| 65987 | 69000 , 67543 , 67435 . . . | 2 , 69000 , 67543 . . . |
| 66848 | . | . |
| 67548 | . | . |
| 66760 | . | . |
| . | . | . |
| . | . | . |
| . | . | . |

In the above cases no headline is allowed when data are arranged in rows, and only one headline is allowed in the case when data are arranged in one column.

The first format (*Data in column*) is the default format of MossWinn when one *saves* data with the program. There is a so-called extended format as well, which allows one to save **the velocity scale** (**in mm/s**) as well as the subspectra together with the original spectrum. This format has the following structure:

**Extended format** of MossWinn:

```
HEADLINE
  -3.2 , 123456 , 123456.432 , . . .
  -3.1 , 123478 , 123478.982 , . . .
  -3.0 , 134578 , 134578.112 , . . .
    .  ,   .    ,     .
    .  ,   .    ,     .
    .  ,   .    ,     .
```

As in the previous case, in the extended format of MossWinn there is only one headline saved together with the data. The first column contains the velocity of the given channel (in mm/s), the second column contains the data which were measured, the third column contains usually the envelope of the fit, and the fourth and further columns contain the envelope of each subspectra one after the other. The program recognizes this format automatically as well.

## 9.2. To make MossWinn understand other ASCII data formats

In most cases ASCII data are arranged either in columns or in rows. The data are furthermore preceded by one or more headlines. One of these headlines in the ASCII data file usually contains enough information to identify the format (here called 'special format') in question. This is the idea how the MossWinn program can be made to recognize a high variety of data formats by several simple definitions put in the file: **..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\SPECFRMT.CFG**

Assuming that a measuring program produces the following ASCII output:

```
Nov 26 1995      7:06:57 pm     Elt: 01969 Seconds
ID: No spectrum identifier defined
Memory Size: 2048 Chls  Conversion Gain: 0512  Adc Offset: 0000 Chls

  Chn   Counts  ROI
   0,   479857  000
   1,   479284  000
   2,   479677  000
   3,   478015  000
   4,   477663  000
          .
          .
```

and furthermore that the strings ***Memory Size:*** and ***Conversion Gain:*** (case is not relevant) always take part in the third row when the measuring program produces an output like the one above, one can use these strings to identify the above data format which contains 5 rows preceding the data, and which contains the data of the measured spectrum in the second column.

To make MossWinn understand the format above, the following lines should be added to the configuration file: **SPECFRMT.CFG**

*.BEGIN.*
*Name of the format: Output of spectrometer A*
*Get spectrum headline from line: 2*
*Search for identification words in headline: 3*
*Identification words in the headline: Memory Size: & Conversion Gain:*
*Irrelevant rows preceding the data: 5*
*Read data from column number: 2*
*.END.*

After these few lines were added to the file **SPECFRMT.CFG**, MossWinn assumes that the data have the above form whenever the strings ***Memory Size:*** and ***Conversion Gain:*** can be found in the third line of a data file. The name of the format can be any string not longer than 80 characters.

In order to load the X-axis (velocity) data from one of the columns, add the following line to the corresponding format definition:

*Read X data from column number: n*

where *n* is the column number of the column containing the velocity data.

As a second example it is assumed that the measuring program produces an output like this:

```
SPECTRUM           DATE         TIME          LIVE        REAL
FE12MMS.TXT     97/01/16     13:11:23       52012          0

PHA NO. 1   SEGMENT NO. 1   SIZE 1024
 2 TMS of Fe  12.0 mm/s

 0  45011  45377  45377  45345  45211  45029  45171  44782  45118
 1  44679  45324  45095  45335  45534  44476  44865  45019  45111
 2  45009  45235  45085  45608  45397  45004  45452  45383  45264
 3  44963  44632  44822  45605  44910  45435  45084  44737  44726
 .    .      .      .      .      .      .      .      .      .
 .    .      .      .      .      .      .      .      .      .
```

The corresponding definition, which should be added to the file **SPECFRMT.CFG**, is the following:

*.BEGIN.*
*Name of the format: Data in numbered rows*
*Get spectrum headline from line: 2*
*Search for identification words in headline: 4*
*Identification words in the headline: SEGMENT & SIZE*
*{& means that both words must be in the fourth line of the data file}*
*Irrelevant rows preceding the data: 6*
*Data are arranged in rows.*
*The rows are numbered.*
*.END.*

If the rows are not numbered then simply omit the sentence: *The rows are numbered.* The maximum number of identification words that can be defined is 4. The identification words cannot be longer than 20 characters. The maximum number of definitions that can be put in the file **SPECFRMT.CFG** is 16.

In the case of the data files defined up to this point, the end of the data should be denoted by a single empty line following the data. This can be changed, if necessary, by putting the following line in any definition in **SPECFRMT.CFG** :

*String of termination: MY OWN END LINE*

{After MossWinn finds a line equal to '*MY OWN END LINE*' the loading terminates.}

If the spectrum data file contains information on the sample temperature and/or velocity axis calibration, i.e. the calibration factor (CAF) and the zero velocity channel (ZVC), then MossWinn can also be instructed to extract and apply these values. To achieve this, one can add instructions to the corresponding definition in **SPECFRMT.CFG** as follows:

*Search for calibration factor in line:* 10
{Calibration factor will be looked for in line 10 of the data file.}
*Search for calibration factor at character position:* 20
{The given character position (20 in line 10) should coincide with one of the characters of the CAF.}
*Search for zero velocity channel in line:* 10
{Zero velocity channel will be looked for in line 10 of the data file.}
*Search for zero velocity channel at character position:* 5
{The given character position (5 in line 10) should coincide with one of the characters of the ZVC.}
*Search for temperature in line:* 3
{Temperature value will be looked for in line 3 of the data file.}
*Search for temperature at character position:* 10
{The given character position (10 in line 3) should coincide with one of the characters of the temperature value.}

Further “very special data formats” can be defined as follows. Let’s assume that MossWinn should be able to load the data from the following ASCII file:

```
SOME TEXT NO DATA
SOME TEXT 15678.89 SOME TEXT
DATA14899.9990 SOME TEXT
CHARAC17899TERS NOT19002.43E0BELONGING
TO16999ANY DATA SHOULD BE 19000SKIPPED.
1.6785E+04HOW TO 156435E-01LOAD THESE DATA
WITH MOSSWINN?18888.77
```

Assuming that the above ASCII data file is a data format in which the data are always at the same place we can make MossWinn to extract the data from the file automatically. To do this one has to create a second text file that contains the so-called *mask* matching the above file. The definition of the mask is rather simple: in the file containing the mask there should be a ***** character wherever a relevant number is present in the data file that should be loaded using the given mask.

In the case of the above example one could create the following mask-file:

```
FIRST ROW. EVERY CHARACTER BUT THE SIGN OF MULTIPLICATION IS SKIPPED
SOME TEXT 156*8.89 SOME TEXT
DATA14899*9990 SOME TEXT
CHARAC17*99TERS NOT19002.4*E0BELONGING
TO16*99ANY DATA SHOULD BE *9000SKIPPED.
1.6785E*04HOW TO 156435E-0*LOAD THESE DATA
WITH MOSSWINN?188*8.77
```

ASCII data file that can be loaded according to the above-defined mask:

```
SOME TEXT NO DATA
SOME TEXT 15678.89 SOME TEXT
DATA14899.9990 SOME TEXT
CHARAC17899TERS NOT19002.43E0BELONGING
TO16999ANY DATA SHOULD BE 19000SKIPPED.
1.6785E+04HOW TO 156435E-01LOAD THESE DATA
WITH MOSSWINN?18888.77
```

In the above case 9 data will be loaded correctly. In the file containing the mask only the ***** characters are relevant. Other characters were included only to make the comparison of the mask with the data file easier. Save the mask with extension **.MSK** (name part is arbitrary) inside the folder **..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\.**

One can load data according to the masks saved into the **STATUS** folder by pressing with the right mouse button on the **LOAD FILE** box in the **LOAD** menu.

The maximum number of data that can be loaded with MossWinn as one spectrum is 8191.

# 10. The LOAD menu

Next follows the description of the menu boxes in the **LOAD** menu.

| NAME | DESCRIPTION |
|---|---|
| **DRIVE LETTER BOXES** | The DRIVE LETTER boxes display the letters for the available drives until the letter R. The current drive can be changed by pressing the DRIVE LETTER box associated with the requested drive or, if the drive letter of the required drive is not visible, either by pressing the corresponding drive letter on the keyboard, or by pressing on the CURRENT DIRECTORY box. Move the mouse pointer over a DRIVE LETTER box to have information displayed about the corresponding drive in the INFO box. |
| **FILE NAME EDIT BOX (THE UPPER BOX)** | Shows the name of the selected file. |
| **FILE MASK EDIT BOX (THE LOWER BOX)** | Shows the file mask that determines the type of files displayed in the EXISTING FILES box. Press with the right mouse button on the MASK box in order to select one of the predefined file masks listed in the file:<br>`..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\MASKS.CFG` |
| **CURRENT DIRECTORY** | Indicates the current directory that contains the listed files and folders. Press on it with the mouse in order to create a new directory or to access drives not visible as a DRIVE LETTER box. |
| **EXISTING FILES** | Shows the files matching the given file mask and being in the current directory. LMC any of the file names in order to display its preview. RMC the file names in order to select them without preview. |
| **DIRECTORIES** | Shows the folders accessible in the current directory. |
| **INFO BOX** | The INFO box displays information concerning the visual element over which the mouse pointer is positioned. The visual elements regarding which the INFO box displays information are the DRIVE LETTER boxes, the FILE NAME EDIT box, the FILE MASK EDIT box, the CURRENT DIRECTORY box, the EXISTING FILES box and the DIRECTORIES box. |
| **LOAD FILE** | Performs the loading of single data files, file groups, and transformation matrices. To load more than one spectrum in succession without leaving the LOAD menu, LMC the file name of the spectra in the EXISTING FILES box, and then LMC the preview of them appearing on the right side of the screen.<br>To load a file according to a special data format, irrespective of whether the file satisfies the file format criteria (see section 9.2) declared for the format in question, RMC the LOAD box. |
| **X,Y[X]** | Performs the loading of data files in X,Y[X] format. First the data are loaded as in the case of the simple LOAD command and after the successful loading process the data in the first column of the data file is loaded separately to serve as the X-axis data of the whole data file. X,Y[X] loading method is selected automatically if the first character in the first row of the data file is the exclamation mark ( ! ).<br>(Spectra saved as X,Y[X] data in the SAVE menu do not require the use of the X,Y[X] method when loading them again. In case of data files loaded as X,Y[X] data the calibration constants have no effect, because the velocity values belonging to the channels are stored in a separate data array in the memory.) |
| **TEXT** | Loads text files. |
| **LOAD ALL** | Loads all files whose name is currently visible — according to the current file mask — in the EXISTING FILES list. |
| **EXIT** | To leave the LOAD menu. |
| **PREVIEW** | Preview of the data & text files is available when the name of a file in the EXISTING FILES box is clicked with the left mouse button (LMC). RMC selects the file, but it does not result in the preview of it. |

# 11. The SAVE menu

| NAME | DESCRIPTION |
|---|---|
| **DRIVE LETTER BOXES** | The DRIVE LETTER boxes display the letters for the available drives until the letter R. The current drive can be changed by pressing the DRIVE LETTER box associated with the requested drive or, if the drive letter of the required drive is not visible, either by pressing the corresponding drive letter on the keyboard, or by pressing on the CURRENT DIRECTORY box. Move the mouse pointer over a DRIVE LETTER box to have information displayed about the corresponding drive in the INFO box. |
| **FILE NAME EDIT BOX (THE UPPER BOX)** | Contains the name by which the file is to save. Press on it to edit. |
| **FILE MASK EDIT BOX (THE LOWER BOX)** | Shows the file mask that determines the type of files displayed in the EXISTING FILES box. Press with the right mouse button on the MASK box in order to select one of the predefined file masks listed in the file:<br>**..\MOSSWINN 4.0\USERS\PUBLIC\STATUS\MASKS.CFG** |
| **CURRENT DIRECTORY** | Indicates the current directory that contains the listed files and folders. Press on it with the mouse in order to create a new directory or to access drives not visible as a DRIVE LETTER box. This is the directory where the content of the selected window is saved when the SAVE FILE box is pressed. |
| **EXISTING FILES** | Shows the files matching the given file mask and being found in the current directory. |
| **DIRECTORIES** | Shows the folders accessible in the current directory. |
| **INFO BOX** | The INFO box displays information concerning the visual element over which the mouse pointer is positioned. The visual elements regarding which the INFO box displays information are the DRIVE LETTER boxes, the FILE NAME EDIT box, the FILE MASK EDIT box, the CURRENT DIRECTORY box, the EXISTING FILES box and the DIRECTORIES box. |
| **SAVE FILE** | Performs the saving of data files and text files. If the X-axis of the saved spectrum is linearly calibrated, then the basic format of MossWinn is used, that is, data will be saved in one column preceded by one headline. |
| **SAVE X,Y[X]** | Performs the saving of data files in the *extended* format (see section 9.1) of MossWinn. The files saved in this way do not require the use of the X,Y[X] loading method, but they can be loaded using the simple LOAD FILE box in the LOAD menu. |
| **SAVE GROUP** | Press on this box to save the list of files associated with the windows on the current project desk to a file group. A *file group* is a text file with a list of data file names following the code words **FILE GROUP** being present in the first line of the file. If a file group is selected for load in the Load menu, then MossWinn will load all the files listed in the file group. The direct use of file groups can be considered as to be obsolete: in order to collect files in a group, create instead a new project desk and load the files - to be grouped - onto that. |
| **EXIT** | To leave the SAVE menu. |

# 12. Managing the windows in the main menu

When the program starts, the default project gets loaded, and the main menu is displayed. In the main menu spectra and text files are framed in windows with several different colors. The default color of a window (-frame) is blue. The red (i.e. red-framed) window is the ***master/target window***, that is, any selected operation gets carried out on the spectrum in this window. The green window is the ***source window***, while the red window takes the role of the target window for various operations. Windows referring to files inside the temporary directory of MossWinn (`..\MOSSWINN 4.0\USERS\PUBLIC\TEMP\`) are displayed with a gray frame unless selected to be red- or green-framed.

Unless there are not any windows loaded on the current desk, there is always exactly one master window on the screen. To make a blue-, gray- or green-framed window to be the master window, press on it with the left mouse button. To make a blue- or gray-framed window to be the source window, press on it with the right mouse button. To remove the source status of the window, press on it with the right mouse button again. In order to have the red window display information on the corresponding data, press on it with the left mouse button. A further press on it will make it display the spectrum graph again.

To move a window on the screen, press on it with the left mouse button, and drag it to a new position without releasing the mouse button. To resize a window, press on its frame, and move the mouse while the frame reaches the required size.

Operations that would change the original spectrum data in the red window result in a new window containing the result of the operation in question, so that the original spectrum data remain unaltered.

## *12.1. Functionality of the headline of the windows*

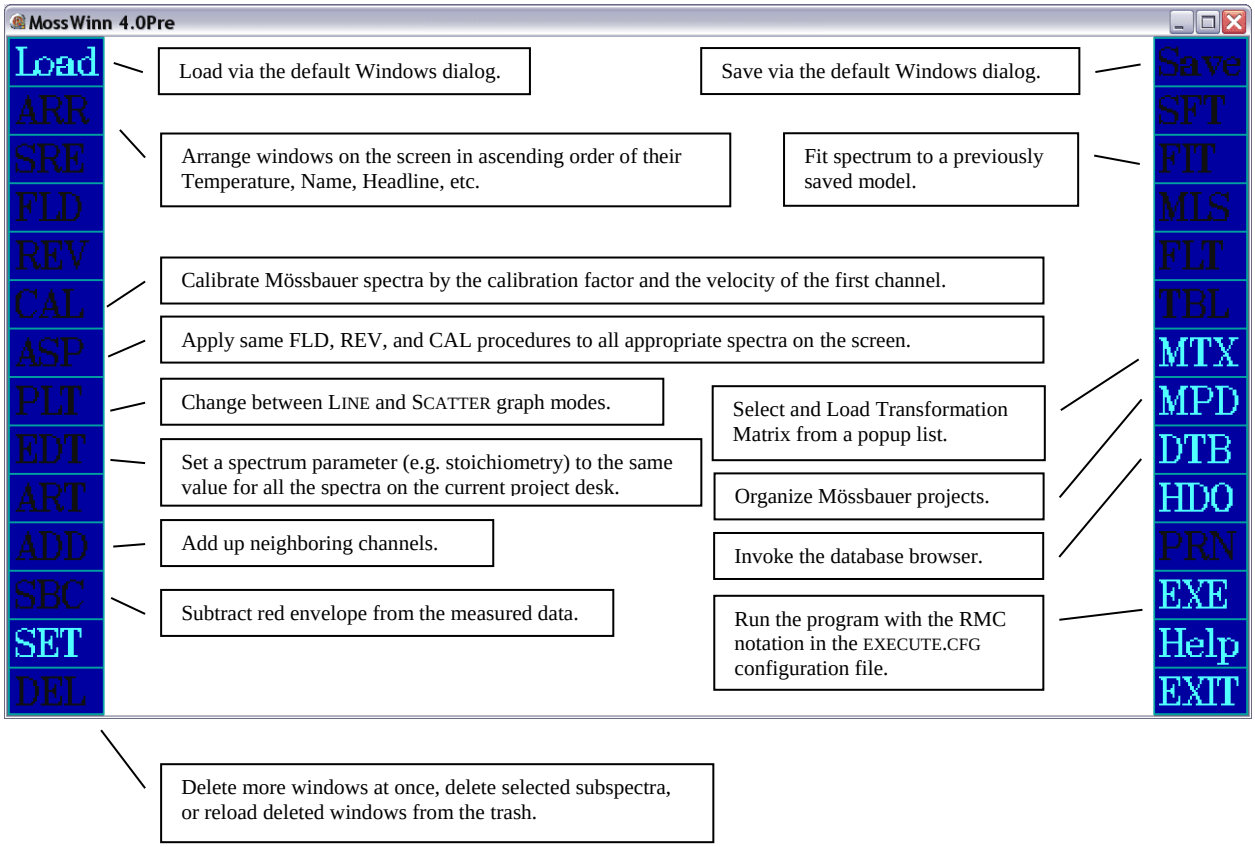
In the bottom of the windows there is a headline that displays information on the corresponding spectrum or text file. Press on the headline to access the following options related to the window in question.

- **Open HTML FitLog** - to open the HTML FitLog file that was created in connection with previous fits of the spectrum in the selected window. The FitLog file is opened in the default web browser application.
- **Create copy** - to create an independent copy of the window and the associated data file. The newly created data file copy is placed inside the host directory of the orginal, and is given a name that differs from that of the original by numbering.
- **Create temporary copy** - to create an independent *temporary* copy of the window and the associated data file. The newly created data file copy is placed inside the temporary directory of MossWinn (`..\MOSSWINN 4.0\USERS\PUBLIC\TEMP\`), and is given a name that has the extension of **TMP**. By 90 days after their creation, temporary files are moved to the trash directory of MossWinn without notice. Windows associated with temporary files are denoted by a gray — rather than blue — frame in MossWinn.
- **Rename associated file** - to rename the file associated with the selected window.
- **Update on disk** - to update the content of the file associated with the selected window according to the actual state of the window. If the window does not have an associated file (i.e. it has not been saved yet), then it will be saved as a temporary file.
- **Reload from disk** - to reload the content of the selected window from the file associated with it.
- **Copy as xls** - to make a copy of the spectrum data in the selected data window in the form of an XLS spreadsheet file. Once created, MossWinn attempts to open the XLS file with an associated software application. *This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.*
- **Print to printer** - Print image of the selected data window either to the default, or to the selected printer.
- **Copy to clipboard** - Copy image of the selected data window into the clipboard of Windows.
- **Copy to clipboard (as text)** – To copy the spectrum data associated with the selected window into the clipboard of Windows as text, including the velocity axis, the measured data, the fit envelope and the subspectra in separate columns as comma delimited numerical data. This option may be used to export numerical data from MossWinn to external graphics software.
- **Show residual** - to show/hide the residual for the selected data window.
- **Recalibrate Y axis** - to adjust the Y axis scale such that all relevant data points are visible.
- **Consider/Ignore zero data points** - to consider/ignore zero valued data points when displaying, fitting, etc. of the selected spectrum. Normally, zero valued data points are ignored, i.e. they are regarded as 'bad points' not to be considered when the spectrum is displayed, fitted or manipulated in any other way.
- **Add to headline content** - to make the selected item to be displayed in the headline of the selected window.
- **Remove from headline content** - to make the selected item *not* to be displayed in the headline of the selected window.
- **Set current as default headline content** - to make the actual headline content to be the default one concerning the items to be displayed. This will influence the window headline of spectra newly loaded/encountered by MossWinn.

## 12.2. Alternative options invoked by the right mouse button

Throughout the MossWinn program menu boxes appear that have different functionality depending on the mouse button that is pressed (left or right). Such menu boxes can be found in the FIT menu, TBL menu, Load menu, MLS menu, FLT menu, as well as in the main menu.

The picture below emphasizes those menu items that have additional functionality when they are pressed on with the right mouse button in the main menu. A short description of the right mouse button functionality is also given. For a detailed description of these extra options, please, see the description of the corresponding menu system.




# 13. The ARRange menu

LMC the ARR box in the main menu of MossWinn in order to make the windows arranged on the screen in rows and columns, according to a predefined shape factor. This shape factor is defined in the MOSSWINN.CFG configuration file (see 'Window attributes' in section 8). RMC the ARR box to arrange the windows on the screen in ascending order of one of their special parameters (alphabetical or numerical order depending on the type of the special parameter). Select the special parameter in question in the appearing popup box. For example, in this way the windows can be made arranged on the screen according to their associated FILE NAME, HEADLINE STRING, TEMPERATURE etc. Whereas special parameters can be defined in the SET menu, their value for the red-framed window can be edited via the EDT menu.

# 14. The SRE menu

Spectrum Recovery and Editing can be done in the **SRE** menu. In this menu there is the possibility:

- To set the value of selected data points to zero.
- To change the value of any data point.
- To change the channel number of the spectrum.
- To correct overflows by hand.

The next table contains the meaning of the boxes visible on the screen in this menu.

| | |
|---|---|
| ***Upper Window*** | The spectrum that should be recovered. At the edges of this window there is a rectangle that can be managed by the mouse. |
| ***Lower Window*** | The resulted recovered spectrum that reflects promptly the changes made during recovering and editing. |
| **REPLACE ON DISK** | Overwrites the original data file with the recovered one on the hard disk. To avoid data loss previously a backup file is saved into the temporary directory of MossWinn. |
| **OVRFLOW** | **LMC** : Adds the overflow number (visible below the word 'OVRFLOW') to all the data counts that are *inside* the rectangle in the upper window. **RMC** : Adds the overflow number (visible below the word 'OVRFLOW') to all the data counts that are *outside* the rectangle in the upper window. The overflow number can be changed after a LMC on its box. |
| **FIX INSIDE** | Set the value of those points that are *inside* the rectangle in the upper window to zero. |
| **FIX OUTSIDE** | Set the value of those points that are *outside* the rectangle in the upper window to zero. |
| **CHANNEL** | Press to change the number of channels to a value less than 8191.<br>If one sets fewer channels then the last ones will be cut. |
| **RESET** | Reset the value of those points that are inside the rectangle in the upper window. |
| **EXIT & KEEP** | Leaves the **SRE** menu. The original and the recovered data both remain in the memory for further processing. |
| **CANCEL** | Leaves the **SRE** menu without keeping the window containing the recovered spectrum. |

When the mouse is positioned above the lower window, then a LMC results in the possibility to edit the value of the selected data point. RMC sets the value of the selected data point to zero.

If the spectrum contains more than 512 channels then difficulties may be encountered by setting the value of individual channels. This is because the resolution of the applied graphics does not allow every data point to have its own pixel on the screen. In these cases one can improve the resolution by a LMC on the ‘+’ sign in the right upper corner of the screen. If the ’−‘ sign is clicked then the original resolution can be recovered. By increasing the resolution, as described above, some part of the spectrum may overstep the edges of the screen. To make the required part of the spectrum displayed, LMC the **arrows** in the left upper corner.

In the case of the ‘+’ and ’−‘ signs as well as in the case of the arrows one can speed up the process by applying RMC rather than LMC. Both mouse buttons can also be pushed at once to achieve an even faster speed.

# 15. The FoLD menu

LMC the FLD menu box to create a new window containing the folded version of the spectrum in the red window. The program selects the best folding point automatically, but it can as well be set manually on the appearing form. The folding procedure of MossWinn works as follows.

The folding point is supposed to have the mathematical form: $F = N/2$ where $N$ is an integer value. After having entered the folding routine one has the possibility to set the minimum and maximum values of $F$. The folding point, $F$, in which case the expression

$$Z(F) = \sum_{i>F}^{N} (C_i - C_{F-(i-F)})^2$$

is minimum will be accepted. ($\boldsymbol{C_i}$ denotes the counts in the $i$th channel of the measured spectrum.)

If $\boldsymbol{D_{last}}$ denotes the last channel of the folded spectrum then $\boldsymbol{D_{last} = C_F + C_F}$ in the case when $F$ is an integer value, and $\boldsymbol{D_{last} = C_{F-1/2} + C_{F+1/2}}$ in the case when $F$ is a half-integer value. Interpolations between counts in neighboring channels are not made.

After the spectrum has been folded the program attaches a certain number of channels with fixed (zero) value to the left (negative) end of the folded spectrum to make it contain a number of channels equal to $2^n$ where $n$ is an integer value. (Mainly for the sake of the MLS and FLT menus that rely on the FFT algorithm.) Note that for folded spectra the calibration constant of the zero velocity channel as evaluated by other programs (that can use a different procedure for folding) may happen not to be the correct one when used in the MossWinn program.

The MossWinn program is able to calibrate and fit unfolded spectra in the **FIT** menu. In this way one can achieve precise fits even if the folding point of the spectrum does not have an integer or half-integer value as assumed in the folding routine. For transmission integral fits, when ultimate precision is required, it is also recommended to fit the unfolded data rather than the folded one. Namely, folding of the spectra always results in a slight broadening of the absorption lines, which could slightly modify the results of transmission integral fits.

# 16. The REVerse menu

After a spectrum was folded, it is usual to want the channels on the left side of the spectrum to belong to negative velocity values, and the channels on the right side to positive velocities. In the case of some Mössbauer setups the folded spectrum needs to be reversed to achieve this. This reversion can be done via the **REV** menu.

LMC the **REV** box to create a new window containing exactly the same data as the original red window did, but in reversed order. If the original spectrum was already calibrated, then the value of the ZVC will be corrected automatically after reversion, so that the – mostly imaginary – channel belonging to the zero velocity will contain exactly the same counts as it did in the case of the original spectrum.

The reversion procedure of MossWinn works as follows. Let $C_i$ denote the original spectrum and $D_i$ denote the reversed spectrum. Then $D_i = C_{N-i+1}$ ($N$ being the number of channels) is true for every $i$.

# 17. The CALibration menu

Use the **CAL** menu to calibrate folded spectra with a linear velocity scale according to known calibration parameters (ZVC and CAF), or to transfer the calibration information from calibrated spectra to uncalibrated ones.

Deselect any green windows on the screen, and LMC the **CAL** box to set the ZVC and CAF calibration constants for the red window. RMC the **CAL** box in order to set the CAF constant, along with the velocity value belonging to the first channel, rather than the channel belonging to the zero velocity (ZVC).

To transfer calibration information from one spectrum to the other, select the source spectrum green, and select the uncalibrated target spectrum red. Then LMC the **CAL** box.

# 18. The ASP menu

**ASP** stands for „**A**pply **S**ame **P**rocedures". LMC the **ASP** box to carry out **FLD**, **REV** and **CAL** operations for the red window exactly as they were carried out for the green window. RMC the **ASP** box to carry out **FLD**, **REV** and **CAL** operations for all the uncalibrated windows on the screen exactly as they were carried out for the green window.

Typical application of this menu is the following. Load a calibration spectrum, and carry out the **FLD** and **REV** operations on it as required. Enter the **FIT** menu and calibrate the velocity axis of the calibration spectrum. Exit the **FIT** menu, and load all the raw (unfolded, non-reversed, and non-calibrated) spectra that were measured according to the same velocity settings as the calibration spectrum. LMC the window of one of the newly loaded spectra in order to make it red. RMC the window of the calibration spectrum to make it green. Then RMC the **ASP** box. As a result, all the newly loaded spectra will be folded, reversed and calibrated exactly according to the calibration spectrum in the green window. The resulted calibrated spectra will be placed in new windows, whereas the original ones will remain unaltered. (As the processed version of the spectra will be positioned above their respective originals, it is convenient to select the option 'DEL → Delete invisible windows on the current desk' in order to remove the original — uncalibrated — spectra from the desk.)

# 19. The PLoT menu

RMC the **PLT** box to make data points in the red window connected/disconnected. When a text file is being shown in the red window a LMC on the **PLT** box makes the red window transparent/not-transparent. A RMC on the **PLT** box makes a text window maximized/minimized in size. LMC the **PLT** box to change the following options of plotting data in the red window.

- **Apply to all** - to apply the selected option to all the windows.
- **Consider/Ignore zero points** - to consider/ignore zero valued data points when displaying, fitting, etc. of the red-framed spectrum. Normally, zero valued data points are regarded as 'bad points' not to be considered when the spectrum is displayed, fitted or manipulated in any other way. 'Fixing' data in the SRE menu also means that the value of the selected data points are set to zero.
- **Show/Hide horizontal line at Y = 0.0** - to show/hide a horizontal line at the ordinate value of Y = 0.0 in the red-framed data window. If the Y axis range does not contain the value of Y = 0.0, then the line won't appear. This option is useful e.g. for inspecting residuals created via the SBC menu box.
- **Point size** - to select Auto/Large/Small data point size for the red-framed spectrum window. When **Auto** is selected, the program chooses between Large and Small point sizes depending on the size of the window.
- **Connect/Disconnect points** - toggle between scatter and line graph modes for the red-framed window.
- **Show/Hide StD bars** - to show/hide StD bars for the red-framed spectrum window. StD bars extend ±σ around the data points where σ is the square root of the data count value. When StD bars are shown, the data points are displayed disconnected from each other.
- **Show/Hide residual** - to show/hide the residual for the red-framed spectrum window. The residual is calculated by subtracting the red fitting envelope from the measured data, then it is shifted to be positioned above the spectrum data. A magenta-colored horizontal line denotes the zero level of the residual, while a grey stripe indicates (approximately) the levels of +1 Std and −1 Std around the zero level. The residual is visible only if the spectrum window contains a fitting envelope.
- **Show/Hide Y axis** - to show/hide the Y (vertical) axis of the red-framed spectrum window.
- **Use/Hide suffix** - to use/hide suffix notation in the numerical labels of the Y axis of the red-framed spectrum window. Suffix notations include k (kilo, $10^3$), M (Mega, $10^6$), G (Giga, $10^9$), T (Tera, $10^{12}$), P (Peta, $10^{15}$) and E (Exa, $10^{18}$). On graphical outputs the suffix notations appear as a **/$10^n$** extension after the Y-axis title.
- **Show percentage/absolute values** - toggle between percentage (i.e. relative) and absolute numerical representation of the Y (ordinate) values in the red-framed spectrum window. In percentage representation the ordinate values are meant relative to the (signed) maximum of the data, $y_i(\%) = 100\times(y_i/y_{max})$. (According to the above, for negative valued data the percentage representation may result in values lower than −100%).
- **Transparent/Not transparent** - to make the red-framed window transparent/not transparent. In transparent mode the white background of the window is not drawn, such that windows being below the transparent window can be seen as well.

- **Ungroup window** - to create a separate data window for all or only one of the fitting envelops being present in the red-framed spectrum window. To create a separate window for all of the fitting envelops, click directly on this item, whereas to create a separate window only for a single fitting envelope, select one of them in the appearing list.
- **Group with green** - to add all the data series being part of the green-framed spectrum window to the red-framed spectrum window. In the red-framed window the newly added data series will appear as additional fitting envelops. Fitting envelops can be removed from a data window via the menu list of the DEL menu box (accessible by a click with the right mouse button).
- **Make a copy of red** - to create an independent copy of the red-framed data window.

# 20. The EDT menu

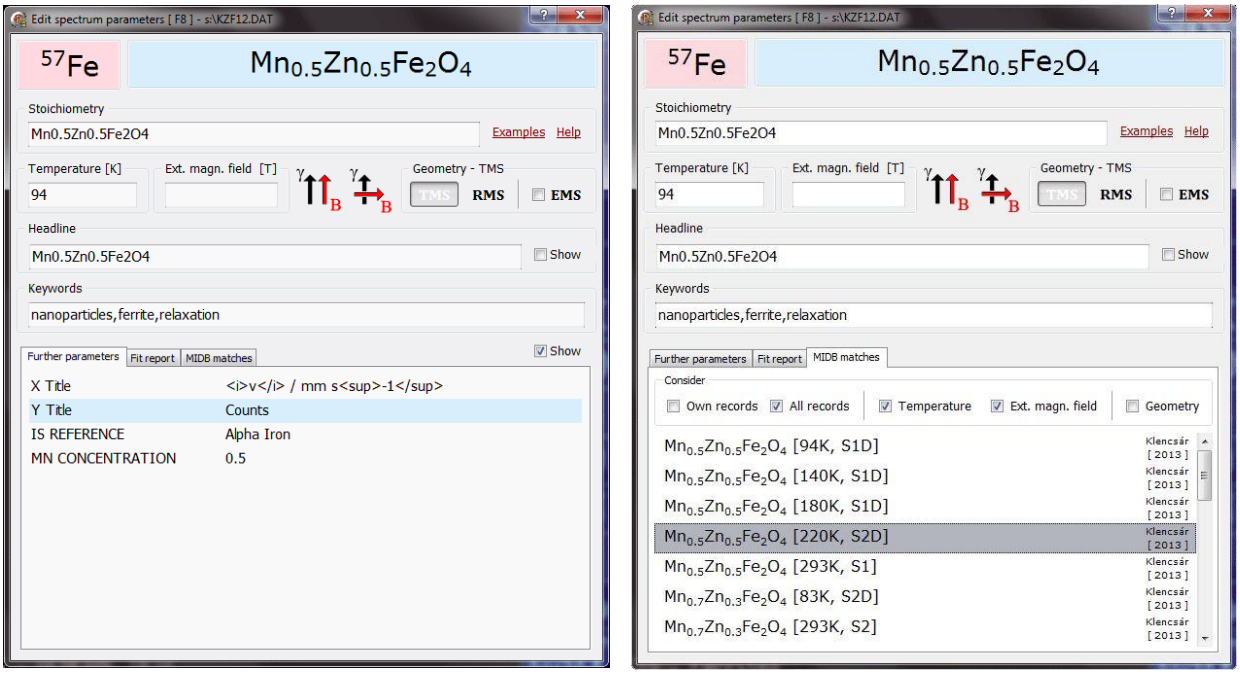
Press on the **EDT** box with the *left mouse button* to display (or hide if already shown) the Edit Spectrum Parameters Dialog that offers multiple functions as explained below. Press on the **EDT** box with the *right mouse button* in order to set a selected special parameter to the same value for all the spectra/datasets shown on the current project desk.

## *20.1. The Edit Spectrum Parameters Dialog*

The Edit Spectrum Parameters Dialog enables one

- to set the value of various spectrum parameters for the spectrum in the red-framed window,
- to monitor the last accepted fit results associated with the spectrum in the red-framed window,
- to monitor the fitness of models in (related) MIDB database records with respect to the spectrum in the red-framed window, and
- to set the fit model of a related MIDB database record as the fit model accepted for the spectrum in the red-framed window.

The dialog offers the following options.




- **Source nuclide** (popup box) - Press on the source nuclide popup box with the left mouse button in order to select the Mössbauer source nuclide associated with the measurement in the red-framed spectrum window.
- **Stoichiometry display** (formatted text) - Displays (by default) the formatted sample stoichiometry in accordance with the content of the stoichiometry edit box. The same area can also display the formatted version of the spectrum headline and further special parameters while the latter are being edited, provided that the corresponding "Show" check boxes are checked. Press on this area with the right mouse button for additional options.

- **Stoichiometry** (edit box) - Write here the stoichiometry of the sample associated with the measurement in the red-framed window. Press on the edit box with the right mouse button in order to select the stoichiometry from a list of previously edited stoichiometry formulas.
- **Examples** (link) - Press on this link in order to open a website with examples of stoichiometry expressions.
- **Help** (link) - Press on this link in order to display the help section about the stoichiometry syntax.
- **Temperature [K]** (edit box) - Write here the sample temperature (measured in kelvin) associated with the spectrum in the red-framed window. (Use a suitable approximate value for room temperature measurements.)
- **Ext. Magn. Field [T]** (edit box) - If the red-framed spectrum was measured in an external magnetic field, write here the value of the applied magnetic field measured in tesla.
- **Parallel field** (button) - Press down this button if the red-framed spectrum was measured in an external magnetic field whose direction was parallel to the γ-ray direction.
- **Perpendicular field** (button) - Press down this button if the red-framed spectrum was measured in an external magnetic field whose direction was perpendicular to the γ-ray direction.
- **TMS** (button) - Press down this button if the spectrum in the red-framed window was measured in transmission geometry.
- **RMS** (button) - Press down this button if the spectrum in the red-framed window was measured in reflection (CEMS, XMS) geometry.
- **EMS** (check box) - Put a check on this box if the spectrum in the red-framed window is the result of an emission Mössbauer spectroscopy measurement where the measured sample takes the role of the radioactive source.
- **Headline** (edit box) - Edit here the headline of the spectrum in the red-framed window. (This will be the first line of the corresponding file.)
- **Show** (Headline) (check box) - Put a check on this box in order to display the formatted version of the headline in the Stoichiometry display area whenever the headline is being edited. To format the headline, HTML style formatting elements (such as  for *italic*,  for **bold**, <u></u> for underline, <sub></sub> for $_{\text{subscript}}$ and <sup></sup> for $^{\text{superscript}}$ text style) can be used.
- **Keywords** (edit box) - List here the keywords (separated by commas) associated with the red-framed spectrum. Press on the edit box area with the right mouse button in order to select keywords from a list compiled on the basis of existing keywords in MIDB database records.
- **Show** (Further parameters) (check box) - Put a check on this box in order to display the formatted version of further parameters in the Stoichiometry display area whenever they are being edited. To format the parameters, HTML style formatting elements (see above) can be used.
- **Further parameters** (page) - set here the value of further parameters associated with the red-framed window, such as axis titles and user-defined special parameters.
- **Fit report** (page) - Displays the complete fit report associated with the last accepted fit (if any) of the red-framed spectrum. Press on the report area with the right mouse button in order to have the report printed or copied to the clipboard of Windows. Use the mouse wheel or press with the left mouse button on the report area in order to scroll the fit report content. (The dialog can also be resized to see a larger section of the fit report.)
- **MIDB matches** (page) - Displays information about MIDB database records that are related to the spectrum in the red-framed window on the basis of the stoichiometry and experimental parameters associated with the latter. Move the mouse pointer over any of the displayed MIDB database records to evaluate the fitness of the corresponding model with respect to the spectrum in the red-framed window. (When the calculation of the selected model would take too long, MossWinn may decide not to display the model in this way.) MIDB records (selected either from all of the records or exclusively from own records depending on the state of the corresponding check boxes) are listed here in the order of their fitness concerning the sample stoichiometry and the experimental parameters (Temperature, Ext. Magn. Field, Geometry) selected here for consideration. In the absence of records with good fitness, it may happen that no record is shown. In order **to set the fit model** of a record as the fit model accepted for the spectrum in the red-framed window, **double-click** on any of the displayed records. As a result, when next time the FIT menu is entered for the given spectrum window, the fit will start with the model accepted here.

The Edit Spectrum Parameters Dialog can remain shown while working in the main menu. The **F8** button can also be used to show or hide the dialog.

# 21. The ART menu

**ART** stands for **AR**i**T**hmetical Operations. Click the **ART** menu to carry out one of the following operations.

- **Multiply by a constant** - to multiply each data value in the red-framed data window by the same constant, and place the result in a new data window.
- **Multiply RED by GREEN** - to multiply each data value in the red-framed data window by the respective data value in the green-framed data window, and place the result in a new data window. Note that this operation disregards the calibration of the X (velocity) axis.
- **Normalize spectrum** - to normalize the red-framed spectrum and place the result in a new window. Normalization is based on an estimated base line value (*BL*) that can be overruled by the user. The normalized spectrum is calculated as $Y_i$(normalized) = **MAX**($BL-Y_i$,0) / **MAXIMUM**$_k$($BL-Y_k$), where **MAX**($a$,$b$) denotes $a$ if $a > b$ and it denotes $b$ otherwise, whereas **MAXIMUM**$_k$($a_k$) denotes the maximum of $a_k$ considering all possible values of $k$. Consequently, the $Y$ (ordinate) values of the normalized spectrum will all lie in the range of [0,1]. Normalization does not work for negative valued data sets.
- **Divide by a constant** - to divide each data value in the red-framed data window by the same constant, and place the result in a new data window.
- **Divide RED by GREEN** - to divide each data value in the red-framed data window by the respective data value in the green-framed data window, and place the result in a new data window. Note that this operation disregards the calibration of the X (velocity) axis.
- **Strip data...** - to strip off the selected subspectrum envelope curve from the measured data in the red-framed spectrum window, and place the result in a new data window. The stripped spectrum is calculated as $Y_i$(stripped) = $Y_i - Y_i$[SUB] + **MAXIMUM**$_k$($Y_k$[SUB]) (for transmission spectra) and
  $Y_i$(stripped) = $Y_i - Y_i$[SUB] + **MINIMUM**$_k$($Y_k$[SUB]) (for scattering – e.g. CEMS – spectra),
  where [SUB] refers to the subspectrum stripped off.
- **Set minimum to zero** - to subtract the minimum of the data in the red-framed data window from every data value of the window, and place the result in a new data window.
- **Set negative to zero** - to set all the negative valued data in the red-framed data window to zero, and place the result in a new data window.
- **Set negative to positive** - to take the absolute value of the data in the red-framed data window, and place the result in a new data window.
- **Horizontal reflection of data** - to turn absorption peaks into emission peaks and vice versa for the red-framed spectrum window, and place the result in a new data window. The transformation is carried out as $Y_i$(transformed) = **MAXIMUM**$_k$($Y_k$) $- Y_i$ + **MINIMUM**$_k$($Y_k$). (Note that applying the transformation twice will give back the original spectrum.)
- **Set zeros equal to red envelope** - to set zeroed data equal to the corresponding value of the red fitting envelope of the red-framed spectrum. This option can be used to eliminate bad/zeroed data points after the spectrum was satisfactorily fitted in the FIT menu, which may prove to be useful when one exports the corresponding spectrum data to an external grapher software.
- **Convolution with a Gaussian** - to convolve the data in the red window with a Gaussian curve, and place the result in a new data window. The convolution is carried out simply by adding up Gaussian curves with appropriate weight factors: $Y_k$(result) = $\Sigma_j$($Y_j$×Gaussian($v_j$,$v_k$)) where Gaussian($v_j$,$v_k$) denotes the value of a Gaussian function centered at $v_j$ and having an **area** of 1, as calculated for the abscissa of $v_k$. The width (FWHM) of the Gaussian is given by the user.
- **Convolution with a Lorentzian** - to convolve the data in the red window with a Lorentzian curve, and place the result in a new data window. The convolution is carried out simply by adding up Lorentzian curves with appropriate weight factors: $Y_k$(result) = $\Sigma_j$($Y_j$×Lorentzian($v_j$,$v_k$)) where Lorentzian($v_j$,$v_k$) denotes the value of a Lorentzian function centered at $v_j$ and having an **amplitude** of 1, as calculated for the abscissa of $v_k$. The width (FWHM) of the Lorentzian is defined by the user.
- **Add normally distributed noise** - to add normal statistical noise to the data in the red-framed window by assuming that for a given data the variance of the noise distribution and the value of the data are equal (referring to the underlying Poisson distribution), and place the result in a new data window.
- **Add noise with fixed variance** - to add normal statistical noise to the data in the red-framed window by assuming that the variance of the noise probability distribution is the same for all data points, and place the result in a new data window. The value of the uniform variance is defined by the user.
- **Recover original baseline** - to estimate and recover the original baseline of a spectrum that was obtained by dividing the measured spectrum data by a constant factor (e.g. the baseline itself). In order to recover the baseline value of a spectrum that was normalized in this way, it has to be fitted to some model previously, so that

the red envelope of the fit estimates well the measured data. Then select this option to calculate and place the spectrum with the recovered baseline in a new window.

- **Recover original baseline (in case of overflows) -** to estimate and recover the original baseline of a spectrum that was obtained by subtracting a constant from the spectrum data (this happens, e.g., during overflows). In order to recover the baseline value of a spectrum, it has to be fitted to some model previously, so that the red envelope of the fit estimates well the measured data. Then select this option to calculate and place the spectrum with the recovered baseline in a new window.
- **Shift velocity axis...** - to add a certain (positive or negative) constant to the velocity value of each channel of the spectrum in the red-framed window, and place the result in a new data window. By the use of this option one can modify the calibration of the velocity axis. For example, in order to transform a calibration relative to alpha iron to a calibration relative to Stainless Steel (SS), one would add *IS* (isomer shift of alpha-Fe relative to SS) = + 0.09 mm/s to the velocity value of each channel.
- **Restrict velocity axis...** - to restrict the velocity axis (either only of the spectrum in the red-framed window or of all spectrum windows on the current desk) to a velocity range to be defined by the user as $[v_{\min} \ldots v_{\max}]$ on the appearing dialog. The resulted spectra are placed in new windows, while the original spectra (and the corresponding files) remain unaltered. The number of channels in the processed spectrum copies will be changed in accordance with the user-defined velocity interval.
- **Shift subspectra for graphics...** - to display the Subspectrum Shifter Dialog that enables the manual vertical shifting of the subspectra and the residual with respect to the measured data in order to create a dataset with a clear visualization of the shape and position of subspectra. The menu is useful to create a visually attractive format of the fitted spectrum data for the creation of spectrum graphics in external graphics software.

# 22. The ADD menu

The **ADD** menu can be used to add two spectra channel by channel, to add a constant to the data points of the spectrum in the red window, as well as to add up neighboring channels of the red window, thus reducing statistical noise.

Deselect any green-framed window on the screen, and click on the **ADD** box with the left mouse button to add a constant to the spectrum in the red window. RMC the **ADD** box to add up the neighboring channels of the spectrum in the red window. In this latter case the resulted spectrum will contain half as many channels as the original spectrum did. If $A_i$ and $B_i$ denote the original spectrum and the resulted spectrum respectively, then $B_i = A_{2i-1}+A_{2i}$ .

In the presence of a green-framed window containing another spectrum, a LMC on the ADD box results in a new window containing the sum of the spectra of the red and green windows. Every channel in this new spectrum bears a value that equals to the sum of the counts in the corresponding channel in the red and in the green windows. If $A_i$ , $B_i$ and $C_i$ denote the spectrum in the red window, the spectrum in the green window and the resulted spectrum respectively, then $C_i = A_i + B_i$. Only those spectra can be added which contain exactly the same number of channels.

# 23. The SBC menu

The **SBC** menu can be used to subtract a constant value from each data point of the spectrum in the red window, to subtract the green window from the red one, and to subtract the red envelope from the spectrum in the red window.

Deselect any green-framed windows and LMC the **SBC** box to subtract a constant from every data point in the spectrum being in the red window. RMC the **SBC** box to subtract the red envelope (if any) from the original spectrum both being present in the red window.

In the presence of a green framed window, LMC the **SBC** box to subtract the spectrum in the green window from the spectrum in the red window. If $A_i$ , $B_i$ and $C_i$ denote the spectrum in the red window, the spectrum in the green window and the resulted spectrum respectively, then $C_i = A_i - B_i$. Only spectra with the same number of channels can be subtracted.

# 24. The SET menu

The SET menu can be used to alter configuration data of MossWinn, as well as to define or delete special parameter types. The corresponding options and recommended settings are listed below.

- **Set user title, name and contact** - to set your preferred title (e.g. Dr.), your name and E-mail address that identify you when you publish data in the MossWinn Internet Database. It is recommended that you give your real name and E-mail here.
- **Set internet access options** - to enable/disable internet access related functions. When enabled, these functions allow MossWinn (1) to automatically detect, download and install updates of its files from the internet, as well as (2) to access the MossWinn Internet Database via the internet.
  - Automatically download updates of the MossWinn manual. [ Enabled ]
  - Automatically download updates of MossWinn help files. [ Enabled ]
  - Automatically check for updates of MossWinn executables. [ Enabled ]
  - MossWinn Internet Database (MIDB) access. [ Enabled ]
- **Set performance options...** - to set options related to various aspects of the performance of MossWinn, e.g. whether MossWinn is allowed to utilize its parallel computing algorithms to speed up the corresponding calculations on multi-core processor systems.
  - Parallel computation on multiple cores [ Enabled ]
  - Automatic HTML FitLog creation on Accept [ Enabled ]
  - Inclusion of related database links into FitLogs [ Enabled ]
  - Resolution of spectrum images in HTML FitLogs [ LOW/MEDIUM/HIGH ]
- **Enable/disable libraries** - to enable the loading and calling of those dynamic link libraries that one intends to use for the calculation of the corresponding subspectrum curve(s) in the FIT menu. The libraries in question should have a file name corresponding to the mask SUB*.DLL , and they should be present in the code library directory of MossWinn.
- **Set mouse type...** - to set whether the mouse is to be treated as a left-handed or as a right-handed mouse. When in Windows the function of the left and right mouse buttons are swapped, then MossWinn will start by assuming a left-handed mouse. Setting the mouse to be left-handed or right-handed in MossWinn will not alter the corresponding (system-wide) setting in Windows.
  - Left-handed - if the mouse is set to be left-handed, then the functions attributed to the left and right mouse buttons are swapped (compared to what is described in this manual).
  - Right-handed - if the mouse is set to be right-handed, then the left and right mouse buttons function as described in this manual.
- **Set color scheme...** - turn to the submenu options of this menu in order to alter the default colors used by MossWinn. This can help to improve perceived color differences of the main MossWinn screen.
  - Default color scheme - to set the default color scheme of MossWinn.
  - Create color scheme... - select this option in order to display the form that allows one to create and save a new, alternative color scheme for MossWinn. Once saved, color schemes can be invoked via the 'Set color scheme…' menu.
  - Delete current color scheme - select this option to delete the currently set alternative color scheme.
- **Set GUI resolution... -** to alter and check on the internal MossWinn GUI (graphical user interface) screen resolution. See page 41 for examples of associated options.
- **Set ASCII keyboard layout** - to display the Customize ASCII keyboard layout dialog that can be used to redefine character inputs in which keystrokes result in MossWinn. When the dialog is displayed, press a key (or shift + key) and then, by using the mouse, in the ASCII list select the character in which the pressed key should result in when entered in MossWinn. Select **Restore** to invalidate all changes and restore the default layout.
- **Set autosave options…** - to set the file extensions used when spectra are saved automatically by MossWinn, as well as to set the frequency by which the status of the fit menu is saved during fitting.
- **Set default calibration options…** - to set the default attributes of calibration spectra:
  - 57Co source matrix (rhodium, chromium or palladium)
  - Calibration material (e.g. Alpha Iron)
  - Isomer shift reference (e.g. Alpha Iron)
- **Default graphics font...** - to set the font that is used when graphical images of spectra are printed to printer, saved to file or copied into the clipboard.
- **Default printer to be used...** - to set the Windows printer that is used when text or graphics is printed by MossWinn.

- **Page orientation when printing...** - to set the default page orientation (portrait or landscape) when graphics is printed by MossWinn.
- **Special parameters...** - to define, delete or set the value of special parameters.
- **Configuration settings...** - to check on and to set of various options initially offered for setting when MossWinn was installed.
- **Edit configuration file...** - to directly edit the content of one of the configuration files, by invoking either the text editor program selected in the EXE menu, or the system's default text editor program (in the case of EDITPROG.CFG).
- **Reload configuration files** - to reload all configuration files in order to make MossWinn aware of their actual state. This option is useful especially after one has directly edited the content of some configuration file and wants the changes to take effect without restarting MossWinn. Normally, configuration files are loaded only when MossWinn starts up.

# 25. The DEL menu

LMC the **DEL** box to delete the red-framed window from the current desk. The window will be placed onto the TRASH desk of the corresponding project group. The file on the hard disk belonging to the red window won't be altered. RMC the **DEL** box to activate one of the following procedures (trashing of the windows won't take place by applying these procedures).

- **Delete all windows on all of the desks** - to delete all the windows loaded in MossWinn. This will make all active project desks empty. With the exception of the *General Projects* . *General Desk* and the *Trash* desks, empty project desks do not get updated on closing the program.
- **Delete all windows on the current desk** - to delete all the windows loaded in MossWinn on the current desk.
- **Unload from memory all desks but current** - to make the actually displayed desk to be the only one that is active. When a new project desk is selected, then the old one may remain in memory, i.e. it may remain active. There can be a maximum of 16 *active project desks* loaded in MossWinn. Press the **TAB** and **Backspace** keys to navigate (i.e. go forward and backward, respectively) among the active project desks.
- **Delete text windows** - to delete all text windows (i.e. windows whose content is not interpreted/displayed as a function of numerical data) on the current project desk.
- **Delete blue-framed windows** - to delete blue-framed windows on the current project desk.
- **Delete gray-framed (temporary) windows** - to delete gray-framed, i.e. temporary windows on the current project desk.
- **Delete invisible windows on the current desk** - to delete those windows on the current project desk that are fully covered by other windows.
- **Delete Subspectrum** - to delete one, all or all but the red one of the fitting envelops (subspectra) being part of the red-framed window.
- **Reload deleted window** - to reload a formerly deleted window from the Trash desk of the current project group.

# 26. The SFT menu

**SFT** stands for „**S**equential **Fi**t of spectra" The **SFT** menu can be used to sequentially fit Mössbauer spectra being on the current desk according to a selected model. The models that are available are those, which were saved in the **FIT** menu previously. The fit of the spectra will happen one after the other, and the fit results will be saved automatically via **ACCEPT** in the **FIT** menu, so that after all the spectra get fitted, one can immediately turn to the **TBL** menu to create a table of the obtained fit results. To break the fitting of the spectra keep pressing the ESC key on the keyboard.

LMC the **SFT** box to enter the dialog box that can be used to customize the sequential fit. The following options are available.

| **Option** | **Functionality** |
|---|---|
| Fit spectra to the model... | |
| **1A**... selected here: | Choose this option to fit all spectra to the fit model selected in the popup box on the right. |
| **1B**... that was used to fit the spectrum in the red window. | Choose this option to fit all spectra to the fit model that was accepted previously for the spectrum in the red window. |
| **1C**... that was accepted for them previously. | Choose this option to refit all spectra to the specific fit model accepted for them previously. |
| **2A** All fits start with the model saved for the red window. | Choose this option to start all fits with the parameters accepted for the spectrum in the red window. |
| **2B** Fit [n+1] takes the end result of Fit [n] as the start.<br><br>These options are not effective if **1C** is selected. | Choose this option to perform a chain-fitting of spectra, in which the $(n+1)^{th}$ fit takes the parameters of the end result of the $n^{th}$ fit as initial fit parameters. |
| **3A** Analyze spectra in ascending order of...<br>**3B** Analyze spectra in descending order of... | With the help of the options **3A** and **3B** one can determine the order in which spectra get analyzed. Select the order parameter (e.g. "Temperature [K]" or "File Name") in the popup box on the right. This has importance especially in the case of chain-fits (**2B** selected) when the spectrum of Fit [n+1] should be as close as possible to the spectrum of Fit [n]. |
| **3C** Analyze only those in the range... | Select this option if only a subset of the spectra on the current desk should be fitted in the sequential fit procedure. Set the extreme values for the order parameter in the string boxes on the right. One can select a numerical value or a non-numerical string value depending on the type of the order parameter. |

| Option | Functionality |
|---|---|
| **4A** Recreate distributions without fitting | Select this option to recreate and invoke distribution curves (if any) associated with fits accepted earlier for the spectra on the current project desk. |
| **4B** Do not perform global fitting. | Select this option to prevent the FIT menu to perform a global search for the optimum set of fit parameters at the beginning of each fitting session. If the initial parameters for the fits can be estimated to be close to the optimum values, then it is recommended to have this option selected. |
| **4C** Do not perform Monte Carlo Error Calculation. | If the standard error calculation routine fails to give reliable results for the standard deviation of the fitting parameters, then Monte Carlo Error Estimation procedure is invoked automatically in the FIT menu. The Monte Carlo Error Calculation, however, can take considerable amount of time depending on the complexity of the applied fit model. Select this option to prevent the program to perform the time consuming Monte Carlo Error calculation even in cases when the standard method failed. |
| **4D** Accept fit results only if chisquare is improved. | Select this option to prevent the program to automatically accept the obtained fit result in cases when a fit accepted earlier for the current spectrum provided a lower normalized chi-square value. |
| **5A** Fix Parameter<br><br>**5B** Unfix Parameter | Use these options to Fix (5A) or Unfix (5B) a fit parameter in all of the spectra on the current desk without entering the fit menu for each of the spectra individually. The fit model, for which the parameters are shown in the popup boxes, is taken from the spectrum of the red window.<br><br>A typical example for the application of this option is when one fits a series of spectra to a fit model in which one of the fit parameters is fixed in order to achieve a better stability of the fit. Then, using this option, the parameter in question gets unfixed, and the sequential fit procedure is repeated to fine-tune the value of the formerly fixed parameter. |

The **SFT** menu could be applied, for example, in the following situation.

- Mössbauer spectra of the same material were taken at 20 different temperatures, and
- all the spectra are already calibrated, and
- all the spectra display the same structure, e.g. two doublets, so that they can all be analyzed using the same fit model, and consequently
- they will differ only in the derived model parameters (e.g. isomer shift and quadrupole splitting).

To let MossWinn do the analysis automatically for all the spectra, LMC the **SFT** box and select the appropriate model. By clicking on **START** the fit will begin immediately, and will proceed automatically until all the spectra get analyzed.

# 27. The FIT menu

Enter the FIT menu with a LMC in order to fit already calibrated Mössbauer spectra, or in order to fit calibration spectra to calibrate the velocity axis. To fit a spectrum according to a model saved previously in the **FIT** menu, one can also RMC the **FIT** box and select the required fit model.

## *27.1. Fitting of calibration spectra*

MossWinn allows the calibration fitting of Mössbauer spectra measured with a $^{57}$Co($^{57}$Fe) — in the followings $^{57}$Fe — Mössbauer source. During calibration-fitting the physical model describing the measured reference material (e.g. α-iron) is assumed to be known, and by fixing the position type parameters (e.g. isomer shift and hyperfine magnetic field) of the model, the velocity axis of the Mössbauer spectrum gets determined by the fit.

In order to calibrate the velocity axis of a calibration spectrum, proceed as follows. Select the — yet uncalibrated — calibration spectrum to be the master window (red framed) in the main menu. Deselect any source (green framed) windows. LMC the **FIT** box. In the **FIT** menu press on the **CALIBRATION** tab in the right upper corner of the screen. Select the **Matrix** (e.g. Rhodium) of the $^{57}$Fe Mössbauer source that was used for the measurement. If the used matrix is not among those displayed, then click on **Define Matrix…** to define the source matrix. After the source matrix has been selected, select the **Absorber** (e.g. α-iron) used for calibration purposes. MossWinn also supports the calibration of the velocity axis according to simultaneously measured reference absorbers. This means, that the velocity axis can be calibrated on the basis of a spectrum that was measured for example with α-iron and Stainless Steel (SS) used simultaneously as absorbers. If the absorber material — used for calibration purposes — is not among those listed, then do the followings. Go to the **MODEL** page and set the known model of the used absorber material (e.g. one doublet). Then set the known, correct values of position type parameters (e.g. isomer shift and quadrupole splitting). The isomer shift value(s) should be set relative to α-iron. Fix all the position type parameters that were set in this way (click on the name of them with the left button of the mouse). Go back to the **CALIBRATION** page, invoke the **Absorber** popup (click on the text **Unknown Absorber**), and select **Define Absorber**.

After the correct absorber material was set, the **Isomer Shift Reference** material should be selected. (When the calibration fit is accepted, then the velocity axis will be calibrated so that isomer shift values will be relative to the reference material selected here.) If the spectra, which are going to be calibrated according to the actually fitted calibration spectrum, were measured with a $^{57}$Fe Mössbauer source, then it is recommended to select α-iron as the calibration material. In all other cases it is recommended to select the **Source material** here as the **Isomer Shift Reference** material. In the latter case the velocity axis will be calibrated according to the real — absolute — velocity of the source, i.e. the velocity values on the X-axis will denote the real velocity the source was moved towards the absorber with while the counts in the particular channel were collected.

After the reference material has been selected, the **Waveform** of the movement of the source should be set. This can be **Triangle** (constant absolute acceleration in time) or **Sinusoid** (Cosine acceleration in time).

Then, it should be set whether the spectrum has been **Folded** (electronically or by software) or it is **Unfolded** displaying all the four quarter periods of the movement of the source.

Then, it should be set whether the very **first channel** of the spectrum bears a negative or positive velocity. (Mössbauer spectra are recorded usually with the negative velocities encountered first. But this may be not the case depending on the settings of the electronics used.) In the folded case a spectrum can display velocities according to the schemes of −/+ and +/− . In the unfolded case, however, the velocity axis can correspond to −/+/+/− or +/−/−/+ schemes.

When all the above settings are completed, the **Cal Mode** should be set active, in order to activate the selected model. As a result, the **Velocity Axis** parameter group appears with three parameters at the top of the parameter list. **Max. Velocity [mm/s]** denotes the maximum velocity of the source during its movement. **Delay [Dwell Time]** denotes a possible time difference in units of Dwell Time (time of continuous counting in a particular channel in one cycle of movement) between the start of the source-movement-period and the start of the counting period. Such delays are not uncommon, and even with good value electronics it may very well have an order of magnitude of 1.0 (one channel sweep).

**Period Length [Channels]** determines the number of channels the whole movement period of the source is divided into. This usually equals to the number of channels in the spectrum. **However, some spectrometers produce an ASCII spectrum output with 512 or 1024 channels, but at the same time divide the whole period into only 500 and 1000 channels, respectively (the rest of the channels are redundant and they are usually zeroed). In such a case the correct setting of the *Period Length [Channels]* parameter (500 instead of 512, and 1000 instead of 1024) is essential to achieve precise calibration.**

To complete the calibration fitting, the calibration spectrum should be fitted according to the model selected as described above. Usually very good fits can be achieved, with $\chi^2 \approx 1.0$ . If this is not the case it is recommended to check carefully whether all the calibration parameters are set correctly.

To finalize the result of calibration fitting, click on **ACCEPT**. As a result, the program will calibrate the velocity axis according to the selected reference material. If the reference material is not the same as the source material, then the fitting will worsen, as the isomer shift parameters of the fit will not be the correct ones relative to the **Isomer Shift Reference** material anymore. This effect, however, does not influence the correctness of the velocity axis calibration.

To transfer the obtained calibration information to other spectra measured with the same velocity settings, exit the **FIT** menu, and in the **main** menu turn either to the **CAL** or to the **ASP** menu.

## *27.2. Fitting of calibrated Mössbauer spectra*

Depending on the existence and content of the master (red) and source (green) windows in the main menu, the FIT menu will proceed as listed below.

| Content of the red window | Content of the green window | What happens after a LMC on the FIT box |
|---|---|---|
| Yet unfitted spectrum | None | Fitting of the spectrum according to a model to be selected later on in the FIT menu. |
| Yet unfitted spectrum | Transformation matrix (text file) | Fitting of the spectrum according to the model represented by the selected transformation matrix. |
| Yet unfitted spectrum | A previously fitted spectrum | Fitting of the spectrum according to the former fit of the spectrum shown in the green framed window |
| Previously fitted spectrum | None | Fitting of the spectrum according to its former fit. |
| Previously fitted spectrum | Transformation matrix (text file) | Fitting of the spectrum according to the model represented by the selected transformation matrix. |
| Previously fitted spectrum | A previously fitted spectrum | Fitting of the spectrum according to the former fit of the spectrum shown in the green framed window. |

A **FIT** can be reloaded only if it was accepted previously by a click on the **ACCEPT** box in the fit menu. To fit a spectrum according to a model selected from the models saved previously in the **FIT** menu, RMC the FIT box and select the required fit model.

The FIT menu is divided into five main pages from which only four are visible by default. The fifth can be invoked by a mouse click on the **DETAILS** box. The **PARAMETERS PAGE** occupies the left of the screen. On the right of it, in the center of the screen, the blue colored menus of the **FUNCTIONS PAGE** can be seen. On the right of it the **MODEL PAGE**, then two identical **INSIGHT PAGES (D,E)**, then the **CALIBRATION PAGE** is located. On the right bottom corner of the screen the **SPECTRUM PAGE** is situated followed by the **RESIDUAL PAGE** and three identical **INSIGHT PAGES (A,B,C)**.

In the followings, the functionality of these pages is described.

## 27.3. The Model page

The Model page can be used to set the physical model according to which the spectrum should be fitted. At the top of the page the **Model Group Popup** box is located. Click on it to select the required model group, or to select directly the previously saved model according to which the current spectrum should be fitted. Below the Model Group Popup box the **Model Popup** box is located, which lists all the models contained by the Model Group actually selected in the Model Group Popup box. On the right of the Model Group Popup box there is the **Source Popup** box in which the nuclide should be selected on which the Mössbauer effect was measured in the case of the current spectrum. Below the Model Popup box the **Subspectrum Popup** box is located. This can be used to select the **current subspectrum** for handling. The **Background** and **Velocity Axis** parameter groups are treated similarly to those of the subspectra. Below the Subspectrum Popup box the **Parameters List** box is located, which lists all the parameters belonging to the current subspectrum. On the right of the Parameters List box, the **Constraints List** box is located that lists the constraints set for the **current parameter** selected for handling in the Parameters List box. On the right of the Subspectrum Popup box, above the Constraints List box, the **Interaction Popup** box is located. This can be used to select the interaction — physical model — of the current subspectrum. When the parameter group of Background is selected, then on the right of the Interaction Popup box the Calculation Mode Popup box is displayed. This popup box can be used to select **Transmission Integral** calculation mode or **Thin Absorber Approximation** calculation mode. When the current parameter group is neither that of the Background nor that of the Velocity Axis, then on the right of the Interaction Popup box the **Line Shape Popup** box is displayed. This popup box can be used to select the shape of absorption lines the absorption pattern of the current model is built from. Below the Parameters List box there are the **ADD**, **REMOVE**, **SAVE**, and **CONSTRAIN** popup boxes, along with the **DETAILS** box. The latter should be clicked to invoke the **DETAILS** page that can be used to fine-tune linear models.

When one of the high-resolution GUI (graphical user interface) modes is selected, then the **Contents** tab becomes visible beside the Calibration tab. Press on the **Contents** tab in order to determine the contents of the free screen area appearing on the right of the Model page in high-resolution GUI modes. While multiple elements can be selected for appearance in the screen area in question, they are displayed only if the available horizontal space allows for it. The following elements are available for this purpose.

| | |
|---|---|
| **Parameter enabled intervals** | Shows a list box that displays the intervals from which the current parameter can take on values according to its constraints list. This list of intervals is identical with the enabled intervals list (see page 106) accessible via the Details page. In addition, the check box **Enable neg. amplitudes** will be displayed above the list box: put a check on this box in order to enable amplitude type parameters to take on negative values. |
| **Subspectrum matrix elements** | Shows the **AFFECTED L.** and **MATRIX** list boxes whose functions are identical to those of the **AFFECTED LINES** and **MATRIX** list boxes accessible via the Details page (see page 103). The **AFFECTED L.** list box lists all the absorption lines belonging to the current subspectrum: the absorption lines that are influenced by the current parameter are selected blue, while those being not influenced remain unselected. The **MATRIX** list box displays the matrix elements belonging to the partial transformation matrix of the current parameter. To each of the parameter types (Amplitude type, Position Type, Line Width type) there is an independent partial transformation matrix maintained (see page 103). In addition two check boxes will be displayed above the list boxes: **Coupled W.** and **Texture**. Put a check on the **Coupled W.** box in order to make all the lines of a linear model to have the same line width. Clear the check box in order to set up independent line width parameters (2 in the case of doublets, 3 in the case of sextets) determining the line widths of the lines. Put a check on the **Texture** box in order to lift powder constraints of a linear model by introducing one additional amplitude type parameter. Clear the check box to return to the constraints of powder geometry. These check boxes can be enabled only for the nuclides $^{57}$Fe, $^{119}$Sn and $^{125}$Te. |
| **Insight A-F** | Shows the insight page selected. Note that unlike in the case of Insights A-E, Insight F does not have its own separate page. |

### *27.3.1.* Functions of the ADD, REMOVE, SAVE, DB, CONSTRAIN, COPY AND GUI menu boxes

**ADD**

| | |
|---|---|
| **New Subspectrum** | To add a new subspectrum only to the model of the current spectrum. The subspectrum can be selected from the collection of previously saved subspectra, or — by simply clicking on „New Subspectrum" — it will be a singlet. |
| **New Subspectrum (DLL)** | To add a new subspectrum available in user programmed and compiled dynamic link libraries, being saved in the **code library directory** (`..\MOSSWINN 4.0\DLLs\`) with a name corresponding to the mask SUB*.DLL, to the model of the current spectrum. |
| **New Subspectrum Group** | To add a subspectrum group only to the model of the current spectrum. The subspectrum group can be selected from the collection of previously saved subspectrum groups (multiple subspectra with arbitrary constraints among them). |
| **New Shared Subspectrum** | To add a new shared subspectrum to the model of all the spectra fitted simultaneously. The subspectrum can be selected from the collection of previously saved subspectra, or — by simply clicking on „New Subspectrum" — it will be a singlet. |
| **New Shared Subspectrum (DLL)** | To add a new shared subspectrum available in user programmed and compiled dynamic link libraries to the model of all the spectra fitted simultaneously. |
| **New Shared Subspectrum Group** | To add a shared subspectrum group to the model of all the spectra (with the same SOURCE setting as the actual one) fitted simultaneously. The subspectrum group can be selected from the collection of subspectrum groups saved earlier via the SAVE \ SAVE SUBSPECTRUM GROUP… option. |
| **Extra Fit Parameter** | A special parameter can be added to the parameter group of the Background. |
| **New Spectrum to fit** | To add a new spectrum to the list of spectra that are fitted simultaneously. Only those spectra are available which are loaded on the current desk in the main menu. |

**REMOVE**

| | |
|---|---|
| **Subspectrum** | To remove a shared/unshared subspectrum from the model of the fitted spectra/current spectrum. |
| **All subspectra / for all the fitted spectra** | To remove all shared and unshared subspectra from the fit model associated with the current spectrum. In case of simultaneous fits of several spectra, select the appearing subitem in order to perform the operation for all the spectra fitted simultaneously. |
| **Spectrum from fit** | To remove a spectrum from the list of spectra fitted simultaneously. |
| **Subspectrum from collection** | To remove a previously saved subspectrum from the collection of subspectra. A separate collection is maintained for each of the nuclides. |
| **Subspectrum Group from collection** | To remove a previously saved subspectrum group from the collection of subspectrum groups. A separate subspectrum group collection is maintained for each of the nuclides. |
| **Fit model from model group** | To remove a previously saved fit model from the model group actually selected in the Model Group Popup. |
| **Model group** | To remove a whole model group with all of its models. |
| **FitLog file** | To delete the HTML FitLog file created earlier for the present spectrum. The FitLog file is located in the same folder as the spectrum to which it belongs. |
| **Parameter** | To remove a parameter from the list of parameters. This function is used first of all to remove Extra Parameters added previously to the list of parameters. |

**SAVE**

| | |
|---|---|
| **Save Subspectrum** | To save one of the subspectra of the model of the current spectrum to the collection of subspectra belonging to the actually selected SOURCE. |
| **Save Subspectrum Group…** | To save one or more of the subspectra of the current model as a group (unit) to the collection of Subspectrum Groups belonging to the actually selected SOURCE. |
| **Save Model As** | To save the model of the current spectrum either to one of the existing model groups or in a newly created model group. |
| **Save HTML FitLog** | To save a HTML FitLog to the FitLog file of the current spectrum, according to the current state of the fit. The FitLog file is saved to the folder that contains also the corresponding spectrum data file. Its name is derived from the file name of the spectrum data file by the addition of **.log.htm**. The saved HTML FitLog can be opened by pressing on the gray headline below the spectrum, and selecting the corresponding menu option of the appearing popup (see page 97). Further FitLog-related functionalities are available via the menu invoked by pressing on the **ACCEPT** menu box with the right mouse button (see page 100). When the corresponding function is enabled in the SET menu (see page 28), then FitLogs are created automatically when fit results are accepted via LMC on the ACCEPT box. MossWinn takes care of duplicates, i.e. it will not save the FitLog if it is essentially identical with a former one. |
| **Save Spectrum** | To save the current spectrum to disk with a different name according to its present state. |
| **Insight Page…** | To save the content of one of the insight pages to disk in ASCII format, according to its present state. |

**DB**

The DB menu box provides access to functions of the **MossWinn Internet Database (MIDB)** service. Full access to the MIDB service requires either the ***DBM version*** of MossWinn or subscription to the ***MossWinn services*** that can be requested, e.g., via the **REQUEST MOSSWINN SERVICES SUBSCRIPTION FOR THE ATTACHED KEY...** submenu of the **HELP** menu in the main menu.

| | |
|---|---|
| **Find and apply best match**<br><br>**Considering own records**<br><br>**Considering all records**<br><br>**Considering all transmission / conversion type records** | To search through the MIDB database records in order to find the spectrum that best matches the fitted spectrum currently on the screen, and to set the corresponding fit model as included in the database record returned by the search. The fitness of the database records with respect to the current spectrum is evaluated by considering the isomer shift of the isomer shift reference material that can be set via the **ISOMER SHIFT REFERENCE** submenu option of the **SET** menu. A press directly on the **FIND AND APPLY BEST MATCH** menu item is equivalent to the option **CONSIDERING OWN RECORDS**. The fit model returned as the best match will be saved automatically as a new model of the MIDB [ * ] model group where * stands for the corresponding source nuclide. Apart from the best match, the search will also return several further records in descending order of their fitness. Select this menu again in order to see the corresponding list and apply another one of the returned records. |
| **Open compound class in database browser** | Turn to this option in order to select one of the records returned by the **FIND AND APPLY BEST MATCH** function, and open the corresponding compound class in the database browser. |
| **Browse the internet database** | Select this option in order to display the database browser that allows one to search through the MIDB database records according to various criteria. The database browser also provides the possibility to try/apply the fit models, represented by the database records, to the fitted spectrum currently on the screen. |
| **Publish record in the internet database** | Select this option in order to publish the current fit model and/or a downsampled version of the current spectrum in the MossWinn Internet Database. If along with the fit parameters you also want to publish their standard deviation in the database, calculate the corresponding standard deviations via the **CAL STD** menu before turning to this option. Once the option is selected, first the **DATABASE RECORD INPUT FORM** becomes displayed on which one can set various parameters associated with the record to be published. Then, the next form provides the possibility to set the downsampled form of the measured spectrum, and to declare whether one wants to publish only the fit model, only the downsampled spectrum, or both. On the next form a preview of the record is displayed, where one can check how the record will appear when published. The record becomes finally published when on the preview form the **PUBLISH RECORD** button is pressed. Once a record is published in the database, it may appear in the MIDB database browser of MIDB subscribers all around the world. The **MIDB Publisher's Guide (`http://www.mosswinn.hu/midbguide.htm`)** contains useful information on recommended practices concerning the publication of MIDB records. |
| **Withdraw record from the internet database** | Select this option in order to withdraw a MIDB record published earlier by using the hardware key that is currently attached to the computer ( own record ). The own record that is to be withdrawn can be selected on the appearing form. **Withdrawal of own records from the MIDB database does not require subscription to the database.** |
| **Edit record published in the internet database** | Select this option to edit one of the own MIDB records by changing the record parameters that can be set on the **DATABASE RECORD INPUT FORM**. The fit model and the downsampled spectrum associated with the record cannot be edited in this way. The own record that is to be edited can be selected on the appearing form. |
| **Synchronize local data with the internet database** | Select this option to carry out pending MIDB publication and withdrawal operations, and to synchronize local database data with the MIDB host server. The frequency of such synchronization events may be subject to a limitation. |
| **Open MIDB Compound Summary in the default browser** | Select this option to open the **MIDB Compound Summary** in the default browser. ( `http://www.mosswinn.hu/midbsummary.htm` ) |
| **Help on the DB menu box** | Select this option in order to open the html help concerning the DB menu box. |

**CONSTRAIN**

| | |
|---|---|
| **Distribution** | Select one of the listed distribution types to fit a distribution of the current parameter. The left and right boundaries of the distribution will be equal to the actual minimum and maximum values of the current parameter, respectively. |
| **Unrestricted (UNR)** | No restriction will be applied when the distribution is derived. Identical to the original method of Hesse and Rübartsch. The Smoothing factor cannot be fitted in this case. |
| **Positive, Free Boundaries (PFB)** | Only positive valued distributions will be considered. |
| **Positive, Zero Left Boundary (PZLB)** | Only those positive valued distributions will be considered, which approaches zero at the left boundary (at the minimum value of the X axis). |
| **Positive, Zero Right Boundary (PZRB)** | Only those positive valued distributions will be considered, which approaches zero at the right boundary (at the maximum value of the X axis). |
| **Positive, Zero Left & Right Boundaries (PZLRB)** | Only those positive valued distributions will be considered, which approaches zero at the left and right boundaries (at the minimum and maximum values of the X axis). |
| **Split distribution** | Select this option in order to split the distribution at some intermediate value by adding the **SPLIT [*x*]** directive to the parameter constraints list box, where *x* denotes an intermediate distribution-parameter value. As a result, the distribution will contribute to the fitting curve by two separate subspectra: one belonging to distribution-parameter values higher than *x*, and the other belonging to distribution-parameter values lower than or equal to *x*. |

**CONSTRAIN**

| | |
|---|---|
| **Relative** | Available only for Amplitude type parameters. The internal absolute value of the selected Amplitude type parameter will be calculated by multiplying its displayed relative value with the absolute value of the *first* of the Amplitude type parameters in the host subspectrum. If the selected parameter is the first Amplitude type parameter in the current subspectrum, then its absolute value will be calculated by multiplying its displayed relative value with the value of the BASE LINE. |

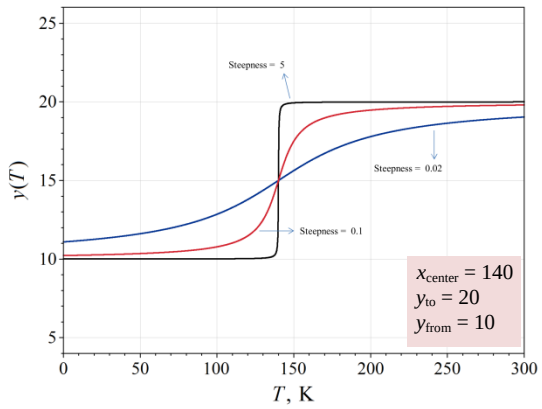
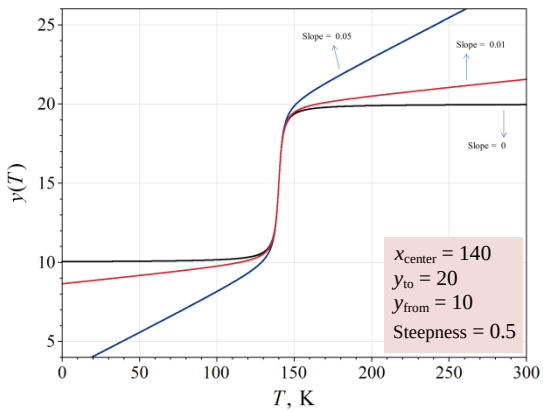
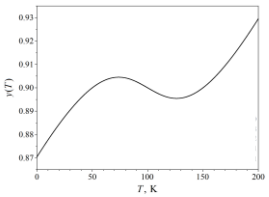
**CONSTRAIN**

| | |
|---|---|
| **Is Equal to** | **:=** constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the value that the current parameter should be equal to. |
| **Is in the Range** | **[ , ]** constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the minimum and maximum values of the current parameter. |
| **INClude Range** | **INC[ , ]** constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the minimum and maximum values of the interval which should be enabled for the current parameter. |
| **EXClude Range** | **EXC[ , ]** constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the minimum and maximum values of the interval which should be excluded from the enabled values of the current parameter. |
| **Higher Than** | > constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the value that the current parameter should exceed. |
| **Higher or Equal** | >= constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the value that the current parameter should exceed or equal. |
| **Less Than** | < constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the value that the current parameter should be lower than. |
| **Less or Equal** | <= constraint will be added to the list of constraints of the current parameter. Click on the Constraints List box to set the value that the current parameter should not exceed. |
| **Hard constraint** | **HARD** constraint will be added to the list of constraints of the current parameter. The above 8 constraints in constraint lists marked with the HARD constraint will be considered whenever the value of the corresponding parameter is set (e.g. during local fitting via the **FIT** menu). **The above 8 constraints in constraint lists without the HARD constraint are in effect only when the Global Fitting procedure is executed via the GLOBAL menu.** |

## CONSTRAIN

| | |
|---|---|
| **Higher Than #PARAMETER** | The value of the current parameter will have to exceed the value of the selected parameter. To remove this constraint click on the name of the current parameter in the list of parameters. |
| **Higher or Equal #PARAMETER** | The value of the current parameter will have to be higher or equal to the value of the selected parameter. To remove this constraint click on the name of the current parameter in the list of parameters. |
| **Less Than #PARAMETER** | The value of the current parameter will have to be less than the value of the selected parameter. To remove this constraint click on the name of the current parameter in the list of parameters. |
| **Less or Equal #PARAMETER** | The value of the current parameter will have to be less than the value of the selected parameter. To remove this constraint click on the name of the current parameter in the list of parameters. |
| **Not Equal to #PARAMETER** | The value of the current parameter must not be equal to the value of the selected parameter. |
| **Is Close to #PARAMETER** | The value of the current parameter must remain close to the value of the selected parameter. What is „close" and what is „far" is determined by the enabled range of #PARAMETER. |
| **Is Far from #PARAMETER** | The value of the current parameter must remain far from the value of the selected parameter. What is „far" and what is „close" is determined by the enabled range of #PARAMETER. |

## CONSTRAIN

| | |
|---|---|
| **:= #PARAMETER** | The value of the current parameter must be equal to the value of the selected parameter. |
| **:= #PARAMETER + CONST** | The value of the current parameter must be equal to the value of the selected parameter + a constant. The constant will be added to the parameter list of the current subspectrum. |
| **:= #PARAMETER * CONST** | The value of the current parameter must be equal to the value of the selected parameter * a constant. The constant will be added to the parameter list of the current subspectrum. |
| **:= #PARAMETER * CONST1 + CONST2** | The value of the current parameter must be equal to the value of the selected parameter * Constant *m* + Constant *b*. The constants *m* and *b* will be added to the parameter list of the current subspectrum. |
| **:= SMOOTH MONOTONIC ( #PARAMETER )**<br>  | This option can be used to set up a more versatile constraint (with respect to linear dependence) that can ensure the smooth, monotonic (increasing or decreasing) dependence of the currently selected fit parameter ($y$) on a physical parameter ($x$) such as the temperature of the sample, but may also model a step-like transition of a parameter as the function of another one. The mathematical form of the constraint is as follows.<br>$$y(x) = (y_{to} - y_{from}) \cdot \frac{\arctan[\text{Steepness} \cdot (x - x_{center})]}{\pi} + \frac{(y_{to} + y_{from})}{2}$$<br>This constraint may also be used to achieve smooth variation of fit parameters in cases where the statistical noise or correlation between fit parameters would otherwise lead to their unphysical oscillations as a function of temperature or other physical parameter.<br>The selected #PARAMETER (e.g. TEMPERATURE [K]) will play the role of $x$ in the above expression.<br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |
| **:= SMOOTH WITH SLOPE ( #PARAMETER )**<br>  | This option can be used to set up a constraint that complements the Smooth Monotonic function (see above) with a slope term as follows:<br>$$y(x) = \text{Slope} \cdot (x - x_{center}) + (y_{to} - y_{from}) \cdot \frac{\arctan[\text{Steepness} \cdot (x - x_{center})]}{\pi} + \frac{(y_{to} + y_{from})}{2}$$<br>The resulting function is not necessarily monotonic anymore:<br>  <br>$x_{center}$ = 100<br>$y_{to}$ = 0.8<br>$y_{from}$ = 1.0<br>Steepness = 0.02<br>Slope = 0.001<br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |

| | |
|---|---|
| **:= User Programmed Function [Quadratic]** | The value of the current parameter will be equal to $\Phi$(SELECTED PARAMETER, NEW PARAMETERS 1..N) where the function $\Phi$ can be an arbitrary function programmed by the user in DEP_DLL1.DLL. The default $\Phi$ function is Quadratic:<br><br>CURRENT PARAMETER := CONSTANT + LINEAR * SELECTED PARAMETER + QUADRATIC * (SELECTED PARAMETER)$^2$<br><br>See page 117 for further details. |
| **:= #Percentage constrained** | The area of the current subspectrum will be constrained by a percentage parameter, and the first of the amplitude type parameters will be fixed. The rest of the amplitude type parameters (if any) will serve as a RELATIVE parameter: to get their real value multiply their displayed relative value with that of the first amplitude type parameter. To remove the percentage constraint, click on the name of the first amplitude type parameter of the corresponding subspectrum in the list of parameters, and select the first row in the appearing popup box. |

**COPY** (available only in high resolution screen mode)

| | |
|---|---|
| **All spectra (as image)** | To copy all simultaneously fitted spectra to the clipboard as a single image. The spectra will follow each other according to the spectrum order set previously via the number of spectra popup box. The resolution of the image can be set via the **Printer Setup Dialog** (see page 137) with **Clipboard - multiple spectra** selected as printer. |
| **All spectra (as text)** | To copy all simultaneously fitted spectra to the clipboard as text, with the velocity values, the measured data, the fit envelope and the subspectra included as comma delimited columns. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. |
| **All spectra (as xls)** | To make a copy of all the simultaneously fitted spectra, all the valid insight pages, the fit results in two different tabular forms as well as the fit reports associated with the current state of the fit in the form of a single XLS spreadsheet file, in which the different spectra/insight pages/tables and the fit reports appear on separate worksheet pages. In order to have the standard deviation of fit parameters included in the XLS file, turn to the Cal StD function before selecting this option. Once created, MossWinn attempts to open the XLS file with an associated software application. The created XLS file is saved inside the folder `..\MOSSWINN 4.0\USERS\PUBLIC\XLS\ .`<br><br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |
| **Current spectrum (as image)** | To copy the currently displayed spectrum to the clipboard as image. The resolution of the image can be set via the **Printer Setup Dialog** (see page 137) with **Clipboard - single spectrum** selected as printer. |
| **Current spectrum (as text)** | To copy the currently displayed spectrum to the clipboard as text, with the velocity values, the measured data, the fit envelope and the subspectra included as comma delimited columns. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. |
| **Current spectrum (as xls)** | To copy the currently selected fitted spectrum, the corresponding fit results in two different tabular forms as well as the associated fit report in the form of a single XLS spreadsheet file, in which the spectrum data, the fit result tables and the fit report appear on separate worksheet pages. In order to have the standard deviation of fit parameters included in the XLS file, turn to the Cal StD function before selecting this option. Once created, MossWinn attempts to open the XLS file with an associated software application. The created XLS file is saved inside the folder `..\MOSSWINN 4.0\USERS\PUBLIC\XLS\ .`<br><br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |
| **All insight pages (as image)** | To copy all the valid insight pages to the clipboard as a single image. |
| **All insight pages (as text)** | To copy the numerical data (including parameter standard errors if calculated) of all the valid insight pages to the clipboard as text. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. |
| **All insight pages (as xls)** | To make a copy of the numerical data of the selected insight page in the form of an XLS spreadsheet file. In order to have standard deviation of fit parameters included in the XLS file, turn to the Cal StD function before selecting this option. Once created, MossWinn attempts to open the XLS file with an associated software application. The created XLS file is saved inside the folder `..\MOSSWINN 4.0\USERS\PUBLIC\XLS\ .`<br><br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |
| **Insight page (as image)...** | To copy a selected insight page to the clipboard of Windows as a single image. |
| **Insight page (as text)...** | To copy the numerical data of a selected insight page to the clipboard of Windows as text. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. |
| **Insight page (as xls)...** | To make a copy of the numerical data of the selected insight page in the form of an XLS spreadsheet file. In order to have standard deviation of fit parameters included in the XLS file, turn to the Cal StD function before selecting this option. Once created, MossWinn attempts to open the XLS file with an associated software application. The created XLS file is saved inside the folder `..\MOSSWINN 4.0\USERS\PUBLIC\XLS\ .`<br><br>*This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.* |

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|---|---|
| **Fit report for the current spectrum** | To copy the results concerning the currently displayed spectrum to the clipboard in the fit report text format. |
| **Fit report for all the fitted spectra** | To copy the fit results of all the simultaneously fitted spectra to the clipboard in the fit report text format. |
| **Fit results as table (with spectra in rows)...** | To copy the numerical results concerning all of the simultaneously fitted spectra into the clipboard as comma delimited numerical data in rows, each of which corresponds to a single spectrum. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. Concerning the format of the standard deviation values, one of the following options can be chosen:<br>• with StD values in separate columns<br>• with StD values in parentheses after values<br>• with StD values in parentheses as error in last digit(s) |
| **Fit results as table (with spectra in columns)...** | To copy the numerical results concerning all of the simultaneously fitted spectra into the clipboard as comma delimited numerical data in columns, each of which corresponds to a single spectrum. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software. Concerning the format of the standard deviation values, one of the following options can be chosen:<br>• with StD values in separate rows<br>• with StD values in parentheses after values<br>• with StD values in parentheses as error in last digit(s) |
| **Correlation matrix...** | To copy the correlation matrix of the fit to the clipboard. When the fit parameter standard deviations are calculated, the following options are available:<br>• As image (for all spectra)<br>• As image (for current spectrum)<br>• As image (value limited, for all spectra)<br>• As text (for all spectra)<br>• As text (for current spectrum)<br>• As text (value limited, for all spectra) |

**GUI** (available only in high resolution screen mode)

The GUI menu box provides the following options to set the internal screen resolution of MossWinn.

| | |
|---|---|
| 800 x 400 | To set the internal MossWinn screen resolution to 800 x 400. |
| 800 x 450 | To set the internal MossWinn screen resolution to 800 x 450. |
| 800 x 500 | To set the internal MossWinn screen resolution to 800 x 500. |
| 800 x 650 | To set the internal MossWinn screen resolution to 800 x 650. |
| 900 x 450 | To set the internal MossWinn screen resolution to 900 x 450. |
| 900 x 500 | To set the internal MossWinn screen resolution to 900 x 500. |
| 900 x 650 | To set the internal MossWinn screen resolution to 900 x 650. |
| Set optimum resolution for full screen mode | To set the internal MossWinn screen resolution equal to a value that is optimum for full screen mode by considering the full resolution of the current screen. |
| Set optimum resolution when entering full screen mode | When selected, the internal MossWinn screen resolution is automatically set to be equal to a value that is optimum for full screen mode whenever the latter is entered by pressing F4. When full screen mode is entered with this option being unselected, the program sets the internal resolution to the one last used in full screen mode. |
| 960 x 540 (Optimum for FHD full screen) | To set the internal MossWinn screen resolution to 960 x 540, which is considered to be optimum in full screen mode on a FHD (1920 x 1080) screen. |
| 960 x 600 (Optimum for WUXGA full screen) | To set the internal MossWinn screen resolution to 960 x 600, which is considered to be optimum in full screen mode on a WUXGA (1920 x 1200) screen. |
| 1280 x 540 (Optimum for UW-UXGA full screen) | To set the internal MossWinn screen resolution to 1280 x 540, which is considered to be optimum in full screen mode on an UW-UXGA (2560 x 1080) screen. |
| 1280 x 720 (Optimum for QHD & 4K HD full screen) | To set the internal MossWinn screen resolution to 1280 x 720, which is considered to be optimum in full screen mode on QHD (2560 x 1440) and 4K HD (3840 x 2160) screens. |
| 1720 x 720 (Optimum for UW-QHD full screen) | To set the internal MossWinn screen resolution to 1720 x 720, which is considered to be optimum in full screen mode on an UW-QHD (3440 x 1440) screen. |
| 1920 x 1080 (Alternative for FHD and 4K HD full screen) | To set the internal MossWinn screen resolution to 1920 x 1080, which is considered as a higher resolution alternative on FHD (1920 x 1080) and 4K HD (3840 x 2160) screens. |
| Set maximum resolution for full screen mode | To set the internal MossWinn screen resolution to its maximum value considering the full resolution of the current screen. This option is available only when the program is in full screen mode.<br><br>The maximum full screen resolution that will be set by MossWinn may be lower than the full resolution of the applied screen. |

Note that one can switch between full screen and windowed modes by pressing **F4** on the keyboard. In order to change the MossWinn window size in windowed mode, press **F1**, **F2** or **F3**.

### *27.3.2.* Selection of source nuclide

On the **MODEL** page click on the **SOURCE** popup box to set the source nuclide used for the Mössbauer measurement. The correct setting of the source nuclide is essential in order to obtain correct values for the fit parameters. The available models in the Interaction Popup depend on the selected source nuclide. The program also passes the source-nuclide information to user written Dynamic Link Libraries (see page 108).

### *27.3.3.* Spectrum background

When the parameter list of the background is selected formally as the current subspectrum, then the Interaction Popup box serves for the selection of various background types. The following types are available. (The ***v*** velocity is measured in [mm/s]).

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|---|---|
| Constant | Constant baseline with one parameter:<br>BASE LINE<br>$Background = BaseLine$ |
| Slope | Baseline with slope, with two parameters:<br>BASE LINE, SLOPE<br>$Background = BaseLine + Slope \cdot v$ |
| Curvature | Baseline modeling slope and curvature, with three parameters:<br>BASE LINE, CURVATURE, CENTER<br>$Background = BaseLine + Curvature \cdot (v - Center)^2$ |
| Third Order | Baseline modeled by a third order polynomial, with four parameters:<br>BASE LINE, CURVATURE, CENTER, CUBIC COEFFICIENT<br>$Background = BaseLine + Curvature \cdot (v - Center)^2 + CubicCoefficient \cdot (v - Center)^3$ |
| Unfolded | Baseline that can be used to model backgrounds of unfolded spectra that are calibrated.<br>Power of a cosine function with five parameters:<br>BASE LINE, COSINE AMPLITUDE, COSINE EXPONENT, MAXIMUM VELOCITY, CENTER [MM/S]<br>$BaseLine \pm COSINEAMPLITUDE \cdot \left[ \cos\left(\frac{\pi}{2} \cdot \frac{(v - Center)}{MaximumVelocity}\right) \right]^{COSINEExponent}$ |
| Unfolded + Slope | Unfolded background with slope, described by six parameters ($v_0$ depends only on the velocity axis, and it is determined internally. Its value is close to the value of the MAXIMUM VELOCITY):<br>BASE LINE, COSINE AMPLITUDE, COSINE EXPONENT, MAXIMUM VELOCITY, CENTER [MM/S], SLOPE<br>$BaseLine \pm slope \cdot ABS(v - v_0) \pm COSINEAMPLITUDE \cdot \left[ \cos\left(\frac{\pi}{2} \cdot \frac{(v - Center)}{MaximumVelocity}\right) \right]^{COSINEExponent}$ |

### *27.3.4.* Built in theories / interactions

For each selected source nuclide, MossWinn provides several theories / interactions that can be selected for any fitted subspectra. Some of these are linear fit models that can be fine-tuned further on the **DETAILS** page. Others, which cannot be modified on the DETAILS page, are based on Hamiltonian calculations. To add a new custom subspectrum model to those already available in the Interaction Popup box, save the model in question to the **Subspectrum Collection** of the corresponding source nuclide (via SAVE → SAVE SUBSPECTRUM). Then the saved model will be available in the Interaction Popup box under SUBSPECTRUM FROM COLLECTION. One can add any subspectrum model to the fitting capability of MossWinn by writing and compiling the corresponding code as DLL (see page 108 for details).

The following table lists the theories / interactions available by default for the various nuclides. The interaction when there is no splitting in the absorption line is called MONOPOLE in MossWinn.

| **Source nuclides: $^{57}$Fe, $^{119}$Sn, $^{125}$Te, $^{151}$Eu, $^{121}$Sb, $^{129}$I, $^{141}$Pr, $^{237}$Np, $^{197}$Au, $^{161}$Dy ( 25.655 keV ), M1/E1, M1+E2, E2** | |
|---|---|
| **Monopole** | **Linear model.**<br>Single absorption line, with three parameters:<br>AMPLITUDE, ISOMER SHIFT, LINE WIDTH |
| **Quadrupole (Powder)**<br>(Available only for $^{57}$Fe, $^{119}$Sn, $^{125}$Te, $^{197}$Au, $^{151}$Eu) | **For $^{57}$Fe, $^{119}$Sn, $^{125}$Te, $^{197}$Au :**<br><br>**Linear model**<br>Symmetrical quadrupole doublet with four parameters:<br>AMPLITUDE, ISOMER SHIFT, Q. SPLITTING, LINE WIDTH<br><br>**For $^{151}$Eu :**<br><br>**Hamiltonian, non-linear model.**<br>The model is calculated by solving the static Hamiltonian for pure quadrupole interaction. Powdered material is assumed. The model is described with five parameters:<br>AMPLITUDE, ISOMER SHIFT, VZZ [10^21 V/M2], ETA [0..1], LINE WIDTH |
| **Magnetic (Powder)**<br>(Not available for M1/E1, M1+E2, E2) | **Linear model.**<br>Magnetically split absorption pattern described with four parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T], LINE WIDTH |
| **First Order Mixed M+Q (Powder)**<br>(Available only for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Linear model.**<br>Magnetically split absorption pattern displaying quadrupole splitting (treated here as the equivalent of 2ε where ε is the first order quadrupole shift), with 6 absorption lines having the amplitude ratio of 3:2:1:1:2:3, with five parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>Q. SPLITTING, LINE WIDTH |
| **Mixed M+Q Static Hamiltonian (Powder)** | **Hamiltonian, non-linear model. H based system**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The *z* axis of the reference coordinate system is chosen to be parallel to the hyperfine magnetic field. BETA (EFG) and ALPHA (EFG) determine the relation between the reference system and the eigensystem of the EFG as explained on page 51. The model is described with eight parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG),<br>BETA (EFG), ALPHA (EFG), LINE WIDTH |
| **Mixed Q+M Static Hamiltonian (Powder)** | **Hamiltonian, non-linear model. $V_{zz}$ based system.**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The eigensystem of the EFG is chosen to be the reference coordinate system. The $\mathbf{e}_z$ basis vector of the reference system is selected such that $\lvert V_{xx}\rvert \le \lvert V_{yy}\rvert \le \lvert V_{zz}\rvert$. BETA (MF) denotes the polar, and ALPHA (MF) denotes the azimuthal angle of the hyperfine magnetic field in the reference system (see page 52). The model is described with eight parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG),<br>BETA (MF), ALPHA (MF), LINE WIDTH |
| **Blume-Tjon Two State Magnetic Relaxation (Powder)**<br>(Available only for $^{57}$Fe) | **Hamiltonian, non-linear model.**<br>Blume-Tjon relaxation model assuming a relaxing magnetic field with two possible, opposite directions for the hyperfine magnetic field at the place of the nucleus. The model is described with eight parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG),<br>JUMP UP RATE, JUMP DOWN RATE, LINE WIDTH |
| **Tjon-Blume Jahn-Teller Quadrupole Relaxation (Powder)**<br>(Available only for $^{57}$Fe) | **Hamiltonian, non-linear model.**<br>Tjon-Blume relaxation model assuming an electric field gradient whose main component ($V_{zz}$), although fixed in magnitude, reorients dynamically and randomly between the $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ directions of the eigensystem of the EFG tensor. The hyperfine magnetic field and $\eta$ are assumed to be zero. The model is described with five parameters:<br>AMPLITUDE, ISOMER SHIFT, VZZ (EFG) [10^21 V/M2],<br>JUMP RATE, LINE WIDTH |

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| **Electron Hopping Relaxation (Paramagnetic, Powder)**<br>(Available only for $^{57}$Fe) | **Hamiltonian, non-linear model.**<br>The theory models a paramagnetic powder where electron hopping takes place either between iron ions of different oxidation states (e.g. $Fe^{2+} \leftrightarrow Fe^{3+}$) or between iron ions and the rest of the system, and as a result of this hopping the Hamiltonian sensed by iron nuclei relaxes between two different forms characterized by different isomer shift and quadrupole splitting values. The model can account for situations encountered, e.g., in the works<br>• F.J. Litterst, G. Amthauer: *Phys. Chem. Minerals* **10** (1984) 250.<br>• R.H. Herber, H. Eckert: *Phys. Rev. B* **31** (1985) 34.<br>The model is described with 8 parameters:<br>AMPLITUDE, ISOMER SHIFT (Fe3+), ISOMER SHIFT (Fe2+), Q. SPLITTING (Fe3+), Q. SPLITTING (Fe2+), Fe3+ RATIO, RELAXATION RATE [Mrad/S], LINE WIDTH |
| **Electron Hopping Relaxation (Magnetic, Powder)**<br>(Available only for $^{57}$Fe) | **Hamiltonian, non-linear model.**<br>The theory models a magnetic powder where electron hopping takes place either between iron ions of different oxidation states (e.g. $Fe^{2+} \leftrightarrow Fe^{3+}$) or between iron ions and the rest of the system, and as a result of this hopping the Hamiltonian sensed by iron nuclei relaxes between two different forms characterized by different isomer shift, hyperfine magnetic field and quadrupole splitting values. The model can account for situations such as the one encountered in the work<br>• K. Ando, J. Nishihara: *J. Phys. Chem. Solids* **41** (1980) 1273.<br>The model is described with 10 parameters:<br>AMPLITUDE, ISOMER SHIFT (Fe3+), ISOMER SHIFT (Fe2+), MAGNETIC FIELD (Fe3+) [T], MAGNETIC FIELD (Fe2+) [T], Q. SPLITTING (Fe3+), Q. SPLITTING (Fe2+), Fe3+ RATIO, RELAXATION RATE [Mrad/S], LINE WIDTH |
| **Random EFG in uniaxial external magnetic field (Powder)**<br>(Available only for $^{57}$Fe) | **Hamiltonian, non-linear model.**<br>The analytical expression for the line shape of the $^{57}$Fe Mössbauer spectrum of a powdered sample, with randomly oriented EFG and $\eta = 0$, subjected to a uniaxial (external) magnetic field, as given by Blaes *et al.* in N. BLAES, H. FISCHER, U. GONSER: NIM B **9** (1985) 201. The model is described with seven parameters ($\eta \equiv 0$ is a fixed parameter):<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T], VZZ (EFG) [10^21 V/M2], ETA (EFG), THETA (GAMMA RAY), LINE WIDTH |

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| **Distributions with parameterized profile (Powder)...** | This is a menu container of the hyperfine parameter distribution models to be detailed below. See also section 27.5 for details. |
| **Gaussian QS and IS distribution (VBF, PM, Powder)**<br>(Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **VBF (Voigt-based fitting) model**<br>The model describes the doublet spectrum of a paramagnetic powder with a Gaussian distribution in the quadrupole splitting, and with an associated Gaussian distribution in the isomer shift values, the latter being coupled to the quadrupole splitting values according to a linear relationship of $\delta = \delta_0+\delta_1\Delta$. It is based on the theory described in<br><br>D.G. Rancourt, J.Y. Ping:<br>*Nuclear Instruments and Methods* B **58** (1991) 85.<br><br>The model is described with the following seven parameters:<br><br>AMPLITUDE, A+/A-, ISOMER SHIFT, Q. SPLITTING, SIGMA (QS), COUPLING (IS,QS), LORENTZIAN LINE WIDTH |
| **Gaussian MF, QS and IS distribution (VBF, M, Powder)**<br>(Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **VBF (Voigt-based fitting) model**<br>The model describes the sextet spectrum of a magnetic powder with a Gaussian distribution in the hyperfine magnetic field, and with an associated Gaussian distribution in the isomer shift and quadrupole splitting (here treated as 2ε) values, the latter ones being coupled to the hyperfine magnetic field values according to the linear relationships of $\delta = \delta_0+m_\delta \cdot B_{hf}$ and $\Delta = \Delta_0+m_\Delta \cdot B_{hf}$. It is based on the theory described in<br><br>D.G. Rancourt, J.Y. Ping:<br>*Nuclear Instruments and Methods* B **58** (1991) 85.<br><br>The model is described with the following nine parameters:<br><br>AMPLITUDE, A25/A34, ISOMER SHIFT, MAGNETIC FIELD [T], Q. SPLITTING, SIGMA (MF), COUPLING (IS,MF), COUPLING (QS,MF), LORENTZIAN LINE WIDTH |
| **Gaussian QS and IS distribution (xVBF, PM, Powder)**<br>(Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **xVBF (extended Voigt-based fitting) model**<br>The model describes the doublet spectrum of a paramagnetic powder with a Gaussian distribution in the quadrupole splitting and isomer shift values, with an arbitrary degree of correlation between the two distributions. It is based on the theory described in<br><br>K. Lagarec, D.G. Rancourt:<br>*Nuclear Instruments and Methods* B **129** (1997) 266.<br><br>The model is described with the following eight parameters:<br><br>AMPLITUDE, A+/A-, ISOMER SHIFT, Q. SPLITTING, SIGMA (IS),<br>SIGMA (QS), CORRELATION (IS,QS), LORENTZIAN LINE WIDTH |
| **Gaussian MF, QS and IS distribution (xVBF, M, Powder)**<br>(Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **xVBF (extended Voigt-based fitting) model**<br>The model describes the sextet spectrum of a magnetic powder with a Gaussian distribution in the isomer shift, hyperfine magnetic field and quadrupole splitting (here treated as 2ε) values, with an adjustable degree of pairwise correlations between the different distributions. It is based on the theory described in<br><br>K. Lagarec, D.G. Rancourt:<br>*Nuclear Instruments and Methods* B **129** (1997) 266.<br><br>The model is described with the following twelve parameters:<br><br>AMPLITUDE, A25/A34, ISOMER SHIFT, MAGNETIC FIELD [T], Q. SPLITTING, SIGMA (IS), SIGMA (MF), SIGMA (QS), CORRELATION (IS,MF), CORRELATION (QS,MF), CORRELATION (IS,QS), LORENTZIAN LINE WIDTH |

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| **Binomial distribution (1 shell, M, Powder)** (Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Binomial atomic distribution model**<br>The model describes the sextet-based spectrum of a magnetic powder sample in which the isomer shift, hyperfine magnetic field and quadrupole splitting (here treated as 2ε) parameters are perturbed in an additive manner by substituent atoms distributed randomly in the first shell of atomic neighbors around the Mössbauer nuclides. Each substituent atom in the shell is assumed to alter the isomer shift, hyperfine magnetic field and quadrupole splitting parameters with the same amount. The maximum number of atomic positions that can contribute to the shell around a Mössbauer nuclide is 14. The model is also suitable to fit doublet- or singlet-based binomial atomic distribution models.<br><br>The model is described with the following eleven parameters:<br><br>AMPLITUDE, A25/A34, ISOMER SHIFT, MAGNETIC FIELD [T], Q. SPLITTING, DELTA IS (NN), DELTA MF (NN), DELTA QS (NN), NEIGHBORS (NN), CONCENTRATION, LINE WIDTH |
| **Binomial distribution (2 shells, M, Powder)** (Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Binomial atomic distribution model**<br>The model describes the sextet-based spectrum of a magnetic powder sample in which the isomer shift, hyperfine magnetic field and quadrupole splitting (here treated as 2ε) parameters are perturbed in an additive manner by substituent atoms distributed randomly in the first and second shells of atomic neighbors around the Mössbauer nuclides. Substituent atoms in the same shell are assumed to alter the isomer shift, hyperfine magnetic field and quadrupole splitting parameters with the same amount, but this amount can be different for atoms in different shells. The maximum number of atomic positions that can contribute to a single shell is 14. The model is also suitable to fit doublet- or singlet-based binomial atomic distribution models.<br><br>The model is described with the following 15 parameters:<br><br>AMPLITUDE, A25/A34, ISOMER SHIFT, MAGNETIC FIELD [T], Q. SPLITTING, DELTA IS (NN), DELTA MF (NN), DELTA QS (NN), DELTA IS (NNN), DELTA MF (NNN), DELTA QS (NNN), NEIGHBORS (NN), NEIGHBORS (NNN), CONCENTRATION, LINE WIDTH |
| **Multinomial distribution (1 shell, AB, M, Powder)** (Available for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Multinomial atomic distribution model**<br>The model describes the sextet-based spectrum of a magnetic powder sample in which the isomer shift, hyperfine magnetic field and quadrupole splitting (here treated as 2ε) parameters are perturbed in an additive manner by **two different kinds (A and B) of substituent atoms** distributed randomly in the first shell of atomic neighbors around the Mössbauer nuclides. Substituent atoms of the same kind are assumed to alter the isomer shift, hyperfine magnetic field and quadrupole splitting parameters with the same amount, but this amount may be different for the **A** and **B** type of substituent atoms. The maximum number of atomic positions that can contribute to the first atomic shell is 14. The model is also suitable to fit doublet- or singlet-based multinomial atomic distribution models.<br><br>The model is described with the following 15 parameters:<br><br>AMPLITUDE, A25/A34, ISOMER SHIFT, MAGNETIC FIELD [T], Q. SPLITTING, DELTA IS (A), DELTA MF (A), DELTA QS (A), DELTA IS (B), DELTA MF (B), DELTA QS (B), NEIGHBORS (NN), CONCENTRATION (A), CONCENTRATION (B), LINE WIDTH |

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| **Paramagnetic Hyperfine Structure (Powder)....**<br>(Available for $^{57}$Fe) | This is a menu container of the paramagnetic hyperfine structure (**PHS**) models listed below. See section 27.6 for details. Note that access to the paramagnetic hyperfine structure models requires either a **MossWinn DBM version licence**, or subscription to the ***MossWinn Services***. |
| **PHS 1/2**<br>**(Powder, ZERO EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system with effective spin $S$ = ½, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident. See page 74 for details. |
| **PHS**<br>**(Powder, ZERO EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 0…5/2, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the *xyz* crystal field system (**CFS**). See page 75 for details. |
| **PHS Trigonal**<br>**(Powder, ZERO EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 0…5/2, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the system of the axial crystal field (**CFS**) whose *z* axis is oriented in the (1,1,1) cube diagonal direction of the cubic crystal field system (trigonal distortion). Tensor **A** is assumed to display axial symmetry ($A_{yy} = A_{xx}$). See page 76 for details. |
| **PHS Angle (Powder, ZERO EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 0…5/2, in the absence of an external magnetic field, by assuming slow electronic relaxation. The relative orientation of the eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are given with respect to the crystal field system (**CFS**) via the respective Euler angles that rotate the CFS system into the **A** or **EFG** tensor eigensystem. The orientation of the *xyz* crystal field system (**CFS**) is given with respect to the cubic system via the Euler angles that rotate the cubic system into the CFS system. See page 82 for details. |
| **PHS 1/2**<br>**(Powder, EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 1/2, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident. See page 78 for details. |
| **PHS**<br>**(Powder, EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 0…5/2, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the crystal field system (**CFS**). See page 79 for details. |
| **PHS Trigonal**<br>**(Powder, EMF, Slow R.)** | This **PHS model** accounts for a powder sample with an electronic system characterized by an effective spin $S$ = 0…5/2, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the crystal field system (**CFS**) whose *z* axis is oriented in the (1,1,1) cube diagonal direction of the cubic crystal field system (trigonal distortion). Tensors **g** and **A** are assumed to display axial symmetry ($g_{yy} = g_{xx}$, $A_{yy} = A_{xx}$). See page 80 for details. |

| | |
|---|---|
| **PHS Angle**<br>**(Powder, EMF, Slow R.)**<br><br>**PHS 1/2**<br>**(Powder, EMF, Decoupled, Fast R.)**<br><br>**PHS**<br>**(Powder, EMF, Decoupled, Fast R.)**<br><br>**PHS Trigonal**<br>**(Powder, EMF, Decoupled, Fast R.)**<br><br>**PHS Angle**<br>**(Powder, EMF, Decoupled, Fast R.)** | This **PHS model** is a general one that includes all the slow-relaxation PHS models treated up to this point as special cases. It accounts for a powder sample with an electronic system characterized by an effective spin $S = 0…5/2$, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The relative orientation of the eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are given with respect to the crystal field system (**CFS**) via the respective Euler angles that rotate the CFS system into the **g**, **A** or **EFG** tensor eigensystem. The orientation of the *xyz* crystal field system (**CFS**) is given with respect to the cubic system via the Euler angles that rotate the cubic system into the CFS system. See page 82 for details.<br><br>**Fast relaxation limit paramagnetic hyperfine structure models.**<br><br>These **PHS models** are fast relaxation limit counterparts of the previous four slow relaxation limit PHS models. See page 84 for details. |

| | |
|---|---|
| **Quadrupole (Single crystal)**<br>(Available only for $^{57}$Fe, $^{119}$Sn, $^{125}$Te, $^{197}$Au) | **Linear model.**<br>Asymmetrical quadrupole doublet with five parameters:<br>AMPLITUDE (1), AMPLITUDE (2), ISOMER SHIFT,<br>Q. SPLITTING, LINE WIDTH |
| **Magnetic (Single crystal)**<br>(Available only for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Linear model.**<br>Magnetically split absorption pattern with 6 absorption lines having the amplitude ratio of 3:*x*:1:1:*x*:3, with five parameters:<br>AMPLITUDE (1,3,4,6), AMPLITUDE (2,5), ISOMER SHIFT,<br>MAGNETIC FIELD [T], LINE WIDTH |
| **First Order Mixed M+Q (Single crystal)**<br>(Available only for $^{57}$Fe, $^{119}$Sn, $^{125}$Te) | **Linear model.**<br>Magnetically split absorption pattern displaying quadrupole splitting (treated here as the equivalent of 2ε where ε is the first order quadrupole shift), with 6 absorption lines having the amplitude ratio of 3:*x*:1:1:*x*:3, with six parameters:<br>AMPLITUDE (1,3,4,6), AMPLITUDE (2,5), ISOMER SHIFT,<br>MAGNETIC FIELD [T], Q. SPLITTING, LINE WIDTH |
| **Mixed M+Q Static Hamiltonian (Single crystal)** | **Hamiltonian, non-linear model. <u>H</u> based system**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The *z* axis of the reference coordinate system is chosen to be parallel to the hyperfine magnetic field. BETA (EFG) and ALPHA (EFG) determine the relation between the reference system and the eigensystem of the EFG as explained on page 51. THETA (GAMMA RAY) denotes the polar, and PHI (GAMMA RAY) denotes the azimuthal angle of the gamma-ray direction in the reference system. The model is described with ten parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG), BETA (EFG), ALPHA (EFG), THETA (GAMMA RAY), PHI (GAMMA RAY), LINE WIDTH |
| **Mixed Q+M Static Hamiltonian (Single crystal)** | **Hamiltonian, non-linear model. <u>$V_{zz}$</u> based system.**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The eigensystem of the EFG is chosen to be the reference coordinate system. The $\mathbf{e}_z$ basis vector of the reference system is selected such that $\lvert V_{xx}\rvert \le \lvert V_{yy}\rvert \le \lvert V_{zz}\rvert$. BETA (MF) denotes the polar, and ALPHA (MF) denotes the azimuthal angle of the hyperfine magnetic field in the reference system (see page 52). THETA (GAMMA RAY) denotes the polar, and PHI (GAMMA RAY) denotes the azimuthal angle of the gamma-ray direction in the reference system. The model is described with ten parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG), BETA (MF), ALPHA (MF), THETA (GAMMA RAY), PHI (GAMMA RAY), LINE WIDTH |

| | |
|---|---|
| **Mixed M+Q Static Hamiltonian (Mosaic)** | **Hamiltonian, non-linear model. <u>H</u> based system**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The *z* axis of the reference coordinate system is chosen to be parallel to the hyperfine magnetic field. BETA (EFG) and ALPHA (EFG) determine the relation between the reference system and the eigensystem of the EFG as explained on page 51. THETA (GAMMA RAY) denotes the polar angle of the gamma-ray direction relative to the direction of the hyperfine magnetic field. The azimuthal angle of the gamma-ray direction is assumed to be random and evenly distributed between 0 deg and 360 deg in the sample (mosaic sample), so that the amplitudes are averaged with respect to this angle {PHI (GAMMA RAY)}. The model is described with nine parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG), BETA (EFG), ALPHA (EFG), THETA (GAMMA RAY) LINE WIDTH |
| **Mixed Q+M Static Hamiltonian (Mosaic)** | **Hamiltonian, non-linear model. <u>$V_{zz}$</u> based system.**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The eigensystem of the EFG is chosen to be the reference coordinate system. The $\mathbf{e}_z$ basis vector of the reference system is selected such that $\lvert V_{xx}\rvert \le \lvert V_{yy}\rvert \le \lvert V_{zz}\rvert$. BETA (MF) denotes the polar, and ALPHA (MF) denotes the azimuthal angle of the hyperfine magnetic field in the reference system (see page 52). THETA (GAMMA RAY) denotes the polar angle of the gamma-ray direction relative to $\mathbf{e}_z$. The azimuthal angle of the gamma-ray direction is assumed to be random and evenly distributed between 0 deg and 360 deg in the sample (mosaic sample), so that the amplitudes are averaged with respect to this angle {PHI (GAMMA RAY)}. The model is described with nine parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG), BETA (MF), ALPHA (MF), THETA (GAMMA RAY), LINE WIDTH |
| **Mixed M+Q Static Hamiltonian (Powder+GKE)** | **Hamiltonian, non-linear model with Goldanskii-Karyagin Effect. <u>H</u> based system**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The *z* axis of the reference coordinate system is chosen to be parallel to the hyperfine magnetic field. BETA (EFG) and ALPHA (EFG) determine the relation between the reference system and the eigensystem of the EFG as explained on page 51.<br>The MSD Tensor is assumed to be diagonal in the reference coordinate system, and furthermore it is assumed to display axial symmetry. D(Z,X) (MSD) denotes $k^2 \cdot \left[\langle z^2\rangle_{\text{av}} - \langle x^2\rangle_{\text{av}}\right]$. The model is described with nine parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG),<br>BETA (EFG), ALPHA (EFG), D(Z,X) (MSD), LINE WIDTH |
| **Mixed Q+M Static Hamiltonian (Powder+GKE)** | **Hamiltonian, non-linear model with Goldanskii-Karyagin Effect. <u>$V_{zz}$</u> based system**<br>The model is calculated by solving the static Hamiltonian for mixed magnetic and quadrupole interactions. The eigensystem of the EFG is chosen to be the reference coordinate system. The $\mathbf{e}_z$ basis vector of the reference system is selected such that $\lvert V_{xx}\rvert \le \lvert V_{yy}\rvert \le \lvert V_{zz}\rvert$. BETA (MF) denotes the polar, and ALPHA (MF) denotes the azimuthal angle of the hyperfine magnetic field in the reference system (see page 52).<br>The MSD Tensor is assumed to be diagonal in the reference coordinate system, and furthermore it is assumed to display axial symmetry. D(Z,X) (MSD) denotes $k^2 \cdot \left[\langle z^2\rangle_{\text{av}} - \langle x^2\rangle_{\text{av}}\right]$. The model is described with nine parameters:<br>AMPLITUDE, ISOMER SHIFT, MAGNETIC FIELD [T],<br>VZZ (EFG) [10^21 V/M2], ETA (EFG),<br>BETA (MF), ALPHA (MF), D(Z,X) (MSD), LINE WIDTH |
| **External libraries** | Turn to this menu option in order to access theories (subspectrum models) programmed and compiled as external dynamic link libraries (see page 108). MossWinn looks for the corresponding libraries in the folder `../MossWinn 4.0/DLLs/` |
| **Subspectrum from collection** | To select any subspectrum saved earlier into the subspectrum collection of the selected source nuclide. |

## *27.3.5.* Nuclear parameters of M1, E1, E2, and M1+E2 transitions

When M1/E1, M1+E2, or E2 is selected formally as the source in the FIT menu, then one has the possibility to customize (or even fit if required) the values of the nuclear parameters of the selected nuclear transition. MossWinn adds/removes the necessary nuclear parameters automatically to/from the parameter list of the background. The name and meaning of these parameters — as used in MossWinn — are as follows.

Parameters used for each type (M1/E1, E2, M1+E2) of nuclear transition:

| **Parameter name** | **Meaning** |
|---|---|
| Energy (Gamma ray) [KeV] | Energy of the γ ray emitted during the Mössbauer transition. |
| Spin (Excited state) | Nuclear spin of the excited state of the Mössbauer nuclide in units of $\hbar$.<br>Constrained to $I_e \le 9/2$ . |
| Spin (Ground state) | Nuclear spin of the ground state of the Mössbauer nuclide in units of $\hbar$.<br>Constrained to $I_g \le 9/2$ . |
| g factor (Excited state) | Gyromagnetic factor of the excited state of the Mössbauer nuclide. |
| g factor (Ground state) | Gyromagnetic factor of the ground state of the Mössbauer nuclide. |
| Q.Mom. (Excited state) [barn] | Nuclear quadrupole moment of the excited state of the Mössbauer nuclide. |
| Q.Mom. (Ground state) [barn] | Nuclear quadrupole moment of the ground state of the Mössbauer nuclide. |
| Natural Line Width [mm/s] | (Experimental) Natural line width, as measurable in an experiment (e.g. 0.194 mm/s for $^{57}$Fe). |

Additional nuclear parameters used only for the M1+E2 type nuclear transition:

| **Parameter name** | **Meaning** |
|---|---|
| Amplitude (E2/M1) | AMPLITUDE ($\delta$) of the E2 / M1 mixing ratio of a mixed M1+E2 Mössbauer transition. It should be non-negative. Equals to the absolute value of the ratio of the corresponding reduced matrix elements:<br>$$\delta \cdot \mathrm{e}^{i\cdot\zeta} = \frac{\left\langle I_\mathrm{g} \middle| \mathbf{M}\,(\mathrm{E2}) \middle| I_\mathrm{e} \right\rangle}{\left\langle I_\mathrm{g} \middle| \mathbf{M}\,(\mathrm{M1}) \middle| I_\mathrm{e} \right\rangle}$$<br>(Most literature quotes $\delta^2$. For $^{197}$Au, for example, $\delta^2 \approx 0.11$) |
| Phase angle (E2/M1) [deg] | PHASE difference between the E2 and M1 radiations. MEASURED IN DEGREES.<br>$180 \cdot \frac{\zeta}{\pi}$ where $\zeta$ appears in $\delta \cdot \mathrm{e}^{i\cdot\zeta}$ . For $^{99}$Ru, for example, Phase angle (E2/M1) [deg] ≈ 180 .<br>(For $^{99}$Ru see O.C. Kistner: *Phys. Rev.* **144** (1966) 1022.) |

## 27.4. Built in Hamiltonian models

### 27.4.1. Static Hamiltonian of mixed magnetic and quadrupole interactions

The model of mixed magnetic and quadrupole interaction is solved in MossWinn by the numerical diagonalization of the nuclear Hamiltonian matrix.

In the reference coordinate system where the $\mathbf{e}_z$ unit vector is chosen to be parallel to the direction of the $\mathbf{B}_{hf}$ hyperfine magnetic field the Hamiltonian is expressed as follows [R.W. Grant: *Mössbauer Spectroscopy in Magnetism: Characterization of Magnetically-ordered Compounds*, in *Mössbauer Spectroscopy* , ed. U. Gonser, Springer-Verlag, **5** (1975) pp. 97.]:

$$H(I)_{m,m} = -\omega_H \hbar \cdot m + \frac{\omega_Q \hbar}{2}(3\cos^2\beta - 1 + \eta \cdot \sin^2\beta \cdot \cos 2\alpha)[3m^2 - I(I+1)]$$

$$H(I)_{m,m+1} = \frac{3\omega_Q \hbar}{2}\sin\beta \cdot \{\cos\beta - \frac{\eta}{6}[(1+\cos\beta)\,e^{2\alpha i} - (1-\cos\beta)e^{-2\alpha i}]\}(2m+1)\sqrt{(I-m)(I+m+1)}$$

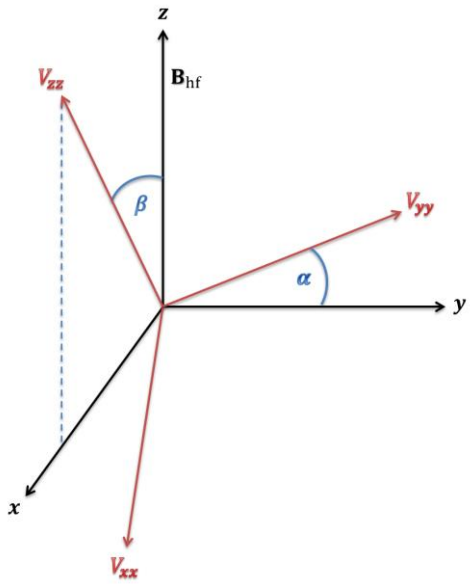
$$H(I)_{m,m+2} = \frac{3\omega_Q \hbar}{4}\{\sin^2\beta + \frac{\eta}{6}[(1+\cos\beta)^2\,e^{2\alpha i} + (1-\cos\beta)^2\,e^{-2\alpha i}]\}\sqrt{(I+m+2)(I+m+1)(I-m)(I-m-1)}$$

$$\omega_H = \frac{g_N(I)\cdot B \cdot \mu_N}{\hbar} \qquad \omega_Q = \frac{1}{\hbar}\cdot\frac{eV_{zz}Q}{4I(2I-1)}$$

where $B$ denotes the flux density of the hyperfine magnetic field, $\boldsymbol{\beta}$ denotes the angle of rotation around the $y$ axis that aligns $\mathbf{B}_{hf}$ with the direction of the eigensystem of the EFG that is associated with its element ($V_{zz}$) having the largest magnitude, $\eta = (V_{xx} - V_{yy}) / V_{zz}$ is the asymmetry parameter of the EFG, $\boldsymbol{\alpha}$ is the angle of rotation around the axis of $V_{zz}$ that is needed to make the correspondingly rotated $y$ axis of the reference system to align with the $V_{yy}$ axis, $I$ denotes the angular momentum quantum number of the excited or ground state of the Mössbauer nucleus, and $m$ goes through the values of $-I$, $-I$+1...$I$−1, $I$. The rest of the elements in the upper triangle are zero. The elements in the lower triangle of the **H(*I*)** matrix are calculated in the following way:

$$\mathbf{H}(\boldsymbol{I})_{i,j}\,[\text{lower triangle}] = \mathbf{H}(\boldsymbol{I})_{j,i}\,[\text{upper triangle}]^*$$

where * denotes the operation of complex conjugation (**H(*I*)** is a Hermitian matrix).




The reference coordinate system (*xyz*, drawn by black color) where the $\mathbf{e}_z$ unit vector is chosen to be parallel to the direction of the $\mathbf{B}_{hf}$ hyperfine magnetic field, and its relation to the eigensystem of the EFG (drawn by red color). **Note that the axis associated with $V_{zz}$ lies in the *xz* plane.** $\beta$ denotes the angle of rotation around the $y$ axis that aligns $z$ with the axis of $V_{zz}$, whereas $\alpha$ denotes the angle of rotation around the axis of $V_{zz}$ that aligns $y$ with the axis of $V_{yy}$. Fit models expressed in this kind of reference coordinate system are designated by a name that includes "**M+Q**", and use the parameters **Beta (EFG)** and **Alpha (EFG)** for the setting of rotation angles $\beta$ and $\alpha$, respectively.

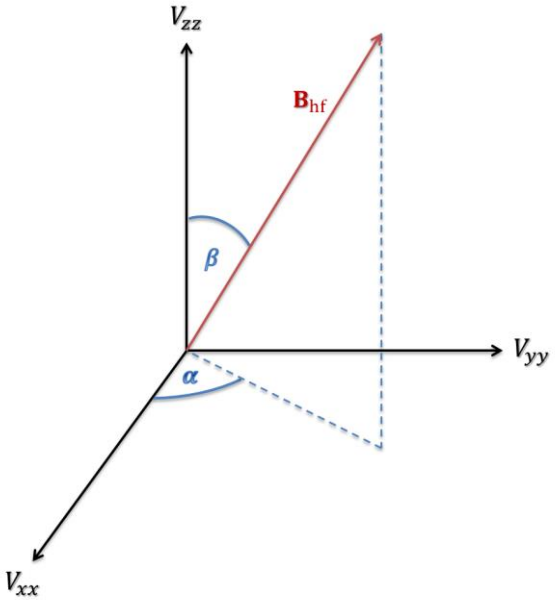
In the reference coordinate system that coincides with the eigensystem of the EFG (where the EFG is diagonal and $|V_{xx}| \le |V_{yy}| \le |V_{zz}|$) the Hamiltonian is expressed as follows [based on W. Kündig: *Nuclear Instruments and Methods* **48** (1967) 219.]:

$$H(I)_{m,m} = \omega_Q \hbar [3m^2 - I(I+1)] - \omega_H \hbar m \cos\beta$$

$$H(I)_{m,m+1} = \frac{-\omega_H \hbar \sin\beta}{2} \sqrt{I(I+1) - m(m+1)} \cdot \mathrm{e}^{i\alpha}$$

$$H(I)_{m,m+2} = \frac{\omega_Q \hbar}{2} \cdot \eta \cdot \sqrt{[I(I+1) - (m+2)(m+1)] \cdot [I(I+1) - m(m+1)]}$$

where the same notations are used as in the previous case, except that here $\beta$ denotes the polar, and $\alpha$ denotes the azimuthal angle of the hyperfine magnetic field in the reference coordinate system. The rest of the elements in the upper triangle are zero. The matrix elements of the lower triangle are calculated in the same way as described in the previous case.




The reference coordinate system ($xyz \equiv V_{xx}V_{yy}V_{zz}$, drawn by black color) fixed to the eigensystem of the EFG where $|V_{xx}| \le |V_{yy}| \le |V_{zz}|$. $\beta$ denotes the polar and $\alpha$ denotes the azimuthal angle of the $\mathbf{B}_{\mathrm{hf}}$ hyperfine magnetic field vector. Fit models expressed in this kind of reference coordinate system are designated by a name that includes "**Q+M**", and use the parameters **Beta (MF)** and **Alpha (MF)** for the setting of angles $\beta$ and $\alpha$, respectively.

The Hamiltonian of the selected model is calculated for the excited as well as for the ground state of the nucleus, and the corresponding eigenproblems are solved numerically. Then the position of the absorption lines is calculated from the obtained eigenvalues, and at each position a Lorentzian, a Lorentzian with dispersion, a Pseudo-Voigt function, or a Cosine Smeared Lorentzian function — depending on the corresponding setting in the FIT menu — is placed. The relative amplitudes of the lines are calculated with the help of the eigenvectors derived during the solution of the eigenproblem. For each handled Mössbauer nuclide three different models (single crystal, mosaic, powder) are available to account for the sample geometry, as described in the next section.

## *27.4.2.* Invariants $S_0$, $S_1$, $S_2$

The invariants $S_0$, $S_1$ and $S_2$ are output by MossWinn on fit reports for subspectra calculated according to those 3/2 – 1/2 Hamiltonian models where the $\mathbf{B}_{hf}$ hyperfine magnetic field vector can have an arbitrary orientation with respect to the eigensystem of the EFG. For powdered samples without texture and Goldanskii-Karyagin effect (see page 56), for a given 3/2 – 1/2 Hamiltonian subspectrum model the invariants $S_0$, $S_1$ and $S_2$, together with the value of the invariant $B_{hf}$, represent the whole class of solutions (i.e. parameter vectors $B_{hf}$, $V_{zz}$, $\eta$, $\beta$, $\alpha$, where $\beta$ and $\alpha$ are the polar and azimuthal angles of the $\mathbf{B}_{hf}$ vector in the eigensystem of the EFG tensor) that would result in the same set of relative positions and intensities of the absorption peaks as the actually output parameter vector. As a consequence, when for Hamiltonian subspectrum models **MIXED M+Q STATIC HAMILTONIAN (POWDER)** and **MIXED Q+M STATIC HAMILTONIAN (POWDER)** different parameter vectors ($B_{hf}$, $V_{zz}$, $\eta$, $\beta$, $\alpha$) result in the same set of invariants $S_0$, $S_1$, $S_2$ and $B_{hf}$, then they also represent the same set of relative positions and intensities of the corresponding absorption peaks. Through this feature the invariants help to treat the so called ambiguity problem characteristic to 3/2 – 1/2 Mössbauer transitions as described in the following papers:

- D. Satuła, K. Szymański, L. Dobrzyński, V.H. Tran, R. Troć: *Phys. Rev. B* **78** (2008) 014411.
- K. Szymański, D. Satuła, L. Dobrzyński, K. Rećko, W. Olszewski, K. Brzózka, J. Jankowska-Kisielińska: *Journal of Physics: Conference Series* **217** (2010) 012010.

In accordance with the above works, MossWinn calculates the invariants as follows:

$$S_0 = a\sqrt{\mathrm{Tr}\,\mathbf{V}^2} = a\sqrt{\frac{3}{2}}\,|V_{zz}|\sqrt{\frac{\eta^2}{3}+1}$$

$$S_1 = a\,(\mathbf{m}^{\mathrm{T}}\cdot\mathbf{V}\cdot\mathbf{m}) = a\,\frac{V_{zz}}{2}(3\cos^2\beta - 1 + \eta\cos 2\alpha\sin^2\beta)$$

$$S_2 = a\sqrt{\mathbf{m}^{\mathrm{T}}\cdot\mathbf{V}^2\cdot\mathbf{m}} = a\,\frac{|V_{zz}|}{2}\sqrt{4-(3+2\eta\cos 2\alpha-\eta^2)\sin^2\beta}$$

where $a = \dfrac{e|Q_{3/2}|c}{E_\gamma}$ is the proportionality constant that makes the invariants to be expressed in units of mm/s, $\mathbf{V}$ denotes the EFG tensor, $\mathbf{m} = \dfrac{\mathbf{B}_{hf}}{B_{hf}}$, $\eta$ is the asymmetry parameter and $V_{zz}$ is the main component of $\mathbf{V}$ expressed in its eigensystem as usual, and finally $\beta$ and $\alpha$ are the polar and azimuthal angles of the $\mathbf{B}_{hf}$ vector in the eigensystem of the EFG tensor.

By default, MossWinn calculates the standard deviation of the above invariants on the basis of the standard deviation of the corresponding $V_{zz}$, $\eta$, $\beta$, $\alpha$ fit parameters by assuming that the latter are uncorrelated. This will usually result in an overestimation of the invariants' StD values. Turn to the Monte Carlo error estimation procedure (see page 99) in order to obtain a more accurate estimation of the standard deviations of $S_0$, $S_1$ and $S_2$.

Beside the above quoted two models of powdered samples, MossWinn outputs the invariants also in the case of models describing mosaic samples, single crystals and powders with Goldanskii-Karyagin effect. In these latter cases, however, the values of the invariants do not determine unequivocally the relative intensities of the absorption peaks.

## *27.4.3.* Relative amplitude of the absorption lines of pure M1/E1 transitions

***Single Crystal case***

In the case of a single crystal the electric field vector of the dipole radiation field can be expressed as follows [R.M. Housley, R.W. Grant, U. Gonser: *Phys. Rev.* **178** (1969) 514.]:

$$\mathbf{E}(\underline{r})_{i\to j} = R(\underline{r})\cdot\{[a_{\mathrm{M}}(1,1)\,\mathrm{e}^{i\varphi} + a_{\mathrm{M}}(1,-1)\,\mathrm{e}^{-i\varphi}]\cdot\hat{\Psi} + \\ + i\cdot[a_{\mathrm{M}}(1,1)\,\mathrm{e}^{i\varphi}\cos(\vartheta) + a_{\mathrm{M}}(1,0)\sqrt{2}\sin(\vartheta) - a_{\mathrm{M}}(1,-1)\,\mathrm{e}^{-i\varphi}\cos(\vartheta)]\cdot\hat{\Xi}\}$$

where $\hat{\Psi}$ and $\hat{\Xi}$ are spherical unit vectors that are both perpendicular to the propagation direction of the radiation, as well as they are perpendicular to each other. $\theta$ and $\varphi$ are the polar and azimuthal angles of the γ-ray direction in the reference coordinate system whose *z* axis coincides either with the direction of the hyperfine magnetic field $\mathbf{B}_{\mathrm{hf}}$ (in case of models denoted with M+Q), or with the $\mathbf{e}_{\mathrm{z}}$ base vector of the eigensystem of the EFG (i.e. with the direction associated with $V_{\mathrm{zz}}$, in case of models denoted with Q+M). The complex coefficients $a_{\mathrm{M}}(1,1)$, $a_{\mathrm{M}}(1,0)$ and $a_{\mathrm{M}}(1,-1)$ are calculated from the eigenvectors of the actual Hamiltonian matrix:

$$a_{\mathrm{M}}(1,m)_{i\to j} = \sum_{m_e - m_g = m} \alpha_i(m_{\mathrm{e}})\cdot\alpha_j^*(m_{\mathrm{g}})\cdot\mathrm{Clebsch}(I_{\mathrm{e}},1,I_{\mathrm{g}},m_{\mathrm{e}},m,m_{\mathrm{g}})$$

where $i\to j$ denotes the transition from the *i*th eigenstate of the excited nucleus, to the *j*th eigenstate of the nucleus in its ground state. $\alpha_{\mathrm{i}}(m_{\mathrm{e}})$ equals to the scalar product of the *i*th eigenstate of the excited nucleus with $|I_{\mathrm{e}},m_{\mathrm{e}}>$. $\alpha_{\mathrm{j}}(m_{\mathrm{g}})$ equals to the scalar product of the *j*th eigenstate of the nucleus in its ground state with $|I_{\mathrm{g}},m_{\mathrm{g}}>$. * denotes the operation of complex conjugation.

The relative amplitude of the absorption line belonging to the transition $i\to j$ is then proportional to $\mathbf{E}^*(\underline{r})_{\mathrm{i}\to\mathrm{j}}\mathbf{E}(\underline{r})_{\mathrm{i}\to\mathrm{j}}$.

***Mosaic Sample case***

In the model for a mosaic sample the relative amplitude of the absorption line belonging to the transition $i\to j$ is proportional to $\int_0^{2\pi}\mathbf{E}^*_{i\to j}\mathbf{E}_{i\to j}\cdot d\varphi$ that is, the amplitudes get averaged with respect to the azimuthal angle of the γ-ray direction.

***Powder Sample case***

In the model for a powder sample the relative amplitude of the absorption line belonging to the transition $i\to j$ is proportional to $\int_0^{2\pi} d\varphi\cdot\int_0^{\pi}\mathbf{E}^*_{i\to j}\mathbf{E}_{i\to j}\cdot\sin(\vartheta)\cdot d\vartheta$ that is, the amplitudes get averaged with respect to the azimuthal angle as well as with respect to the polar angle of the γ-ray direction.

***True for all the three cases***

For the case of Hamiltonian models, independent of the setting of the AREA/AMPLITUDE mode, the relative amplitudes of the absorption lines get normalized so that the area of their sum — that is the area of the whole subspectrum — will be equal to the AMPLITUDE parameter of the corresponding subspectrum.

### *27.4.4.* Relative amplitude of the absorption lines of mixed M1+E2 transitions

In the case of a mixed M1+E2 nuclear transition — apart from a constant factor — the electric radiation field can be expressed as follows:

$$\vec{\mathrm{E}}(\vartheta,\varphi) = \sum_{m=-2}^{+2} i \cdot \left[\delta \cdot \mathrm{e}^{i\cdot\zeta} \cdot a(2,m)\right] \cdot (\vec{\mathrm{X}}_{2,m} \times \vec{\mathbf{e}}_r) - \sum_{m=-1}^{+1} a(1,m) \cdot \vec{\mathrm{X}}_{1,m}$$

(For pure E2 nuclear transition the radiation field is expressed as $\mathrm{E}(\vartheta,\varphi) = \sum_{m=-2}^{+2} i \cdot a(2,m) \cdot (\mathrm{X}_{2,m} \times \mathbf{e}_r)$ )

where $\mathbf{e_r} = \mathbf{e_r}(\vartheta,\varphi)$ is the direction of propagation of the radiation, $\mathbf{X_{l,m}} = \mathbf{X_{l,m}}(\vartheta,\varphi)$ denotes the vector spherical harmonics (for their definition, see for example J.M. Blatt, V.F. Weisskopf: *Theoretische Kernphysik*, Teubner verlag, Leipzig 1959, pp. 500). The ratio of the reduced matrix elements appears as:

$$\delta \cdot \mathrm{e}^{i\cdot\zeta} = \frac{\left\langle I_\mathrm{g} \left| \mathbf{M}(\mathrm{E2}) \right| I_\mathrm{e} \right\rangle}{\left\langle I_\mathrm{g} \left| \mathbf{M}(\mathrm{M1}) \right| I_\mathrm{e} \right\rangle}$$

$\boldsymbol{a(1,m)} = \boldsymbol{a_\mathrm{M}(1,m)}$ is defined as described in the previous section, and $\boldsymbol{a(2,m)}$ is expressed as:

$$a(2,m)_{i\to j} = \sum_{m_e - m_g = m} \alpha_i(m_\mathrm{e}) \cdot \alpha_j^*(m_\mathrm{g}) \cdot \mathrm{Clebsch}(I_\mathrm{e}, 2, I_\mathrm{g}, m_\mathrm{e}, m, m_\mathrm{g})$$

For single crystals the relative amplitudes of the absorption lines are then proportional to

$$\mathrm{Amplitude} \propto \vec{\mathrm{E}}^*(\vartheta,\varphi) \cdot \vec{\mathrm{E}}(\vartheta,\varphi)$$

Powder and Mosaic geometries are handled in a way similar to that described in the previous section.

## *27.4.5.* The Goldanskii-Karyagin Effect

The Goldanskii-Karyagin Effect (GKE) is implemented for all the handled (M1, E1, E2, M1+E2) Mössbauer transitions for powder geometry. The Mean Square Displacement (MSD) tensor is assumed to be diagonal in the chosen reference coordinate system (fixed either to the eigensystem of the EFG, see page 52, or to the $\mathbf{B}_{\mathrm{hf}}$ hyperfine magnetic field, see page 51), and furthermore it is assumed to display axial symmetry.

Accordingly, for a given $i \to j$ (excited state level → ground state level) transition, in the case of a powder sample the relative intensity of the absorption lines can be expressed as:

$$\mathrm{Amplitude}_{i\to j} \propto \int_0^{\pi} d\vartheta \cdot \left[ \mathrm{e}^{-k^2 \cdot \left[\langle z^2\rangle_{\mathrm{av}} - \langle x^2\rangle_{\mathrm{av}}\right]\cos^2(\vartheta)} \cdot \sin(\vartheta) \cdot \int_0^{2\pi} \mathbf{E}^*_{i\to j}\mathbf{E}_{i\to j} \cdot d\varphi \right]$$

where $k$ is the absolute value of the wave vector of the radiation, $\langle z^2\rangle_{\mathrm{av}}$ and $\langle x^2\rangle_{\mathrm{av}}$ denote the average of the squared displacement of the Mössbauer nucleus from its equilibrium state in the $\mathbf{e}_z$ and $\mathbf{e}_x$ direction of the reference coordinate system, respectively. As before, $\theta$ and $\varphi$ are the polar and azimuthal angles of the γ-ray direction in the reference coordinate system whose $z$ axis coincides either with the direction of the hyperfine magnetic field $\mathbf{B}_{\mathrm{hf}}$ (model M+Q), or with the $\mathbf{e}_z$ base vector of the eigensystem of the EFG (model Q+M).

In MossWinn $D(z,x)(\mathrm{MSD}) = k^2 \cdot \left[\langle z^2\rangle_{\mathrm{av}} - \langle x^2\rangle_{\mathrm{av}}\right]$ appears as fitting parameter when one of the following models is selected:

1, MIXED M+Q STATIC HAMILTONIAN (POWDER + GKE)
2, MIXED Q+M STATIC HAMILTONIAN (POWDER + GKE)

References:

H.-D. Pfannes, U. Gonser: *Appl. Phys.* **1** (1973) 93.
G.K. Shenoy, J.M. Friedt: *Nuclear Instruments and Methods* **136** (1976) 569.

## *27.4.6.* Randomly oriented EFG ($\eta$ = 0) in uniaxial magnetic field ($^{57}$Fe, powdered sample)

The analytical expression for the line shape of the $^{57}$Fe Mössbauer spectrum of a powdered sample, with randomly oriented EFG and $\eta$ = 0, subjected to a uniaxial (external) magnetic field has been given in

N. Blaes, H. Fischer, U. Gonser: *NIM B* **9** (1985) 201.

This analytical expression is implemented in MossWinn as

$$F(v) = \frac{A}{8\pi} \cdot \mathrm{Re}(N_0(H) + N_0(-H))$$

where ***A*** is the area of the corresponding subspectrum (having the name AMPLITUDE as a fit parameter), and apart from the 8π normalization factor, the remaining quantities are essentially the same as those in Eq. (5) of the above mentioned paper of Blaes *et al.* In the FIT menu of MossWinn the model is described with the following parameters:

| | |
|---|---|
| AMPLITUDE | Area of the subspectrum. |
| ISOMER SHIFT | $^{57}$Fe isomer shift. |
| MAGNETIC FIELD [T] | The amplitude *H* of the uniaxial magnetic field. |
| Vzz (EFG) 10^21 [V/m2] | The main component of the EFG in its eigensystem. |
| ETA (EFG) | Asymmetry parameter of the EFG, fixed to zero. |
| Theta (Gamma ray) | Polar angle of the γ-ray direction relative to the direction of the *H* magnetic field. |
| LINE WIDTH | Internal line width ($\Gamma$). |

To initialize a subspectrum with the above model select RANDOM EFG IN UNIAXIAL EXTERNAL MAGNETIC FIELD (POWDER) in the interaction popup on the MODEL PAGE.

## *27.4.7.* Blume-Tjon two-state magnetic relaxation ($^{57}$Fe, powdered sample)

The $^{57}$Fe Blume-Tjon two state magnetic relaxation model implemented in the MossWinn program describes the physical model for a powdered sample that contains $^{57}$Fe nuclei experiencing fluctuating hyperfine magnetic field. The theoretical background and calculation of this model can be found in:

M. Blume, J.A. Tjon: *Phys. Rev.* **165** (1968) 446.

It is assumed that the $^{57}$Fe nucleus experiences a magnetic field that relaxes between two values: $H_1 = -h$ and $H_2 = +h$ . That is, the magnetic field can either point „upwards" ($+h$) or „downwards" ($-h$). The direction of the magnetic field is assumed to be along one of the principal axes of the EFG. The relaxation between the two states $+h$ and $-h$ is described by the two transition rates $W_1 = 2\pi f_1$ and $W_2 = 2\pi f_2$, expressed as angular frequencies associated with the corresponding $f_1$ and $f_2$ transition frequencies.

MossWinn fits the following model:

$$W(p(v)) \propto \mathrm{Re} \sum_{m_0,m_1} \frac{1}{4} \left| \langle I_0 m_0 \left| \mathrm{H} \right| I_1 m_1 \rangle \right|^2 \cdot \sum_{i,j} p_i \cdot \langle j \left| \left[ A^{-1}(p) + 3Q^2\eta^2 B(p) \right]^{-1} \right| i \rangle$$

Without giving a detailed explanation of the above expression, we simply note that this function is essentially identical with expression (B1) of APPENDIX B in the above-mentioned paper of Blume and Tjon. The model makes it possible to describe relaxation effects in the presence of nonzero electric field gradient and an arbitrary asymmetry parameter $\eta$. It contains eight parameters.

| | |
|---|---|
| AMPLITUDE | Area of the subspectrum |
| ISOMER SHIFT | $^{57}$Fe isomer shift |
| MAGNETIC FIELD [T] | The amplitude $h$ of the relaxing magnetic field. |
| VZZ (EFG) [10^21 V/m2] | The component of the EFG in the direction of the hyperfine magnetic field $+h$. |
| ETA (EFG) | Asymmetry parameter of the EFG. |
| JUMP UP RATE | $\log_{10} W_2$ |
| JUMP DOWN RATE | $\log_{10} W_1$ |
| LINE WIDTH | Internal line width ($\Gamma$) |

The quantities $\log_{10} W_1$ and $\log_{10} W_2$ are called *Jump down rate* and *Jump up rate* in MossWinn, respectively. The total relaxation frequency of the process is given by $f_{\mathrm{total}} = f_1 + f_2$, whereas the corresponding characteristic relaxation time is given by $\boldsymbol{\tau_r = 2\pi/(W_1+W_2)} = 1/(f_1+f_2) = 1/f_{\mathrm{total}}$.

Note that some relaxation time values given in the literature (see, e.g., Blume 1965 and Wickman 1966) are apparently in accordance with a relaxation time calculated as $\tau = 1/(W_1+W_2)$, whereas other works (see, e.g., Stoian *et al.* 2005) quote relaxation time as $\tau_r = 1/(f_1+f_2)$.

The *Jump up rate* and *Jump down rate* values are forced to be equal by default. In this case $W_1 = W_2 = W$, and the $\tau_r$ relaxation time is given by $\tau_r = 1/f_{\mathrm{total}} = \pi/W$.

Similarly to other Hamiltonian models, area fitting mode is the default mode when fitting Blume-Tjon magnetic relaxation model, independent of the setting of the AREA/AMPLITUDE mode. Consequently, the Amplitude parameter denotes the area of the corresponding subspectrum.

M. Blume: *Phys. Rev. Lett.* **14** (1965) 96.

H.H. Wickman (1966): Mossbauer Paramagnetic Hyperfine Structure, In: MÖSSBAUER EFFECT METHODOLOGY (ed. I.J. Gruverman), Vol. 2, p. 39. (See Figure 6 on page 55.) The same figure is reprinted in: S. Mørup, J.A. Dumesic, H. Topsøe (1980) Magnetic Microcrystals, In: APPLICATIONS OF MÖSSBAUER SPECTROSCOPY (ed. R.L. Cohen), Vol. 2, p. 1. (See Figure 4 on page 18.)

S.A. Stoian, Y. Yu, J.M. Smith, P.L. Holland, E.L. Bominaar, E. Münck: *Inorganic Chemistry* **44** (2005) 4915.

## *27.4.8.* Tjon-Blume Jahn-Teller quadrupole relaxation ($^{57}$Fe, powdered sample)

The $^{57}$Fe Tjon-Blume Jahn-Teller quadrupole relaxation model implemented in the MossWinn program describes the physical model for a powdered sample that contains $^{57}$Fe nuclei experiencing an electric field gradient whose main component ($V_{zz}$), although fixed in magnitude, reorients dynamically and randomly between the $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ directions of the eigensystem of the EFG tensor. All the three directions are assumed to be equally probable. The asymmetry parameter, $\eta$, and the hyperfine magnetic field, $H$, are both assumed to be equal to zero. The "Jahn-Teller" effect enters the name of the model because the assumptions of the model are expected to get realized in the presence of a dynamic Jahn-Teller effect. The theoretical background and calculation of this model can be found in:

J.A. Tjon, M. Blume: *Phys. Rev.* **165** (1968) 456.

MossWinn fits the following absorption shape:

$$W(p(v)) \propto \mathrm{Re} \sum_{m_0,m_1} \frac{1}{4} \left| \left\langle I_0 m_0 \left| \mathrm{H}^{(+)} \right| I_1 m_1 \right\rangle \right|^2 \cdot \sum_{i,j} p_i \cdot \left\langle j \left| A(p) \cdot \left[ 1 + 3\alpha^2 B(p) A(p) \right]^{-1} \right| i \right\rangle$$

Without giving a detailed explanation of the above expression, we simply note that this function is essentially identical with equation (15) of the above-mentioned paper of Tjon and Blume. (MossWinn evaluates the above expression by utilizing equation (16) of the same paper.)

The model is described with five parameters.

| | |
|---|---|
| AMPLITUDE | Area of the subspectrum |
| ISOMER SHIFT | $^{57}$Fe isomer shift |
| VZZ (EFG) [10^21 V/m2] | The main component of the EFG. |
| JUMP RATE | $\log_{10}W$ , logarithm of the **angular relaxation frequency**, $W = 2\pi f$, where $f$ is the transition frequency between the different states. |
| LINE WIDTH | Internal line width ($\Gamma$) |

Similarly to other Hamiltonian models, AREA fitting mode is the default mode when fitting Tjon-Blume Jahn-Teller relaxation model, independent of the setting of the AREA/AMPLITUDE mode. Consequently, the Amplitude parameter denotes the area of the corresponding subspectrum.

## *27.4.9.* Electron hopping relaxation ($^{57}$Fe, paramagnetic powdered sample)

The theory is implemented for $^{57}$Fe in paramagnetic substances where electron hopping occurs either between iron ions of different oxidation states (e.g. $Fe^{2+} \leftrightarrow Fe^{3+}$) or between iron ions and the rest of the system. It can account for situations encountered, e.g., in the papers

- F.J. Litterst, G. Amthauer: *Phys. Chem. Minerals* **10** (1984) 250.
- R.H. Herber, H. Eckert: *Phys. Rev. B* **31** (1985) 34.

The actual implementation is based on the theory and formalism put forward by M. Blume in M. Blume: *Phys. Rev.* **174** (1968) 351. It is assumed that in the studied sample $^{57}$Fe nuclei can experience the following two different forms of the Hamiltonian:

$$H_1 = \frac{\Delta_1}{6}(3m^2 - I(I+1)) + \delta_1 I$$

,

$$H_2 = \frac{\Delta_2}{6}(3m^2 - I(I+1)) + \delta_2 I$$

where both $H_1$ and $H_2$ result in a quadrupole split doublet, respectively with isomer shifts of $\delta_1$ and $\delta_2$, and quadrupole splittings of $\Delta_1$ and $\Delta_2$. $I$ and $m$ denote, as usual, the nuclear spin quantum number and the magnetic quantum number ($m = I_z$) of the nuclear state, respectively. The first term in the Hamiltonians accounts for the nuclear quadrupole interaction, whereas the second term ($\delta_1 I$ and $\delta_2 I$) accounts (formally) for the isomer shift.

It is assumed, furthermore, that the Hamiltonian sensed by a given $^{57}$Fe nucleus alternates/relaxes between $H_1$ and $H_2$ with a relaxation rate of $\omega$ [rad/s]. The probability $p$ of finding iron nuclei being subject to $H_1$ is allowed to differ from that of finding them being subject to $H_2$, i.e. $p$ is allowed to take on any value in the range of [0..1]. The transition rates $W_{1\to2}$ and $W_{2\to1}$ (probabilities of transition per unit time, being the elements of the stochastic matrix **W** in Blume's theory) are calculated as

$$W_{2\to1} = p\omega$$
$$W_{1\to2} = (1-p)\omega$$

such that detailed balance between the states '1' and '2', i.e. $pW_{1\to2} = (1-p)W_{2\to1}$, is satisfied.

The implemented model assumes, by default, that states '1' and '2' correspond to high-spin $Fe^{3+}$ and high-spin $Fe^{2+}$, respectively. It is described with 8 parameters as follows.

| | |
|---|---|
| AMPLITUDE | Area of the subspectrum. |
| ISOMER SHIFT (Fe3+) | $^{57}$Fe isomer shift characterizing the state $Fe^{3+}$ ($\delta_1$). |
| ISOMER SHIFT (Fe2+) | $^{57}$Fe isomer shift characterizing the state $Fe^{2+}$ ($\delta_2$). |
| Q. SPLITTING (Fe3+) | Quadrupole splitting characterizing the state $Fe^{3+}$ ($\Delta_1$). |
| Q. SPLITTING (Fe2+) | Quadrupole splitting characterizing the state $Fe^{2+}$ ($\Delta_2$). |
| Fe3+ RATIO | The probability $p$ of finding iron in the state of $Fe^{3+}$ (corresponding to state '1'). |
| RELAXATION RATE [Mrad/s] | The relaxation rate $\omega$ measured in $10^6$ rad/s. |
| LINE WIDTH | Common line width characterizing states '1' and '2'. |

The boundaries set by default for the isomer shift parameters are meant relative to α-Fe at room temperature. If the fitted spectrum has a different velocity scale, then these boundaries may need to be altered.

Note that in the frame of this model the spectral shape also depends on the sign of $\Delta_1/\Delta_2$, and therefore the quadrupole splitting parameters are by default allowed to take on negative values as well.

## *27.4.10.* Electron hopping relaxation ($^{57}$Fe, magnetic powdered sample)

The theory is implemented for $^{57}$Fe in magnetic substances where electron hopping occurs either between iron ions of different oxidation states (e.g. $Fe^{2+} \leftrightarrow Fe^{3+}$) or between iron ions and the rest of the system. It can account for situations encountered, e.g., in the paper

- K. Ando, J. Nishihara: *J. Phys. Chem. Solids* **41** (1980) 1273.

The actual implementation is based on the theory and formalism put forward by M. Blume in M. Blume: *Phys. Rev.* **174** (1968) 351. It is assumed that in the studied sample $^{57}$Fe nuclei can experience the following two different forms of the Hamiltonian:

$$H_1 = -g_I \mu_N m B_1 + \frac{\Delta_1}{6}(3m^2 - I(I+1)) + \delta_1 I$$

,

$$H_2 = -g_I \mu_N m B_2 + \frac{\Delta_2}{6}(3m^2 - I(I+1)) + \delta_2 I$$

where both $H_1$ and $H_2$ can describe a sextet respectively with isomer shifts of $\delta_1$ and $\delta_2$, hyperfine magnetic fields of $B_1$ and $B_2$ and apparent quadrupole splittings of $\Delta_1$ and $\Delta_2$. $I$ and $m$ denote, as usual, the nuclear spin quantum number and the magnetic quantum number ($m = I_z$) of the nuclear state, respectively, $g_I$ is the nuclear gyromagnetic factor of the $^{57}$Fe nucleus in the state characterized with nuclear spin quantum number $I$, and $\mu_N$ denotes the nuclear magneton (see page 145). The last terms ($\delta_1 I$ and $\delta_2 I$) account (formally) for the isomer shift. Note that compared to the general Hamiltonian (see page 51), $H_1$ and $H_2$ correspond to the case when $\eta = 0$ and $\beta = 0$.

It is assumed, furthermore, that the Hamiltonian sensed by a given $^{57}$Fe nucleus alternates/relaxes between $H_1$ and $H_2$ with a relaxation rate of $\omega$ [rad/s]. The probability $p$ of finding iron nuclei being subject to $H_1$ is allowed to differ from that of finding them being subject to $H_2$, i.e. $p$ is allowed to take on any value in the range of [0..1]. The transition rates $W_{1\to2}$ and $W_{2\to1}$ (probabilities of transition per unit time, being the elements of the stochastic matrix **W** in Blume's theory) are calculated as

$$W_{2\to1} = p\omega$$
$$W_{1\to2} = (1-p)\omega$$

such that detailed balance between the states '1' and '2', i.e. $pW_{1\to2} = (1-p)W_{2\to1}$, is satisfied.

The implemented model assumes, by default, that states '1' and '2' correspond to high-spin $Fe^{3+}$ and high-spin $Fe^{2+}$, respectively. It is described with 10 parameters as follows.

| | |
|---|---|
| AMPLITUDE | Area of the subspectrum. |
| ISOMER SHIFT (Fe3+) | $^{57}$Fe isomer shift characterizing the state $Fe^{3+}$ ($\delta_1$). |
| ISOMER SHIFT (Fe2+) | $^{57}$Fe isomer shift characterizing the state $Fe^{2+}$ ($\delta_2$). |
| MAGNETIC FIELD (Fe3+) [T] | Hyperfine magnetic field characterizing the state $Fe^{3+}$ ($B_1$). |
| MAGNETIC FIELD (Fe2+) [T] | Hyperfine magnetic field characterizing the state $Fe^{2+}$ ($B_2$). |
| Q. SPLITTING (Fe3+) | Quadrupole splitting characterizing the state $Fe^{3+}$ ($\Delta_1$). |
| Q. SPLITTING (Fe2+) | Quadrupole splitting characterizing the state $Fe^{2+}$ ($\Delta_2$). |
| Fe3+ RATIO | The probability $p$ of finding iron in the state of $Fe^{3+}$ (corresponding to state '1'). |
| RELAXATION RATE [Mrad/s] | The relaxation rate $\omega$ measured in $10^6$ rad/s. |
| LINE WIDTH | Common line width characterizing states '1' and '2'. |

Note that the relation between the relaxation rate $\omega$ as used in MossWinn and the $\Omega$ electron transfer rate given by Ando & Nishihara in the above paper is $\Omega = p\omega / (2\pi)$.

## *27.4.11.* Pure quadrupole splitting ($^{151}$Eu, powdered sample)

This routine was originally implemented in MossWinn 2.0 . In order to preserve compatibility with earlier versions, it appears in MossWinn 4.0 in an unchanged form.

A quadrupole split spectrum of $^{151}$Eu in general consists of 12 Lorentzian lines (8 when $\eta$ = 0) according to the 7/2 $\rightarrow$ 5/2 nuclear transition. MossWinn displays only the envelope of the 12 absorption lines on the screen. Zero hyperfine magnetic field and randomly oriented powdered sample is assumed in the calculations. The model is described with five parameters:

| | |
|---|---|
| AMPLITUDE | Denotes the whole area of the subspectrum. |
| ISOMER SHIFT | $^{151}$Eu isomer shift |
| Vzz [10^21 V/m2] | $V_{zz}$ denotes the element with the highest absolute value in the diagonal form of the EFG (Electric Field Gradient) tensor. The $V_{zz}$ parameter has the unit: $10^{21}$ [V/m$^2$]. |
| ETA [0..1] | ETA denotes the asymmetry parameter ($\eta$) of the EFG: $$ETA = \frac{V_{xx} - V_{yy}}{V_{zz}} \qquad (0 \le ETA \le 1)$$ $V_{xx}$,$V_{yy}$ and $V_{zz}$ being the diagonal elements of the EFG tensor, defined as usual. |
| LINE WIDTH | Line width of the absorption lines building up the quadrupole split absorption pattern of $^{151}$Eu. Each of the 12 lines has the same line width. |

In this routine MossWinn solves the Hamiltonian of the $^{151}$Eu nucleus as described in the paper:

J. Lindén, J. Hietaniemi, E. Ikonen, M. Lippmaa, I. Tittonen, T. Katila, T. Karlemo, M. Karppinen, L. Niinistö, K. Ullakko: *Phys. Rev. B* **46** (1992) 8534.

## *27.5. Distributions with parameterized profile*

Distributions with parameterized profile have a shape that is fully determined by its parameters, independent from the actual measurement data to which they are fitted. Distributions of this type available in MossWinn are described in the followings. Among these, the cumulative distribution curves (probability density functions) of VBF and xVBF distributions can be visualized on the insight pages (see section 27.14 on page 97) in the FIT menu.

Note that MossWinn allows fitting arbitrary-profile distributions in position type parameters of distribution subspectra with parameterized profile. This is, however, best avoided, unless the physical nature of the studied material unambiguously calls for the application of such a fit model. Also note that VBF and xVBF subspectra with a parameter being subject to an arbitrary-profile distribution are not included in the cumulative VBF/xVBF distribution plots that can be displayed on the insight pages.

Note that VBF and xVBF distribution curves are presented by MossWinn via discrete data point samples of the underlying continuous probability density functions whose integral area is 1. This is in contrast with the arbitrary profile distributions derived via the method of Hesse and Rübartsch (see page 107), which latter are discrete probability distribution functions.

Note that VBF and xVBF models require at least the SELECT version of MossWinn.

### *27.5.1.* Gaussian QS and IS distribution (VBF, PM, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered paramagnetic sample with possible texture. It consists of a quadrupole doublet component with a possible Gaussian distribution in the corresponding quadrupole splitting (QS) and isomer shift (IS) parameters, with a linear correlation between the QS and IS values. The model and implementation is based on the Voigt-based fitting (VBF) method described in

- D.G. Rancourt, J.Y. Ping: *Nuclear Instruments and Methods* B **58** (1991) 85.

The model is calculated according to Eq. (12) of the above paper, by setting $N = 1$ and $p_i = 1.0$ (single Gaussian describes the distribution of the quadrupole splitting values). The model parameters are given in the next table where in the last column associated quantities are also given with notations from the above reference (in the present case, index $i$ can take the value 1 only, and is thus skipped for clarity).

| **Parameter name** | **Meaning** | **Associated quantity in the above paper** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $\frac{\gamma\pi}{2}(h_+ + h_-)$ |
| A+/A- | Relative area of the peak centered at IS + QS/2 with respect to that centered at IS – QS/2. The parameter can be used to account for a textured sample. It is fixed to 1.0 by default (suitable for a powder without texture). | $h_+/h_-$ |
| ISOMER SHIFT | Isomer shift (if coupling is zero), or center of the Gaussian isomer shift distribution profile. | $\delta_0+\delta_1\Delta_0$ |
| Q. SPLITTING | Center of the Gaussian quadrupole splitting distribution profile. | $\Delta_0$ |
| SIGMA (QS) | Standard deviation of the Gaussian quadrupole splitting distribution profile. | $\sigma_\Delta$ |
| COUPLING (IS,QS) | Linear coupling coefficient ($\delta_1$) between the distributed isomer shift ($\delta$) and quadrupole splitting ($\Delta$) values: $\delta = \delta_0+\delta_1\Delta$ | $\delta_1$ |
| LORENTZIAN LINE WIDTH | Full width at half maximum (FWHM) of the Lorentzian peaks that are broadened by the coupled Gaussian distributions in the isomer shift and quadrupole splitting parameters. Equals to the FWHM width of the peaks when SIGMA (QS) is set to zero. | $\gamma$ |

In order to extend the quadrupole splitting distribution with further Gaussians (corresponding to $N > 1$), simply add more subspectra of this type to the fit model, and define constraints among the distributions as required (such as for example constraining the coupling parameter to be the same for all such distribution subspectra).

Note concerning QS distributions where negative QS values have appreciable probability, that MossWinn does not fold back the part of distribution curve belonging to negative QS values onto the corresponding positive QS distribution part. Also note that a change in the sign of QS results in the exchange of the position of the two peaks.

## *27.5.2.* Gaussian MF, QS and IS distribution (VBF, M, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered magnetic sample with possible texture. It consists of a sextet component with a possible Gaussian distribution in the corresponding (hyperfine) magnetic field (MF), quadrupole splitting (QS) and isomer shift (IS) parameters, with a linear correlation between the MF, IS and QS values. Quadrupole interaction is taken into account in the first-order perturbation limit. The model and implementation is based on the Voigt-based fitting (VBF) method described in

- D.G. Rancourt, J.Y. Ping: *Nuclear Instruments and Methods* B **58** (1991) 85.

The model is calculated according to Eq. (18) of the above paper, by setting $N = 1$ and $p_i = 1.0$ (single Gaussian describes the distribution of the hyperfine magnetic field values). The model parameters are given in the next table where in the last column associated quantities are also given with notations from the above reference (in the present case, index $i$ can take the value 1 only, and is thus skipped for clarity, $c$ denotes the speed of light in vacuum, and $E_\gamma$ is the energy of the Mössbauer transition).

| **Parameter name** | **Meaning** | **Associated quantity in the above paper** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $\frac{\gamma\pi}{2}\sum_{k=1}^{6} h_k$ |
| A25/A34 | Relative area of the 2nd and 5th peaks with respect to that of the 3rd and 4th peaks of the sextet component. The parameter can be used to account for magnetic texture. It is fixed to 2.0 by default (suitable for a powder without texture). Note that $A_{16}/A_{34}$ is fixed to 3.0 in MossWinn. In order to account for thickness effects, turn to transmission integral fitting (see section 27.8). | $\alpha$ |
| ISOMER SHIFT | Isomer shift (if coupling is zero), or center of the Gaussian isomer shift distribution profile. Equals to $\delta_0+m_\delta \cdot B_{\mathrm{hf},0}$. | $\delta_0+\delta_1 z_0$ |
| MAGNETIC FIELD [T] | Center of the Gaussian hyperfine magnetic field distribution profile ($B_{\mathrm{hf},0}$). | $\frac{z_0}{\lvert g^* \rvert \mu_\mathrm{N}} \cdot \left[\frac{E_\gamma}{c}\right]$ |
| Q. SPLITTING | Quadrupole splitting (if coupling is zero), or center of the Gaussian quadrupole splitting distribution profile. Note that quadrupole splitting is taken here to be equal to 2ε where ε denotes the first order quadrupole shift. Equals to $\Delta_0+m_\Delta \cdot B_{\mathrm{hf},0}$. | $2(\varepsilon_0+\varepsilon_1 z_0)$ |
| SIGMA (MF) | Standard deviation of the Gaussian hyperfine magnetic field distribution profile. | $\frac{\sigma_z}{\lvert g^* \rvert \mu_\mathrm{N}} \cdot \left[\frac{E_\gamma}{c}\right]$ |
| COUPLING (IS,MF) | Linear coupling coefficient ($m_\delta$) between the distributed isomer shift (δ) and hyperfine magnetic field ($B_\mathrm{hf}$) values: $\delta = \delta_0+m_\delta \cdot B_\mathrm{hf}$ | $\delta_1 \lvert g^* \rvert \mu_\mathrm{N} \cdot \left[\frac{c}{E_\gamma}\right]$ |
| COUPLING (QS,MF) | Linear coupling coefficient ($m_\Delta$) between the distributed quadrupole splitting (Δ) and hyperfine magnetic field ($B_\mathrm{hf}$) values: $\Delta = \Delta_0+m_\Delta \cdot B_\mathrm{hf}$ | $2\varepsilon_1 \lvert g^* \rvert \mu_\mathrm{N} \cdot \left[\frac{c}{E_\gamma}\right]$ |
| LORENTZIAN LINE WIDTH | Full width at half maximum (FWHM) of the Lorentzian peaks that are broadened by the coupled Gaussian distributions in the magnetic field, isomer shift, and quadrupole splitting parameters. Equals to the FWHM width of the peaks when SIGMA (MF) is set to zero. | $\gamma$ |

In order to extend the hyperfine magnetic field distribution with further Gaussians (corresponding to $N > 1$), simply add more subspectra of this type to the fit model, and define constraints among the distributions as required (such as for example constraining the coupling parameters to be the same for all such distribution subspectra).

Note that $E_\gamma / (|g^*|\mu_\mathrm{N} c) \approx 14.768$ T/(mm s$^{-1}$) for the case of $^{57}$Fe.

### *27.5.3.* Gaussian QS and IS distribution (xVBF, PM, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered paramagnetic sample with possible texture. It consists of a quadrupole doublet component with a possible Gaussian distribution in the corresponding quadrupole splitting (QS) and isomer shift (IS) parameters, with an arbitrary degree of correlation between the QS and IS values. The model and implementation is based on the extended Voigt-based fitting (xVBF) method described in

- K. Lagarec, D.G. Rancourt: *Nuclear Instruments and Methods* B **129** (1997) 266.

The model is calculated according to Eq. (11) of the above paper, by setting $n_\delta = 1$, $n_\Delta = 1$, $p_\delta = 1.0$ and $p_\Delta = 1.0$ (single Gaussian describes the distribution of the isomer shift and the quadrupole splitting values). The model parameters are given in the next table where in the last column associated quantities are also given with notations from the above reference (in the present case *i* and *j* indexes can take the value 1 only, and are therefore skipped for clarity).

| **Parameter name** | **Meaning** | **Associated quantity in the above paper** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $A_1+A_2$ |
| A+/A- | Relative area of the peak centered at IS + QS/2 with respect to that centered at IS – QS/2. The parameter can be used to account for a textured sample. It is fixed to 1.0 by default (suitable for a powder without texture). | $A_2/A_1$ |
| ISOMER SHIFT | Center of the Gaussian isomer shift distribution profile. | $\delta_0$ |
| Q. SPLITTING | Center of the Gaussian quadrupole splitting distribution profile. | $\Delta_0$ |
| SIGMA (IS) | Standard deviation of the Gaussian isomer shift distribution profile. | $\sigma_\delta$ |
| SIGMA (QS) | Standard deviation of the Gaussian quadrupole splitting distribution profile. | $\sigma_\Delta$ |
| CORRELATION (IS,QS) | Correlation between the isomer shift and quadrupole splitting values. It can take on values from the range −1…+1, the lower and upper limiting values being equivalent to (deterministic) linear correlation. | $\rho$ |
| LORENTZIAN LINE WIDTH | Full width at half maximum (FWHM) of the Lorentzian peaks that are broadened by the Gaussian distributions in the isomer shift and quadrupole splitting parameters. Equals to the FWHM width of the peaks when SIGMA (IS) and SIGMA (QS) are both set to zero. | $2\gamma$ |

In order to extend the isomer shift and/or quadrupole splitting distribution with further Gaussians (corresponding to $n_\delta > 1$ and $n_\Delta > 1$, respectively), simply add more subspectra of this type to the fit model, and define constraints among the distributions as required (such as for example constraining the correlation parameter to be the same for all such distribution subspectra). As an example, check out the corresponding MossWinn video tutorial (at http://www.mosswinn.com/english/videotutorials.htm) that shows how to set up the xVBF model associated with Figure 3 and Table 1 of the above reference.

Note concerning QS distributions where negative QS values have appreciable probability, that MossWinn does not fold back the part of distribution curve belonging to negative QS values onto the corresponding positive QS distribution part. Also note that a change in the sign of QS results in the exchange of the position of the two peaks.

## *27.5.4.* Gaussian MF, QS and IS distribution (xVBF, M, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered magnetic sample with possible texture. It consists of a sextet component with a possible Gaussian distribution in the corresponding (hyperfine) magnetic field (MF), quadrupole splitting (QS) and isomer shift (IS) parameters, with an arbitrary degree of correlation between the MF, QS and IS values. Quadrupole interaction is taken into account in the first-order perturbation limit. The model and implementation is based on the extended Voigt-based fitting (xVBF) method described in

- K. Lagarec, D.G. Rancourt: *Nuclear Instruments and Methods* B **129** (1997) 266.

The model is calculated according to Eq. (19) in the above paper, by setting $n_\delta = 1$, $n_\varepsilon = 1$, $n_z = 1$, $p_\delta = 1.0$, $p_\varepsilon = 1.0$ and $p_z = 1.0$ (single Gaussian describes the distribution of the isomer shift, the quadrupole splitting and the hyperfine magnetic field). The model parameters are given in the next table where in the last column associated quantities are also given with notations from the above reference (in the present case *i*, *j* and *k* indexes can only take the value 1 and are therefore skipped for clarity, *c* denotes the speed of light in vacuum, and $E_\gamma$ is the energy of the Mössbauer transition).

| **Parameter name** | **Meaning** | **Associated quantity in the above paper** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $\sum_{l=1}^{6} A_l$ |
| A25/A34 | Relative area of the 2nd and 5th peaks with respect to that of the 3rd and 4th peaks of the sextet component. The parameter can be used to account for magnetic texture. It is fixed to 2.0 by default (suitable for a powder without texture). Note that $A_{16}/A_{34}$ is fixed to 3.0 in MossWinn. In order to account for thickness effects, turn to transmission integral fitting (see section 27.8). | $A_2/A_3$ |
| ISOMER SHIFT | Center of the Gaussian isomer shift distribution profile. | $\delta_0$ |
| MAGNETIC FIELD [T] | Center of the Gaussian magnetic field distribution profile. | $\frac{z_0}{\lvert g^* \rvert \mu_N} \cdot \left[ \frac{E_\gamma}{c} \right]$ |
| Q. SPLITTING | Center of the Gaussian quadrupole splitting distribution profile. | $2\varepsilon_0$ |
| SIGMA (IS) | Standard deviation of the Gaussian isomer shift distribution profile. | $\sigma_\delta$ |
| SIGMA (MF) | Standard deviation of the Gaussian magnetic field distribution profile. | $\frac{\sigma_z}{\lvert g^* \rvert \mu_N} \cdot \left[ \frac{E_\gamma}{c} \right]$ |
| SIGMA (QS) | Standard deviation of the Gaussian quadrupole splitting distribution profile. | $2\sigma_\varepsilon$ |
| CORRELATION (IS,MF) | Correlation between the isomer shift and magnetic field values. It can take on values from the range −1…+1, the lower and upper limiting values being equivalent to (deterministic) linear correlation. | $\rho_{\delta z}$ |
| CORRELATION (QS,MF) | Correlation between the quadrupole splitting and magnetic field values. It can take on values from the range −1…+1, the lower and upper limiting values being equivalent to (deterministic) linear correlation. | $\rho_{\varepsilon z}$ |
| CORRELATION (IS,QS) | Correlation between the isomer shift and quadrupole splitting values. It can take on values from the range −1…+1, the lower and upper limiting values being equivalent to (deterministic) linear correlation. | $\rho_{\delta\varepsilon}$ |
| LORENTZIAN LINE WIDTH | Full width at half maximum (FWHM) of the Lorentzian peaks that are broadened by the Gaussian distributions in the isomer shift, magnetic field and quadrupole splitting parameters. Equals to the FWHM width of the peaks when SIGMA (IS), SIGMA (MF) and SIGMA (QS) are all set to zero. | $2\gamma$ |

Note that $E_\gamma / (|g^*|\mu_N c) \approx 14.768$ T/(mm s$^{-1}$) for the case of $^{57}$Fe.

In order to extend the isomer shift, magnetic field and quadrupole splitting distribution with further Gaussians (corresponding to $n_\delta > 1$, $n_z > 1$ and $n_\varepsilon > 1$, respectively), simply add more subspectra of this type to the fit model, and define constraints among the distributions as required (such as for example constraining the corresponding correlation parameters to be the same for all such distribution subspectra).

Note that in accordance with the above reference, validity of this model requires that the quantity $\rho_0 = \rho_{\delta\varepsilon}^2 + \rho_{\delta z}^2 + \rho_{\varepsilon z}^2 - 2\rho_{\delta\varepsilon}\rho_{\delta z}\rho_{\varepsilon z}$ does not exceed 1.0, and therefore not all combinations of $\rho_{\delta z}$, $\rho_{\varepsilon z}$ and $\rho_{\delta\varepsilon}$ represent a valid solution. For invalid combinations MossWinn calculates the subspectrum as if its area was set to zero. Note that setting two of the correlation parameters to zero will always result in a valid solution (as long as the third one is valid, i.e. it lies in the range of [−1,+1]).

## *27.5.5.* Binomial distribution (1 shell, M, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered magnetic sample with possible texture. It consists of several sextet components (with the quadrupole interaction being taken into account in the first-order perturbation limit) whose relative weights and hyperfine parameters are determined by assuming that the isomer shift ($\delta$), hyperfine magnetic field ($B_{\mathrm{hf}}$) and quadrupole splitting ($QS$, here treated as to be equal to 2ε where ε is the first order quadrupole shift) parameters characterizing a given Mössbauer nuclide depend on the number of randomly distributed substituent atoms in its 1$^{st}$ shell of atomic neighborhood. It is assumed that all substituent atoms in the 1$^{st}$ shell change the $\delta$, $B_{\mathrm{hf}}$ and $QS$ Mössbauer parameters by equal amounts of $\Delta\delta$, $\Delta B_{\mathrm{hf}}$ and $\Delta QS$, respectively. Assuming that the atomic concentration of the substituent atoms is $c$, and that their number in the 1$^{st}$ shell can take on values from the range of 0…$n$, the spectrum is calculated as the sum of $n$+1 sextet components with weights chosen according to the corresponding binomial distribution:

$$A \cdot \sum_{i=0}^{n} \binom{n}{i} c^i (1-c)^{n-i} \cdot \mathrm{S}(\delta_0 + i \cdot \Delta\delta, QS_0 + i \cdot \Delta QS, B_{\mathrm{hf},0} + i \cdot \Delta B_{\mathrm{hf}})$$

where $A$ denotes the total area of the subspectrum, $i$ denotes the number of substituent atoms in the 1$^{st}$ shell of atomic neighborhood of the Mössbauer nuclide, and $S(\delta_0 + i \cdot \Delta\delta, QS_0 + i \cdot \Delta QS, B_{\mathrm{hf},0} + i \cdot \Delta B_{\mathrm{hf}})$ denotes a sextet with unit area and with Mössbauer parameters of $\delta = \delta_0 + i \cdot \Delta\delta$, $QS = QS_0 + i \cdot \Delta QS$ and $B_{\mathrm{hf}} = \mathrm{MAX}(B_{\mathrm{hf},0} + i \cdot \Delta B_{\mathrm{hf}}, 0)$, where the latter notation means that negative $B_{\mathrm{hf}}$ values are treated as zero.

The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above expression.

| **Parameter name** | **Meaning** | **Associated quantity in the above expression** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $A$ |
| A25/A34 | Relative area of the 2$^{nd}$ and 5$^{th}$ peaks with respect to that of the 3$^{rd}$ and 4$^{th}$ peaks of the sextet component. The parameter can be used to account for magnetic texture. It is fixed to 2.0 by default (suitable for a powder without texture). Note that $A_{16}/A_{34}$ is fixed to 3.0. In order to account for thickness effects, turn to transmission integral fitting (see section 27.8). | |
| ISOMER SHIFT | Isomer shift characterizing Mössbauer nuclides without substituent atoms in their 1$^{st}$ shell of atomic neighbors. Equals to the isomer shift when the value of the CONCENTRATION parameter is zero. | $\delta_0$ |
| MAGNETIC FIELD [T] | Hyperfine magnetic field characterizing Mössbauer nuclides without substituent atoms in their 1$^{st}$ shell of atomic neighbors. Equals to the hyperfine magnetic field when the value of the CONCENTRATION parameter is zero. | $B_{\mathrm{hf},0}$ |
| Q. SPLITTING | Quadrupole splitting (here taken to be equal to 2ε where ε denotes the first order quadrupole shift) characterizing Mössbauer nuclides without substituent atoms in their 1$^{st}$ shell of atomic neighbors. Equals to the quadrupole splitting when the value of the CONCENTRATION parameter is zero. | $QS_0$ |
| DELTA IS (nn) | Change in the isomer shift due to one additional substituent atom in the 1$^{st}$ shell of atomic neighbors of a Mössbauer nuclide. | $\Delta\delta$ |
| DELTA MF (nn) | Change in the hyperfine magnetic field due to one additional substituent atom in the 1$^{st}$ shell of atomic neighbors of a Mössbauer nuclide. | $\Delta B_{\mathrm{hf}}$ |
| DELTA QS (nn) | Change in the quadrupole splitting (2ε) due to one additional substituent atom in the 1$^{st}$ shell of atomic neighbors of a Mössbauer nuclide. | $\Delta QS$ |
| NEIGHBORS (nn) | Number of atomic positions contributing to (and the maximum number of substituent atoms in) the 1$^{st}$ shell of atomic neighbors of a Mössbauer nuclide. The value can be any integer in the range of 1…14. | $n$ |
| CONCENTRATION | Atomic concentration of substituent atoms. | $c$ |
| LINE WIDTH | FWHM width of the Lorentzian peaks of the individual sextet components (each being associated with a certain number of substituent atoms in the 1$^{st}$ shell of atomic neighbors of Mössbauer nuclides). Note that when Pseudo-Voigt peak shape is selected for the subspectrum, the "LINE WIDTH" parameter refers to the FWHM width of the *Gaussian* component of the (Pseudo-) Voigt peaks used in this case as the profile of individual lines of the sextets. | |

The possible number of atoms in the 1st shell of atomic neighborhood of a Mössbauer nuclide depends on the physical model under consideration. For example, in the bcc lattice of a disordered $Fe_{1-c}X_c$ alloy one could assume (as a first approximation) that the maximum 8 nearest-neighbor (nn) and the maximum 6 next-nearest-neighbor (nnn) X atoms surrounding a $^{57}$Fe nuclide each change the hyperfine parameters characteristic to the latter with roughly equal amounts, whereas the effect of X atoms being further away can be neglected in comparison. Then, under such assumptions, one could take nn and nnn lattice sites both contributing to the 1st shell of atomic neighborhood that in this case would include altogether $n = 14$ atoms.

Note that beside the number of substituent atoms, their configuration around the Mössbauer nuclide may also be of importance, which effect is not taken into account in the present model.

## *27.5.6.* Binomial distribution (2 shells, M, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered magnetic sample with possible texture. It consists of several sextet components (with the quadrupole interaction being taken into account in the first-order perturbation limit) whose relative weights and hyperfine parameters are determined by assuming that the isomer shift ($\delta$), hyperfine magnetic field ($B_{\mathrm{hf}}$) and quadrupole splitting ($QS$, here treated as to be equal to $2\varepsilon$ where $\varepsilon$ is the first order quadrupole shift) parameters characterizing a given Mössbauer nuclide depend on the number of randomly distributed substituent atoms in its 1st and 2nd shell of atomic neighborhood. It is assumed that substituent atoms in the 1st and 2nd shells change the $\delta$, $B_{\mathrm{hf}}$ and $QS$ Mössbauer parameters by amounts of $\Delta\delta_1$, $\Delta B_{\mathrm{hf},1}$, $\Delta QS_1$ and $\Delta\delta_2$, $\Delta B_{\mathrm{hf},2}$, $\Delta QS_2$, respectively. Assuming that the atomic concentration of the substituent atoms is $c$, and that their number in the 1st and 2nd shells can take on values from the range of $0\ldots n_1$ and $0\ldots n_2$, respectively, the spectrum is calculated as the sum of $(n_1+1)\cdot(n_2+1)$ sextet components with weights chosen according to the corresponding binomial distributions:

$$A\cdot\sum_{j=0}^{n_2}\binom{n_2}{j}c^j(1-c)^{n_2-j}\sum_{i=0}^{n_1}\binom{n_1}{i}c^i(1-c)^{n_1-i}\cdot \mathrm{S}(\delta_0+i\cdot\Delta\delta_1+j\cdot\Delta\delta_2, QS_0+i\cdot\Delta QS_1+j\cdot\Delta QS_2, B_{\mathrm{hf},0}+i\cdot\Delta B_{\mathrm{hf},1}+j\cdot\Delta B_{\mathrm{hf},2})$$

where $A$ denotes the total area of the subspectrum, $i$ and $j$ denote the number of substituent atoms respectively in the 1st and 2nd shell of atomic neighborhood of the Mössbauer nuclide, and $S(\delta_0+i\cdot\Delta\delta_1+j\cdot\Delta\delta_2, QS_0+i\cdot\Delta QS_1+j\cdot\Delta QS_2, B_{\mathrm{hf},0}+i\cdot\Delta B_{\mathrm{hf},1}+j\cdot\Delta B_{\mathrm{hf},2})$ denotes a sextet with unit area and with Mössbauer parameters of $\delta = \delta_0 + i\cdot\Delta\delta_1 + j\cdot\Delta\delta_2$, $QS = QS_0 + i\cdot\Delta QS_1 + j\cdot\Delta QS_2$ and $B_{\mathrm{hf}} = \mathrm{MAX}(B_{\mathrm{hf},0} + i\cdot\Delta B_{\mathrm{hf},1} + j\cdot\Delta B_{\mathrm{hf},2}, 0)$, where the latter notation means that negative $B_{\mathrm{hf}}$ values are treated as zero. The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above expression.

Similarly to the case of the previous (section 27.5.5) binomial model, the possible number of atoms in the 1st and 2nd shells of atomic neighborhood of a Mössbauer nuclide depends on the physical model under consideration. For example, in the bcc lattice of a disordered $Fe_{1-c}X_c$ alloy one could assume that the maximum 8 nearest-neighbor (nn) and the maximum 6 next-nearest-neighbor (nnn) X atoms surrounding a $^{57}$Fe nuclide change the hyperfine parameters characteristic to the latter with different amounts, whereas the effect of X atoms being further away can be neglected in comparison. Then, under such assumptions, one could take nn and nnn lattice sites contributing respectively to the 1st and 2nd shells of atomic neighborhood, and consequently one could set $n_1 = 8$ and $n_2 = 6$ in the above expression.

Note that beside the number of substituent atoms, their configuration around the Mössbauer nuclide may also be of importance, which effect is not taken into account in the present model.

For the case of $Fe_{1-c}X_c$ alloys, see for example

G.K. Wertheim, V. Jaccarino, J.H. Wernick, D.N.E. Buchanan, *Phys. Rev. Lett.* **12** (1964) 24-27.
R. Idczak, R. Konieczny, J. Chojcan: *Solid State Communications* **159** (2013) 22-25.

| **Parameter name** | **Meaning** | **Associated quantity in the above expression** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $A$ |
| A25/A34 | Relative area of the 2nd and 5th peaks with respect to that of the 3rd and 4th peaks of the sextet component. The parameter can be used to account for magnetic texture. It is fixed to 2.0 by default (suitable for a powder without texture). Note that $A_{16}/A_{34}$ is fixed to 3.0. In order to account for thickness effects, turn to transmission integral fitting (see section 27.8). | |
| ISOMER SHIFT | Isomer shift characterizing Mössbauer nuclides without substituent atoms in their 1st and 2nd shells of atomic neighbors. Equals to the isomer shift when the value of the CONCENTRATION parameter is zero. | $\delta_0$ |
| MAGNETIC FIELD [T] | Hyperfine magnetic field characterizing Mössbauer nuclides without substituent atoms in their 1st and 2nd shells of atomic of neighbors. Equals to the hyperfine magnetic field when the value of the CONCENTRATION parameter is zero. | $B_{\mathrm{hf},0}$ |
| Q. SPLITTING | Quadrupole splitting (here taken to be equal to 2ε where ε denotes the first order quadrupole shift) characterizing Mössbauer nuclides without substituent atoms in their 1st and 2nd shells of atomic neighbors. Equals to the quadrupole splitting when the value of the CONCENTRATION parameter is zero. | $QS_0$ |
| DELTA IS (nn) | Change in the isomer shift due to one additional substituent atom in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta\delta_1$ |
| DELTA MF (nn) | Change in the hyperfine magnetic field due to one additional substituent atom in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta B_{\mathrm{hf},1}$ |
| DELTA QS (nn) | Change in the quadrupole splitting (2ε) due to one additional substituent atom in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta QS_1$ |
| DELTA IS (nnn) | Change in the isomer shift due to one additional substituent atom in the 2nd shell of atomic neighbors of a Mössbauer nuclide. | $\Delta\delta_2$ |
| DELTA MF (nnn) | Change in the hyperfine magnetic field due to one additional substituent atom in the 2nd shell of atomic neighbors of a Mössbauer nuclide. | $\Delta B_{\mathrm{hf},2}$ |
| DELTA QS (nnn) | Change in the quadrupole splitting (2ε) due to one additional substituent atom in the 2nd shell of atomic neighbors of a Mössbauer nuclide. | $\Delta QS_2$ |
| NEIGHBORS (nn) | Number of atomic positions contributing to (and the maximum number of substituent atoms in) the 1st shell of atomic neighbors of a Mössbauer nuclide. The value can be any integer in the range of 1…14. | $n_1$ |
| NEIGHBORS (nnn) | Number of atomic positions contributing to (and the maximum number of substituent atoms in) the 2nd shell of atomic neighbors of a Mössbauer nuclide. The value can be any integer in the range of 1…14. | $n_2$ |
| CONCENTRATION | Atomic concentration of substituent atoms. | $c$ |
| LINE WIDTH | FWHM width of the Lorentzian peaks of the individual sextet components. Note that when Pseudo-Voigt peak shape is selected for the subspectrum, the "LINE WIDTH" parameter refers to the FWHM width of the *Gaussian* component of the (Pseudo-) Voigt peaks used in this case as the profile of individual lines of the sextets. | |

## *27.5.7.* Multinomial distribution (1 shell, AB, M, Powder)

This theory (available for $^{57}$Fe, $^{119}$Sn and $^{125}$Te) models a Mössbauer spectrum of a powdered magnetic sample with possible texture. It consists of several sextet components (with the quadrupole interaction being taken into account in the first-order perturbation limit) whose relative weights and hyperfine parameters are determined by assuming that the isomer shift ($\delta$), hyperfine magnetic field ($B_{\mathrm{hf}}$) and quadrupole splitting ($QS$, here treated as to be equal to 2ε where ε is the first order quadrupole shift) parameters characterizing a given Mössbauer nuclide depend on the number and kind of randomly distributed substituent atoms in its 1$^{\mathrm{st}}$ shell of atomic neighborhood. It is assumed that there are two different types of *substituent* atoms in the system, atom types 'A' and 'B'. It is assumed that the Mössbauer nuclide may be surrounded by 'A' and 'B' substituent atoms in a random manner, with corresponding changes in the $\delta$, $B_{\mathrm{hf}}$ and $QS$ Mössbauer parameters by the amounts of $\Delta\delta_{\mathrm{A}}$, $\Delta B_{\mathrm{hf,A}}$, $\Delta QS_{\mathrm{A}}$ and $\Delta\delta_{\mathrm{B}}$, $\Delta B_{\mathrm{hf,B}}$, $\Delta QS_{\mathrm{B}}$, respectively, for each of the substituent atoms. Assuming that the atomic concentration of the substituent atoms is $c_{\mathrm{A}}$ and $c_{\mathrm{B}}$, and that their number in the 1$^{\mathrm{st}}$ shell of atomic neighborhood can take on values from the range of 0…$n$ (such that their *total* number is maximum $n$), the spectrum is calculated as the sum of ½($n$+1)·($n$+2) sextet components with weights chosen according to the corresponding multinomial distribution:

$$A\cdot\sum_{j=0}^{n}\sum_{i=0}^{n-j}\frac{n!}{i!\cdot j!(n-i-j)!}(c_{\mathrm{B}})^{j}(c_{\mathrm{A}})^{i}(1-c_{\mathrm{A}}-c_{\mathrm{B}})^{n-i-j}\cdot\mathrm{S}(\delta_0+i\cdot\Delta\delta_{\mathrm{A}}+j\cdot\Delta\delta_{\mathrm{B}},QS_0+i\cdot\Delta QS_{\mathrm{A}}+j\cdot\Delta QS_{\mathrm{B}},B_{\mathrm{hf},0}+i\cdot\Delta B_{\mathrm{hf,A}}+j\cdot\Delta B_{\mathrm{hf,B}})$$

where $A$ denotes the total area of the subspectrum, $i$ and $j$ denote the number of substituent atoms A and B, respectively, in the 1$^{\mathrm{st}}$ shell of atomic neighborhood of the Mössbauer nuclide, and

$$\mathrm{S}(\delta_0+i\cdot\Delta\delta_{\mathrm{A}}+j\cdot\Delta\delta_{\mathrm{B}},QS_0+i\cdot\Delta QS_{\mathrm{A}}+j\cdot\Delta QS_{\mathrm{B}},B_{\mathrm{hf},0}+i\cdot\Delta B_{\mathrm{hf,A}}+j\cdot\Delta B_{\mathrm{hf,B}})$$

denotes a sextet with unit area and with Mössbauer parameters of $\delta=\delta_0+i\cdot\Delta\delta_{\mathrm{A}}+j\cdot\Delta\delta_{\mathrm{B}}$, $QS=QS_0+i\cdot\Delta QS_{\mathrm{A}}+j\cdot\Delta QS_{\mathrm{B}}$ and $B_{\mathrm{hf}}=\mathrm{MAX}(B_{\mathrm{hf},0}+i\cdot\Delta B_{\mathrm{hf,A}}+j\cdot\Delta B_{\mathrm{hf,B}}\ ,\ 0)$, where the latter notation means that negative $B_{\mathrm{hf}}$ values are treated as zero. The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above expressions.

Similarly to the case of the previously treated binomial models, the possible number of atoms in the 1$^{\mathrm{st}}$ shell of atomic neighborhood of a Mössbauer nuclide depends on the physical model under consideration. For example, in the bcc lattice of a disordered $\mathrm{Fe}_{1-c_{\mathrm{A}}-c_{\mathrm{B}}}\mathrm{A}_{c_{\mathrm{A}}}\mathrm{B}_{c_{\mathrm{B}}}$ alloy one could assume that the hyperfine parameters characteristic to $^{57}$Fe are influenced mainly by the 8 nearest-neighbor (nn) atoms in the 1$^{\mathrm{st}}$ shell of atomic neighborhood of $^{57}$Fe, whereas the effect of atoms being further away can be neglected in comparison. Then, under such assumptions, one could take 8 lattice sites contributing to the 1$^{\mathrm{st}}$ shell of atomic neighborhood, and consequently one could set $n$ = 8 in the above expression.

MossWinn allows setting $c_{\mathrm{A}}$ and $c_{\mathrm{B}}$ values independently such that $c_{\mathrm{A}}+c_{\mathrm{B}}\geq 1$ may occur, but it will not calculate the corresponding subspectrum for such values.

Note that beside the number of substituent atoms, their configuration around the Mössbauer nuclide may also be of importance, which effect is not taken into account in the present model.

| **Parameter name** | **Meaning** | **Associated quantity in the above expressions** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | $A$ |
| A25/A34 | Relative area of the 2nd and 5th peaks with respect to that of the 3rd and 4th peaks of the sextet component. The parameter can be used to account for magnetic texture. It is fixed to 2.0 by default (suitable for a powder without texture). Note that $A_{16}/A_{34}$ is fixed to 3.0. In order to account for thickness effects, turn to transmission integral fitting (see section 27.8). | |
| ISOMER SHIFT | Isomer shift characterizing Mössbauer nuclides without substituent atoms in their 1st shell of atomic neighbors. Equals to the isomer shift when the value of the CONCENTRATION (A) and CONCENTRATION (B) parameters are both zero. | $\delta_0$ |
| MAGNETIC FIELD [T] | Hyperfine magnetic field characterizing Mössbauer nuclides without substituent atoms in their 1st shell of atomic of neighbors. Equals to the hyperfine magnetic field when the value of the CONCENTRATION (A) and CONCENTRATION (B) parameters are both zero. | $B_{\mathrm{hf},0}$ |
| Q. SPLITTING | Quadrupole splitting (here taken to be equal to 2ε where ε denotes the first order quadrupole shift) characterizing Mössbauer nuclides without substituent atoms in their 1st shell of atomic neighbors. Equals to the quadrupole splitting when the value of the CONCENTRATION (A) and CONCENTRATION (B) parameters are both zero. | $QS_0$ |
| DELTA IS (A) | Change in the isomer shift due to one additional substituent atom of the type 'A' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta\delta_{\mathrm{A}}$ |
| DELTA MF (A) | Change in the hyperfine magnetic field due to one additional substituent atom of the type 'A' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta B_{\mathrm{hf,A}}$ |
| DELTA QS (A) | Change in the quadrupole splitting (2ε) due to one additional substituent atom of the type 'A' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta QS_{\mathrm{A}}$ |
| DELTA IS (B) | Change in the isomer shift due to one additional substituent atom of the type 'B' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta\delta_{\mathrm{B}}$ |
| DELTA MF (B) | Change in the hyperfine magnetic field due to one additional substituent atom of the type 'B' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta B_{\mathrm{hf,B}}$ |
| DELTA QS (B) | Change in the quadrupole splitting (2ε) due to one additional substituent atom of the type 'B' in the 1st shell of atomic neighbors of a Mössbauer nuclide. | $\Delta QS_{\mathrm{B}}$ |
| NEIGHBORS (nn) | Number of atomic positions contributing to (and the maximum number of substituent atoms in) the 1st shell of atomic neighbors of a Mössbauer nuclide. The value can be any integer in the range of 1…14. | $n$ |
| CONCENTRATION (A) | Atomic concentration of substituent atoms of the type 'A'. | $c_{\mathrm{A}}$ |
| CONCENTRATION (B) | Atomic concentration of substituent atoms of the type 'B'. | $c_{\mathrm{B}}$ |
| LINE WIDTH | FWHM width of the Lorentzian peaks of the individual sextet components. Note that when Pseudo-Voigt peak shape is selected for the subspectrum, the "LINE WIDTH" parameter refers to the FWHM width of the *Gaussian* component of the (Pseudo-) Voigt peaks used in this case as the profile of individual lines of the sextets. | |

## 27.6. Paramagnetic Hyperfine Structure (PHS)

*This theory requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.*

To account for Mössbauer spectra displaying paramagnetic hyperfine structure of the Mössbauer nuclide, the combined Hamiltonian of the electronic and the nuclear system has to be considered. As the electronic state of the Mössbauer ion depends on the crystal/ligand field it is situated in, corresponding terms appear in the combined Hamiltonian that operates on product states built from electronic and nuclear basis states. The latter are written in terms of the electronic and nuclear spin states as $|S,S_z\rangle|I,I_z\rangle$ where $S$ refers to the **effective spin** characteristic of the apparent state of the electronic system. The combination of the electronic and nuclear degrees of freedom leads to a Hamiltonian with a dimension equal to the product of the respective spin multiplicities, i.e. $(2S+1)(2I+1)$. Assuming high-spin $Fe^{3+}$ ($S = 5/2$), this dimension takes on the value of 24 and 12 for the $^{57}Fe$ excited and ground state, respectively, with a corresponding number of associated eigenstates in each case. Depending on the actual form of the Hamiltonian, these eigenstates may be a mixture (linear combination) of the mentioned basis states, which in the treated example (high-spin $Fe^{3+}$) may lead to a maximum of 24×12 absorption peaks contributing to a corresponding Mössbauer spectrum. Interdependence between the electronic and nuclear states is established by the Hamiltonian term of $\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}$ — where $\mathbf{S} = (\mathbf{S}_x,\mathbf{S}_y,\mathbf{S}_z)$ and $\mathbf{I} = (\mathbf{I}_x,\mathbf{I}_y,\mathbf{I}_z)$ — that accounts for the hyperfine magnetic interaction. Assuming the presence of an externally applied magnetic field (being useful for the elucidation of details of the electronic state and the corresponding crystal/ligand field) this term may turn out to be negligible in comparison with the term accounting for the electronic Zeeman energy. In the latter case the electronic and nuclear states may be seen as being **decoupled** from each other, and the electronic state may be described without considering the nuclear state, by solving the separate electronic Hamiltonian with dimensions of $(2S+1)$. The nuclear Hamiltonian (including also the hyperfine magnetic interaction and having dimensions of $2I+1$) can then be written and solved by using the spin expectation values $(\langle S_x\rangle,\langle S_y\rangle,\langle S_z\rangle)$ for each of the derived eigenstates of the electronic system. In this **slow relaxation** (**SR**) approach there belongs a separate Mössbauer spectrum component to each of the possible electronic states. The relative intensities of these components are determined by the respective Boltzmann factors of the ground state levels, meaning that the shape of the compound spectrum will depend on the sample temperature. At the same time, relaxation among eigenstates of the electronic subsystem may also be fast compared to the characteristic time scale of the Mössbauer measurement, in which case the appearance of only one spectrum component is expected, reflecting the $(\langle S_x\rangle_T,\langle S_y\rangle_T,\langle S_z\rangle_T)$ thermal averages of the electronic spin component expectation values. Due to the involvement of Boltzmann factors in the calculation of the thermal averages, in this latter **decoupled & fast relaxation** (**DFR**) case the spectral shape will also depend on the sample temperature.

The combined Hamiltonian of the electronic and nuclear states is usually expressed in the coordinate system defined by the part of the **crystal field Hamiltonian** (**CFH**) that accounts for the deviation from a purely cubic crystal field. In the case of an axial distortion of the crystal field, the orientation of the corresponding symmetry axis is chosen as the $z$ axis, whereas the orthogonal $x$ and $y$ axes are then chosen in the corresponding perpendicular plane. We refer to this coordinate system as the **crystal field system** (**CFS**). Considering a single crystal in an external magnetic field, the resulting Mössbauer spectrum will depend on the orientation of the magnetic field with respect to the CFS. In the case of powder samples this makes it necessary to consider all the possible orientations of the **external magnetic field** (**EMF**) with respect to the CFSs of the individual crystallites. The corresponding Mössbauer spectra can therefore be calculated only in an approximate manner, by applying a **numerical spherical integral** accounting for all the possible relative orientations of the EMF with respect to the CFS. The symmetry reflected by the Hamiltonian may allow for a reduction of the solid angle over which the integration has to be performed, from that of the full sphere to that of a hemisphere or of a spherical octant. In case of axial symmetry, only a line integral needs to be performed over a spherical (quarter-circular) arc.

The need for the execution of a numerical spherical integral makes the **calculation speed of PHS models** in general much slower than that of other theories in MossWinn. The accuracy and calculation time will increase simultaneously with the increase of resolution chosen for the spherical integral. In MossWinn the latter is based on the method put forward by Alderman *et al.* (1986), which represents a considerable advance in accuracy with respect to previously applied methods. To take advantage of the power offered by recent multicore processors, a corresponding spherical integral method was implemented in MossWinn by making use of **parallel (multithreaded) computing techniques** that will result in higher computing speeds on processors with a higher number of cores (or simultaneously executed threads). A higher-end processor is thus recommended for the fit of PHS models.

For each of the subspectra calculated according to a PHS theory involving the numerical spherical integral, MossWinn allows for the setting of several different accuracy levels as follows.

| Accuracy level | Spherical numerical integral resolution |
|---|---|
| 0 | Automatically chosen depending on the actual calculation speed. It will mostly be equivalent to accuracy level 1 or 2. This is the default setting. |
| 1 | 64 points over a spherical octant. This is the fastest but the least accurate setting. Suitable for rough fitting. |
| 2 | 256 points over a spherical octant. High accuracy, usually suitable for final fitting and publications. |
| 3 | 1024 points over a spherical octant. Very high accuracy, usually brings only minor improvements over accuracy level 2. |
| 4 | 4096 points over a spherical octant. Slow, the calculations may be sluggish even on a higher-end computer. |

In practice it is recommended to start the fit with accuracy level 1, finalize the fit with accuracy level 2, and check the end result by setting accuracy level 3 manually in order to make sure that accuracy provided by level 2 was high enough. Though accuracy level 0 is practical in the sense that it adjusts the accuracy level automatically in accordance with the speed of the computer, it may lead to unexpected changes between accuracy levels (and corresponding changes in the fitting curve) depending on the workload of the computer. In such cases it is better to set the accuracy level manually to some higher than zero value.

For the case of slow relaxation, MossWinn also offers a choice between coupled and decoupled treatment of the electronic and nuclear levels. Calculation via the **decoupled** way will in general be **considerably faster than** via the **coupled** one. Note, however, that below EMFs of around 0.01 T **the decoupled way of calculations may produce invalid results** due to the hyperfine magnetic interaction being not negligible anymore with respect to the electronic Zeeman interaction. MossWinn will call attention to such circumstances in HTML fitlogs created when the fit results are accepted. It should also be noted that the program cannot itself decide automatically whether the relaxation of the electronic subsystem is slow or fast. It depends on the choice of the user to select the model variant that corresponds to the actual physical situation.

For cases when an external magnetic field is applied, **the relative orientation of the EMF with respect to the direction of the Mössbauer γ-ray** will also influence the spectral shape through the relative intensities of the absorption peaks. Corresponding PHS models of MossWinn can account for the two most commonly applied geometries in this respect: the geometry where the EMF is applied parallel to the Mössbauer γ-ray direction, and the one where it is applied perpendicular to it.

In the followings the different PHS models available in the present version of MossWinn are introduced. Note that the parameter **TEMPERATURE [K]**, **EXTERNAL MAGNETIC FIELD [T]** and **EMF PAR (0) / PERP (1)** accounting respectively for the sample temperature, the magnitude and the orientation of the external magnetic field applied may be added to the parameter list of the baseline whenever a PHS model is invoked for the actual spectrum. The orientation of the external magnetic field (**PAR** for parallel, **PERP** for perpendicular) is meant with respect to the Mössbauer γ-ray direction. The value of the parameter **EMF PAR (0) / PERP (1)** should be set to 0 for an EMF that is parallel to the Mössbauer γ-ray direction, or to 1 for an EMF that is perpendicular to it.

Parameters of the crystal field and the hyperfine interaction are given in various units in the literature. See page 149 for some useful conversion constants in this regard.

In order to apply PHS models in MossWinn one needs either a **DBM version licence**, or subscription to the ***MossWinn Services***.

## *27.6.1.* PHS 1/2 (Powder, ZERO EMF, Slow R.)

This model accounts for a powder sample with an electronic system with effective spin $S = ½$, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident. The effective Hamiltonian can be written as

$$\mathbf{H} = g_n \mu_N [A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where *n* can stand either for the ground state or for the excited state of the nucleus. (The quadrupole term can be omitted for the ground nuclear state of $^{57}$Fe.) Note that with this definition of the hyperfine Hamiltonian the $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus.

The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression.

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\,\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{xx}$ |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{zz}$ |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

Corresponding theoretical cases are treated for example in the paper

H.H. Wickman, M.P. Klein, D.A. Shirley: *Phys. Rev.* **152** (1966) 345.

## *27.6.2.* PHS (Powder, ZERO EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 0\ldots5/2$, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the crystal field system (**CFS**). The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1) + \frac{E}{D}(\mathbf{S}_x^2 - \mathbf{S}_y^2)] + \frac{a}{6}\cdot[\mathbf{S}_x^4 + \mathbf{S}_y^4 + \mathbf{S}_z^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$

$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2] +$$

$$g_n\mu_N[A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where *n* can stand either for the ground state or for the excited state of the nucleus. (The quadrupole term can be omitted for the ground nuclear state of $^{57}$Fe.) The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. When $a \neq 0$ the model can account only for orthorhombic distortions of the cubic crystal field potential, where the system of cubic axes coincide with the CFS.

The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression. (Quantities *h* and *c* denote the Planck constant and the speed of light in vacuum, respectively.)

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\,\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{D}{100hc}$ |
| E/D | Relative value of the multiplier of the rhombic term of the CFH with respect to that of the axial term (*D*). It can describe a rhombic distortion of the cubic crystal field. (Rhombicity parameter.) | $\frac{E}{D}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{xx}$ |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{zz}$ |
| 2S+1 (multiplicity) | 2*S*+1 where *S* is the effective spin. Can take on integer values from the range 0…6. | 2*S*+1 |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

For the corresponding Hamiltonian expression see for example the following works:

B. Bleaney, K.W.H. Stevens: *Rep. Prog. Phys.* **16** (1953) 108-159. (See page 138.)
H.H. Wickman, G.K. Wertheim: *Phys. Rev.* **148** (1966) 211.

## *27.6.3.* PHS Trigonal (Powder, ZERO EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 0\ldots5/2$, in the absence of an external magnetic field, by assuming slow electronic relaxation. The eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the system of the axial crystal field (**CFS**) whose *z* axis is oriented in the (1,1,1) cube diagonal direction of the cubic crystal field system (trigonal distortion). Tensor **A** is assumed to display axial symmetry ($A_{yy} = A_{xx}$). The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1)] + \frac{a}{6}\cdot[\mathbf{S}_{100}^4 + \mathbf{S}_{010}^4 + \mathbf{S}_{001}^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$

$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2]$$

$$g_n\mu_N[A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where *n* can stand either for the ground state or for the excited state of the nucleus. (The quadrupole term can be omitted for the ground nuclear state of $^{57}$Fe.) The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. When $a \neq 0$ the model can account only for trigonal distortions of the cubic crystal field potential. When $\eta = 0$, in this model the orientation of the orthogonal *x* and *y* axes is immaterial. For $\eta \neq 0$, consider that in this particular model the $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ unit vectors of the CFS are expressed in the cubic system as follows (being equivalent with Euler angles $\{\theta,\varphi,\gamma\} = \{\arccos(1/\sqrt{3}), 45^\circ, -45^\circ\}$)

$$\mathbf{e}_x = (\frac{\sqrt{3}+3}{6}, \frac{\sqrt{3}-3}{6}, -\frac{1}{\sqrt{3}}),\ \mathbf{e}_y = (\frac{\sqrt{3}-3}{6}, \frac{\sqrt{3}+3}{6}, -\frac{1}{\sqrt{3}}),\ \mathbf{e}_z = (\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})$$

The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression. (Quantities *h* and *c* denote the Planck constant and the speed of light in vacuum, respectively.)

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{D}{100hc}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. It is assumed to be identical with the *yy* element (axial symmetry). | $A_{xx} = A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{zz}$ |
| 2S+1 (multiplicity) | 2*S*+1 where *S* is the effective spin. Can take on integer values from the range 1…6. | 2*S*+1 |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

See for example:

B. Bleaney, K.W.H. Stevens: *Rep. Prog. Phys.* **16** (1953) 108-159. (See page 129.)
W.T. Oosterhuis: *Biochemistry* (Structure and Bonding) **20** (1974) 59.

## *27.6.4.* PHS Angle (Powder, ZERO EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 0…5/2$, in the absence of an external magnetic field, by assuming slow electronic relaxation. The relative orientation of the eigensystem of the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are given with respect to the crystal field system (**CFS**) via the respective Euler angles that rotate the CFS system into the **A** or **EFG** tensor eigensystem. The orientation of the *xyz* CFS system is given with respect to the [100, 010, 001] cubic system via the Euler angles that rotate the cubic system into the CFS system. The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1) + \frac{E}{D}(\mathbf{S}_x^2 - \mathbf{S}_y^2)] + \frac{a}{6}\cdot[\mathbf{S}_{100}^4 + \mathbf{S}_{010}^4 + \mathbf{S}_{001}^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$

$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2] +$$

$$g_n\mu_N[\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}] + \frac{eQ_n}{4I(2I-1)}\sum_{i,j=x,y,z} V_{ij}\left[\mathbf{I}_i\cdot\mathbf{I}_j + \mathbf{I}_j\cdot\mathbf{I}_i - \delta_{ij}\frac{2}{3}I(I+1)\right]$$

where *n* can stand either for the ground state or for the excited state of the nucleus. The model parameters are given in the next table. For the meaning of Euler angles see the description on page 82.

| **Parameter name** | **Meaning** | **Associated quantity** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum. (Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{D}{100hc}$ |
| E/D | Relative value of the multiplier of the rhombic term of the CFH with respect to that of the axial term (*D*). It can describe a rhombic distortion of the cubic crystal field. (Rhombicity parameter.) | $\frac{E}{D}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{xx}$ |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{zz}$ |
| 2S+1 (multiplicity) | 2*S*+1 where *S* is the effective spin. Can take on integer values from the range 1…6. | 2*S*+1 |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |
| THETA (A) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| PHI (A) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| GAMMA (A) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| THETA (EFG) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| PHI (EFG) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| GAMMA (EFG) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| THETA (CFS) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |
| PHI (CFS) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |
| GAMMA (CFS) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |

## *27.6.5.* PHS 1/2 (Powder, EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 1/2$, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the $g$ tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident. The effective Hamiltonian can be written as

$$\mathbf{H} = \mu_{\mathrm{B}}[g_{xx}B_x\mathbf{S}_x + g_{yy}B_y\mathbf{S}_y + g_{zz}B_z\mathbf{S}_z] + g_n\mu_{\mathrm{N}}[A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z]$$
$$- g_n\mu_{\mathrm{N}}[B_x\mathbf{I}_x + B_y\mathbf{I}_y + B_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where $B_x$, $B_y$ and $B_z$ stands respectively for the $x$, $y$ and $z$ component of the external magnetic field vector that is applied either parallel or perpendicular to the Mössbauer γ-ray direction, and $n$ can stand either for the ground state or for the excited state of the nucleus. (The quadrupole term can be omitted for the ground nuclear state of $^{57}$Fe.) The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. The model parameters are given in the next table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression. (Quantities $h$ and $c$ denote the Planck constant and the speed of light in vacuum, respectively.)

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\,\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{xx}$ |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. | $A_{zz}$ |
| gxx | *xx* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{xx}$ |
| gyy | *yy* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{yy}$ |
| gzz | *zz* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{zz}$ |
| Accuracy level | Sets the accuracy of calculations by influencing the resolution of the spherical integral. Possible values are in the range of 0…4. Default value is 0 (automatic accuracy setting). See page 73 for the meaning of the different accuracy levels. | |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

In the case of this PHS model the spherical integration is performed over the $x,y,z \geq 0$ spherical octant by default, unless the parameter values correspond to axial symmetry, when a line integral is performed over a quarter-circular arc.

## *27.6.6.* PHS (Powder, EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 0\ldots5/2$, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the crystal field system (**CFS**). The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1) + \frac{E}{D}(\mathbf{S}_x^2 - \mathbf{S}_y^2)] + \frac{a}{6}\cdot[\mathbf{S}_x^4 + \mathbf{S}_y^4 + \mathbf{S}_z^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$
$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2] +$$
$$\mu_B[g_{xx}B_x\mathbf{S}_x + g_{yy}B_y\mathbf{S}_y + g_{zz}B_z\mathbf{S}_z] + g_n\mu_N[A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z]$$
$$- g_n\mu_N[B_x\mathbf{I}_x + B_y\mathbf{I}_y + B_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where $B_x$, $B_y$ and $B_z$ stands respectively for the *x*, *y* and *z* component of the external magnetic field vector that is applied either parallel or perpendicular to the Mössbauer γ-ray direction, and *n* can stand either for the ground state or for the excited state of the nucleus.

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. | $\frac{D}{100hc}$ |
| E/D | Relative value of the multiplier of the rhombic term of the CFH with respect to that of the axial term (*D*). It can describe a rhombic distortion of the cubic crystal field. (Rhombicity parameter.) | $\frac{E}{D}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | $A_{xx}$ |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | $A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | $A_{zz}$ |
| gxx | *xx* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{xx}$ |
| gyy | *yy* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{yy}$ |
| gzz | *zz* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{zz}$ |
| 2S+1 (multiplicity) | 2*S*+1 where *S* is the effective spin. Can take on integer values from the range 1…6. Set it to 1 in order to model a diamagnetic ion (*S* = 0). | 2*S*+1 |
| Coupled (0) / Decoupled (1) | Set it to 0 to perform the calculations by taking into account the coupled electronic and nuclear Hamiltonian directly as given above. Set it to 1 in order to treat the electronic part of the Hamiltonian as being decoupled from the nuclear part as described on page 72. | |
| Accuracy level | Sets the accuracy of calculations by influencing the resolution of the spherical integral. Possible values are in the range of 0…4. Default value is 0 (automatic accuracy setting). See page 73 for the meaning of the different accuracy levels. | |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. The model parameters are given in the table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression. (Quantities $h$ and $c$ denote the Planck constant and the speed of light in vacuum, respectively.) By default the model is initialized according to isotropic **g** and **A** tensors ($g_{zz} = g_{yy} = g_{xx}$, $A_{zz} = A_{yy} = A_{xx}$ ), which constraints can be lifted (one by one) by pressing on the name of the constrained parameters with the left mouse button.

In the case of this PHS model the spherical integration is performed over the $x,y,z \geq 0$ spherical octant by default, unless the parameter values correspond to axial symmetry, when a line integral is performed over a quarter-circular arc.

## *27.6.7.* PHS Trigonal (Powder, EMF, Slow R.)

This model accounts for a powder sample with an electronic system characterized by an effective spin $S = 0\ldots5/2$, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The eigensystem of the $g$ tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are assumed to be coincident with the crystal field system (**CFS**) whose $z$ axis is oriented in the (1,1,1) cube diagonal direction of the cubic crystal field system (trigonal distortion). Tensors **g** and **A** are assumed to display axial symmetry ($g_{yy} = g_{xx}$, $A_{yy} = A_{xx}$). The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1)] + \frac{a}{6}\cdot[\mathbf{S}_{100}^4 + \mathbf{S}_{010}^4 + \mathbf{S}_{001}^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$
$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2] +$$
$$\mu_B[g_{xx}B_x\mathbf{S}_x + g_{yy}B_y\mathbf{S}_y + g_{zz}B_z\mathbf{S}_z] + g_n\mu_N[A_{xx}\mathbf{S}_x\mathbf{I}_x + A_{yy}\mathbf{S}_y\mathbf{I}_y + A_{zz}\mathbf{S}_z\mathbf{I}_z]$$
$$- g_n\mu_N[B_x\mathbf{I}_x + B_y\mathbf{I}_y + B_z\mathbf{I}_z] + \frac{eQ_nV_{zz}}{4I(2I-1)}[3\mathbf{I}_z^2 - I(I+1) + \eta(\mathbf{I}_x^2 - \mathbf{I}_y^2)]$$

where $B_x$, $B_y$ and $B_z$ stands respectively for the $x$, $y$ and $z$ component of the external magnetic field vector that is applied either parallel or perpendicular to the Mössbauer γ-ray direction, and $n$ can stand either for the ground state or for the excited state of the nucleus. The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. When $a \neq 0$ the model can account only for trigonal distortions of the cubic crystal field potential. When $\eta = 0$, in this model the orientation of the orthogonal $x$ and $y$ axes is immaterial. For $\eta \neq 0$, consider that in this particular model the $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$ unit vectors of the CFS are expressed in the cubic system as follows

$$\mathbf{e}_x = (\frac{\sqrt{3}+3}{6}, \frac{\sqrt{3}-3}{6}, -\frac{1}{\sqrt{3}}),\ \mathbf{e}_y = (\frac{\sqrt{3}-3}{6}, \frac{\sqrt{3}+3}{6}, -\frac{1}{\sqrt{3}}),\ \mathbf{e}_z = (\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})$$

(being equivalent with Euler angles $\{\theta,\varphi,\gamma\} = \{\arccos(1/\sqrt{3}), 45^\circ, -45^\circ\}$ ). The $A_{xx}$, $A_{yy}$ and $A_{zz}$ values are measured in magnetic flux density units (Tesla), and their value is the same in the ground and in the excited state of the nucleus. The model parameters are given in the table where in the last column associated quantities are also given with notations taken from the above Hamiltonian expression. (Quantities $h$ and $c$ denote the Planck constant and the speed of light in vacuum, respectively.) By default the model is initialized according to isotropic **g** and **A** tensors ($g_{zz} = g_{xx}$, $A_{zz} = A_{xx}$ ), which constraints can be lifted by pressing on the name of the constrained parameters with the left mouse button.

In the case of the PHS Triangle models the spherical integration is performed over all the four $z \geq 0$ spherical octants regardless of the actual value of the fit parameters.

| **Parameter name** | **Meaning** | **Associated quantity** **with notations taken from the above expression.** |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | $\frac{V_{zz}}{10^{21}\frac{\mathrm{V}}{\mathrm{m}^2}}$ |
| ETA | Asymmetry parameter of the EFG. | $\eta$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. | $\frac{D}{100hc}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor expressed in its eigensystem. It is assumed to be identical with the *yy* element (axial symmetry). | $A_{xx} = A_{yy}$ |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | $A_{zz}$ |
| gxx | *xx* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. It is assumed to be identical with the *yy* element (axial symmetry). | $g_{xx} = g_{yy}$ |
| gzz | *zz* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | $g_{zz}$ |
| 2S+1 (multiplicity) | 2*S*+1 where *S* is the effective spin. Can take on integer values from the range 1…6. Set it to 1 in order to model a diamagnetic ion (*S* = 0). | 2*S*+1 |
| Coupled (0) / Decoupled (1) | Set it to 0 to perform the calculations by taking into account the coupled electronic and nuclear Hamiltonian directly as given above. Set it to 1 in order to treat the electronic part of the Hamiltonian as being decoupled from the nuclear part as described on page 72. | |
| Accuracy level | Sets the accuracy of calculations by influencing the resolution of the spherical integral. Possible values are in the range of 0…4. Default value is 0 (automatic accuracy setting). See page 73 for the meaning of the different accuracy levels. | |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |

## *27.6.8.* PHS Angle (Powder, EMF, Slow R.)

This is a general model that includes all the slow-relaxation PHS models treated up to this point as special cases. It accounts for a powder sample with an electronic system characterized by an effective spin $S = 0\ldots5/2$, being situated in an external magnetic field oriented either parallel or perpendicular to the Mössbauer γ-ray direction. The model assumes slow electronic relaxation. The relative orientation of the eigensystem of the *g* tensor (**g**), the hyperfine magnetic interaction tensor (**A**) and the electric field gradient tensor (**EFG**) are given with respect to the crystal field system (**CFS**) via the respective Euler angles that rotate the CFS system into the **g**, **A** or **EFG** tensor eigensystem. The orientation of the *xyz* CFS system is given with respect to the cubic system via the Euler angles that rotate the cubic system into the CFS system. In the followings Euler rotations are expressed as $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_{z''}(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta) = \mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)\mathbf{R}_z(\gamma)$ where $\mathbf{R}_{z''}(\gamma)$ denotes rotation with angle γ around the new direction of the *z* axis obtained after rotations $\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$, where $\mathbf{R}_z(\varphi)$ and $\mathbf{R}_y(\theta)$ denote rotation around the original *z* axis with angle φ and rotation around the original *y* axis with angle θ, respectively.

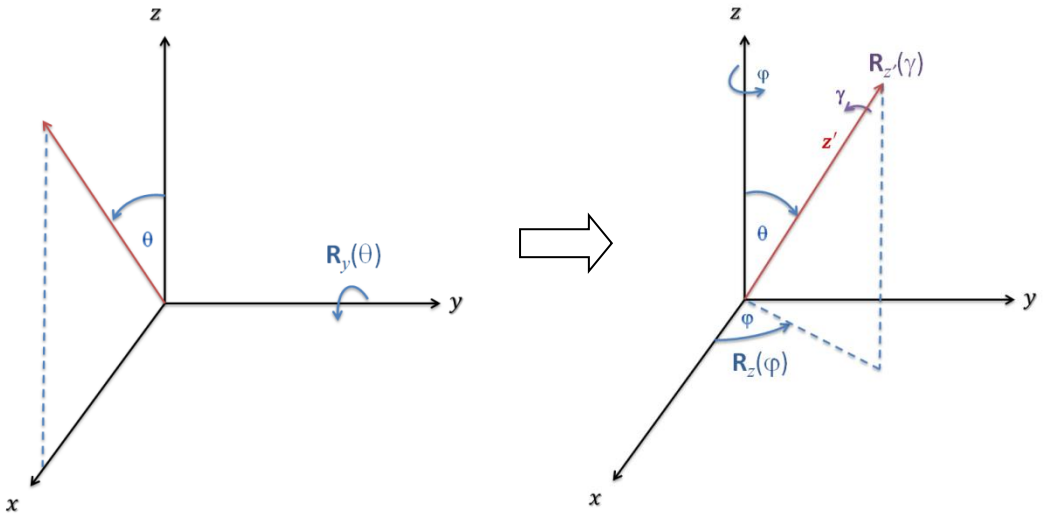



Illustration of Euler rotations as they are meant in MossWinn's PHS models. The *xyz* system is rotated into the *x*'*y*'*z*' system via successive rotations of $\mathbf{R}_y(\theta)$ followed by $\mathbf{R}_z(\varphi)$ followed by $\mathbf{R}_{z''}(\gamma)$. The *x*' and *y*' axes are omitted for clarity.

The **g**, **A** and **EFG** tensors are defined with their parameters given in their eigensystem ($g_{xx}$, $g_{yy}$, $g_{zz}$ for **g**, $A_{xx}$, $A_{yy}$, $A_{zz}$ for **A**, and $V_{zz}$, $\eta$ for the **EFG**) along with the Euler angles θ, φ, γ that rotate the *xyz* CFS system into their respective eigensystem. With these parameters the form of the corresponding diagonal tensors (in the following **Λ**, where **Λ** can stand for the diagonal form of **g**, **A** and **EFG**) are expressed in the CFS system as

$$\mathbf{R}_{\theta\varphi\gamma} \cdot \mathbf{\Lambda} \cdot \mathbf{R}^{-1}_{\theta\varphi\gamma} .$$

The effective Hamiltonian can be written as

$$\mathbf{H} = D[\mathbf{S}_z^2 - \frac{1}{3}S(S+1) + \frac{E}{D}(\mathbf{S}_x^2 - \mathbf{S}_y^2)] + \frac{a}{6}\cdot[\mathbf{S}_{100}^4 + \mathbf{S}_{010}^4 + \mathbf{S}_{001}^4 - \frac{1}{5}\cdot S(S+1)(3S^2+3S-1)] +$$
$$\frac{F}{180}\cdot[35\mathbf{S}_z^4 - 30\cdot S(S+1)\mathbf{S}_z^2 + 25\mathbf{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2] +$$
$$\mu_B[\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}] + g_n\mu_N[\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}]$$
$$- g_n\mu_N[B_x\mathbf{I}_x + B_y\mathbf{I}_y + B_z\mathbf{I}_z] + \frac{eQ_n}{4I(2I-1)}\sum_{i,j=x,y,z} V_{ij}\left[\mathbf{I}_i\cdot\mathbf{I}_j + \mathbf{I}_j\cdot\mathbf{I}_i - \delta_{ij}\frac{2}{3}I(I+1)\right]$$

where **B**, $B_x$, $B_y$ and $B_z$ stands respectively for the EMF vector, and the *x*, *y* and *z* component of the EMF vector that is applied either parallel or perpendicular to the Mössbauer γ-ray direction, *n* can stand either for the ground state or for the excited state of the nucleus, $V_{ij}$ is the form of the **EFG** tensor expressed in the *xyz* system, calculated from the diagonal form of the EFG (defined by the $V_{zz}$ and $\eta$ fit parameters) by

using the corresponding Euler angle fit parameters that bring the CFS into the **EFG** eigensystem. Similarly, **g** and **A** are respectively the electron gyromagnetic tensor and the hyperfine magnetic interaction tensor expressed in the *xyz* system, as calculated from their diagonal form they have in their respective eigensystem (defined by the respective fit parameters of $g_{xx}$, $g_{yy}$, $g_{zz}$ and $A_{xx}$, $A_{yy}$, $A_{zz}$) by taking into account the corresponding Euler angle fit parameters that bring the *xyz* CFS system into their respective eigensystem. $\mathbf{S}_{100}$, $\mathbf{S}_{010}$ and $\mathbf{S}_{001}$ are the spin operators associated with the base vector directions of the cubic system, as calculated by taking into account the Euler angle fit parameters that bring the cubic system into the *xyz* CFS system. The fit model is described with the following parameters.

| **Parameter name** | **Meaning** | **Associated quantity** with notations taken from the above expression. |
|---|---|---|
| AMPLITUDE | Area of the subspectrum.<br>(Regardless of whether AREA or AMPLITUDE calculation mode is set.) | |
| ISOMER SHIFT | Isomer shift. | |
| Vzz (EFG) [10^21 V/m2] | Main component of the electric field gradient tensor expressed in its eigensystem, given in units of $10^{21}$ V/m$^2$. | Influences $V_{ij}$ |
| ETA | Asymmetry parameter of the EFG. | Influences $V_{ij}$ |
| D [1/cm] | Multiplier of the — second order — axial term of the CFH that can describe uniaxial distortion of the cubic crystal field. | $\frac{D}{100hc}$ |
| E/D | Relative value of the multiplier of the rhombic term of the CFH with respect to that of the axial term ($D$). It can describe a rhombic distortion of the cubic crystal field. (Rhombicity parameter.) | $\frac{E}{D}$ |
| a [1/cm] | Multiplier of the cubic term of the CFH that describes the effect of a cubic crystal field. It is converted to energy unit in the actual calculations. | $\frac{a}{100hc}$ |
| F [1/cm] | Multiplier of the — fourth order — axial term of the CFH that can account for a contribution to the uniaxial distortion of the cubic crystal field. | $\frac{F}{100hc}$ |
| Axx [T] | *xx* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | Influences **A** |
| Ayy [T] | *yy* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | Influences **A** |
| Azz [T] | *zz* diagonal element of the hyperfine magnetic interaction tensor in its eigensystem. | Influences **A** |
| gxx | *xx* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | Influences **g** |
| gyy | *yy* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | Influences **g** |
| gzz | *zz* diagonal element of the electron gyromagnetic tensor expressed in its eigensystem. | Influences **g** |
| 2S+1 (multiplicity) | $2S+1$ where $S$ is the effective spin. Can take on integer values from the range 1…6. Set it to 1 in order to model a diamagnetic ion ($S = 0$). | $2S+1$ |
| Coupled (0) / Decoupled (1) | Set it to 0 to perform the calculations by taking into account the coupled electronic and nuclear Hamiltonian directly as given above. Set it to 1 in order to treat the electronic part of the Hamiltonian as being decoupled from the nuclear part as described on page 72. | |
| Accuracy level | Sets the accuracy of calculations by influencing the resolution of the spherical integral. Possible values are in the range of 0…4. Default value is 0 (automatic accuracy setting). See page 73 for the meaning of the different accuracy levels. | |
| LINE WIDTH | FWHM of the Lorentzian peaks building up the spectra. | |
| THETA (g) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **g** tensor. See Euler rotations on page 82. | Influences **g** |
| PHI (g) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **g** tensor. See Euler rotations on page 82. | Influences **g** |
| GAMMA (g) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **g** tensor. See Euler rotations on page 82. | Influences **g** |
| THETA (A) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| PHI (A) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| GAMMA (A) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **A** tensor. See Euler rotations on page 82. | Influences **A** |
| THETA (EFG) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| PHI (EFG) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| GAMMA (EFG) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the *xyz* CFS system into the eigensystem of the **EFG** tensor. See Euler rotations on page 82. | Influences $V_{ij}$ |
| THETA (CFS) | Euler angle θ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |
| PHI (CFS) | Euler angle φ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |
| GAMMA (CFS) | Euler angle γ (expressed in deg) where $\mathbf{R}_{\theta\varphi\gamma} \equiv \mathbf{R}_z(\gamma)\mathbf{R}_z(\varphi)\mathbf{R}_y(\theta)$ brings the cubic system into the *xyz* CFS system. See Euler rotations on page 82. | Influences $\mathbf{S}_{100}$, $\mathbf{S}_{010}$, $\mathbf{S}_{001}$ |

Concerning the Euler angles that define the orientation of the *xyz* CFS system with respect to the cubic system [100, 010, 001] in which the cubic crystal field term is expressed, the corresponding Euler angle values of {THETA (CFS), PHI (CFS), GAMMA (CFS)} = $\{\arccos(1/\sqrt{3}), 45^\circ, -45^\circ\}$ realize the situation preset for the Trigonal PHS models (see pages 76 and 80), where the *z* axis of the CFS system points in the (1,1,1) cube diagonal direction of the cubic system. These Euler angles are also automatically set by MossWinn when one changes a **PHS Trigonal** model to the more general **PHS Angle** model.

By default the model is initialized according to isotropic **g** and **A** tensors ($g_{zz} = g_{yy} = g_{xx}$, $A_{zz} = A_{yy} = A_{xx}$ ), which constraints can be lifted (one by one) by pressing on the name of the constrained parameters with the left mouse button.

In the case of the PHS Angle models the spherical integration is performed over all the four $z \geq 0$ spherical octants regardless of the actual value of the fit parameters.

## *27.6.9.* Fast relaxation PHS models

The models listed in the first column of the table below are fast relaxation limit counterparts of the previously treated slow relaxation models. They treat the same Hamiltonian as their slow relaxation counterpart, but only in a decoupled manner, and in the fast relaxation limit, as explained on page 72. The number and the meaning of the fit parameters are also the same in the fast and slow relaxation cases.

| **Fast relaxation PHS model name** | **Slow relaxation PHS model counterpart** |
|---|---|
| PHS 1/2 (Powder, EMF, Decoupled, Fast R.) | PHS 1/2 (Powder, EMF, Slow R.) (see page 78) |
| PHS (Powder, EMF, Decoupled, Fast R.) | PHS (Powder, EMF, Slow R.) (see page 79) |
| PHS Trigonal (Powder, EMF, Decoupled, Fast R.) | PHS Trigonal (Powder, EMF, Slow R.) (see page 80) |
| PHS Angle (Powder, EMF, Decoupled, Fast R.) | PHS Angle (Powder, EMF, Slow R.) (see page 82) |

## 27.7. Absorption line shapes

In MossWinn the following functions can be selected as the line shape of the absorption lines:

| | |
|---|---|
| **Lorentzian**<br><br>**(LOR)** | For AMPLITUDE calculation mode:<br>$$\frac{\Gamma^2}{4}\cdot\frac{Amplitude}{(v-IS)^2+\frac{\Gamma^2}{4}}$$<br>For AREA calculation mode:<br>$$\frac{\Gamma}{2\pi}\cdot\frac{Area}{(v-IS)^2+\frac{\Gamma^2}{4}}$$ |
| **Pseudo-Voigt**<br><br>**(PVOI)** | The Pseudo-Voigt line shape approximates the Voigt line profile, which latter is resulted by the convolution of a Lorentzian line ( l(y) ) with a Gaussian line profile ( g(x-y) ):<br>$$V(x)=\int_{-\infty}^{\infty} l(y)\cdot g(x-y)\cdot \mathrm{d}y$$<br>This line shape can describe small distributions in the measured sample (e.g. quadrupole splitting distribution). The MossWinn program uses the Pseudo-Voigt Line Shape described in the paper: W. I. F. David: *J. Appl. Cryst.* **19** (1986) 63-64.<br>When the Pseudo-Voigt line shape is selected for a subspectrum, then the former line width parameters will determine the line width (FWHM) of the Gaussian that takes part in the convolution above. The Lorentzian line width is then added to the parameter list of the subspectrum as an additional parameter.<br>If the subspectrum model contains more than one absorption line, then they all can have different Gaussian line widths, but all of them will share the same Lorentzian line width. The value of this common Lorentzian line width in this case should be close to the line width obtained by fitting a spectrum corresponding to a caliber (e.g. α-iron foil) which was measured using the same radioactive source. The remaining width of the individual lines in the spectrum will be present then in the Gaussian line and will be characteristic of the distribution of Mössbauer nuclides in the measured sample.<br>By setting the Lorentzian Line Width of the Pseudo-Voigt function to zero one obtains a perfect Gaussian line shape that can be used to decompose previously calculated distributions.<br>In AMPLITUDE calculation mode the amplitude type parameters will denote the height of the Pseudo-Voigt peak. In AREA calculation mode the amplitude type parameters will denote the area of the Pseudo-Voigt peak. |
| **Lorentzian with dispersion**<br><br>**(LOR-DI)** | If there is a considerable interference between the nuclear resonance absorption of γ rays and the atomic photoelectric effect (most pronounced in the case of E1 type nuclear transitions), then a so called "Dispersion term" appears in the Mössbauer absorption line. The resulting line shape can be expressed as follows (see for example F.E. Wagner, B.D. Dunlap, G.M. Kalvius, H. Schaller, R. Felscher, H. Spieler: *Phys. Rev. Lett.* **28** (1972) 530. and D.J. Erickson, M.W.J. Prins, L.D. Roberts: *Phys. Rev. C* **8** (1973) 1916.):<br><br>For AMPLITUDE calculation mode:<br>$$\frac{\Gamma^2}{4}\cdot\frac{Amplitude\cdot\left(1-2\cdot\xi\cdot(v-IS)\cdot\frac{2}{\Gamma}\right)}{(v-IS)^2+\frac{\Gamma^2}{4}}$$<br>For AREA calculation mode:<br>$$\frac{\Gamma}{2\pi}\cdot\frac{Area\cdot\left(1-2\cdot\xi\cdot(v-IS)\cdot\frac{2}{\Gamma}\right)}{(v-IS)^2+\frac{\Gamma^2}{4}}$$<br>where $\xi$ is called "**DISPERSION AMPLITUDE**" in MossWinn. |

Table continued on the next page.

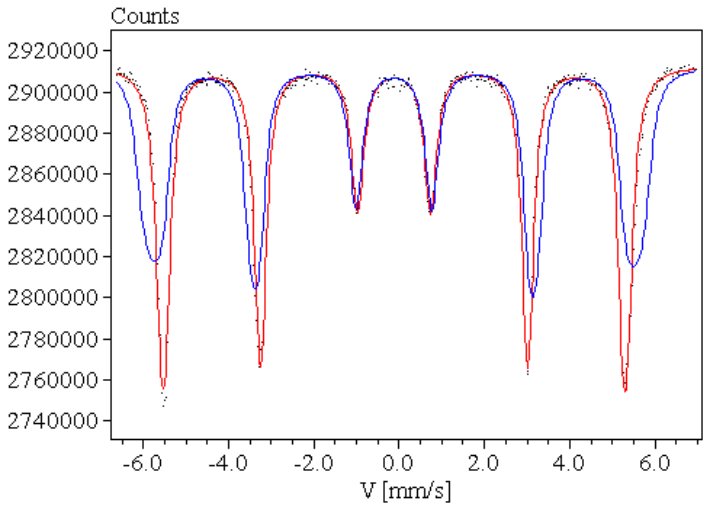
**Lorentzian with Cosine smearing**

**(LOR-CS)**

This line shape is available only in thin absorber approximation mode. The smeared Lorentzian line shape can be used to model ***cosine broadening*** caused by geometrical effects. MossWinn fits the line shape described by D. Crespo and J. Parellada in *Hyp. Int.* **29** (1986) 1539. (Eq. 3). This line shape is exact in the case of a point source moving along the line defined by the center of a circular absorber, placed normally and coaxially to the source velocity, and the point source itself. However, as the authors point out in the above paper, this line shape works well even if the conditions are not exactly those mentioned above.

In the case of this smeared Lorentzian line shape the amplitude, area and percentage values displayed or printed by MossWinn are exactly those which you would get for a Lorentzian line if cosine smearing was not present in the spectrum. That is, apart from possible f factor differences, relative areas in this case reflect the relative occurrence of Mössbauer nuclides in different microenvironments just as in the case of Lorentzian lines when Cosine broadening is not present. At the same time the area values are not equal to the apparent spectral area.

When smeared Lorentzian is selected as line shape in MossWinn, a new parameter **— VISUAL ANGLE [deg] —** will be added to the parameter list of the subspectrum in question. This is the visual angle of the absorber or the detector aperture (which is smaller depending on the actual geometrical conditions) viewed from the point source. Certainly, in real geometrical conditions this value will be only some kind of average mainly because the source always has a finite diameter, which often makes it differ strongly from the ideal picture of a point source. An example of the cosine broadened line shape can be seen below.




$^{57}$Fe Mössbauer spectrum of alpha iron recorded using bad geometrical conditions. The red curve has been calculated using the „Lorentzian with Cosine smearing" line shape (Visual Angle=16°). The blue curve shows the case when Visual Angle=30°.

In AMPLITUDE calculation mode the amplitude type parameters will denote the height of the corresponding Lorentzian peak. This may deviate from the actual, apparent height of the peak. In AREA calculation mode the amplitude type parameters will denote the area of the corresponding Lorentzian peak. This may deviate from the actual, apparent area of the peak.

## 27.8. Thin Absorber Approximation and Transmission Integral

To change between the calculation modes of thin absorber approximation (**Thin A.**), transmission integral (**T-INT**) and transmission integral with special source line shape, select a parameter from the parameter list of the background. As a result, in the place of the former Line Shape Popup box, the actual calculation mode (Thin A., T-INT, TI-L2) will be displayed. Press on the box to change the calculation mode.

In thin absorber approximation mode the spectra are calculated by adding (in REFLECTION mode) / subtracting (in TRANSMISSION mode) the absorption lines to / from the background. The transmission integral mode is available only for TRANSMISSION mode. In transmission integral mode the calculation assumes an infinitely thin source, and is carried out in the following way.

First the absorption lines are calculated as in the case of the thin absorber approximation mode, but without subtraction from the baseline. In the resulting curve, denoted below as $A(v)$, the absorption peaks point upwards. $A(v)$ gets then normalized to have a full area equal to

$$\int_{-\infty}^{+\infty} A(v)\cdot dv = \frac{\pi}{2}\cdot \Gamma_0$$

where $\Gamma_0$ equals to the Lorentzian line width (full width at half maximum) of the corresponding nuclear transition (for $^{57}$Fe, for example, $\Gamma_0$ equals to 0.097 mm/s). The resulting normalized function, $A_n(v)$, is then used to calculate the transmission spectrum, $N(v)$, in the following way.

$$N(v) = N(\infty)\cdot((1-b)\cdot\frac{T(v)}{T(\infty)}+b)$$

where

$$T(v) = (1- f_S + f_S\cdot\int L_S(w-v,\Gamma_S)\cdot \mathrm{e}^{-\tau\cdot A_n(w)}\cdot \mathrm{d}w)$$

where the source line shape is expressed as follows, depending on the selected calculation mode:

| Selected transmission integral calculation mode | Source line shape |
|---|---|
| 'Transmission Integral' (T-INT) | $L_S(w-v,\Gamma_S) = \frac{\Gamma_S}{2\pi}\cdot\frac{1}{(w-v)^2+\frac{\Gamma_S^2}{4}}$ |
| 'TI source function…' → Squared Lorentzian (TI-L2)<br>Note that this source line shape may be useful in the analysis of spectra recorded with a $^{57}$Fe Synchrotron Mössbauer Source, as described in G.V. Smirnov, A.I. Chumakov, V.B. Potapkin, R. Rüffer, S.L. Popov: *Phys. Rev. A* **84** (2011) 053851.<br><br>For the case of traditional laboratory Mössbauer spectroscopy the previous option (T-INT) should be used. | $L_S(w-v,\Gamma_S) = \pi\Gamma_S\left(\frac{\Gamma_S}{2\pi}\cdot\frac{1}{(w-v)^2+\frac{\Gamma_S^2}{4}}\right)^2$ |

$N(v)$ = The envelope of the fitting curve
$N(\infty)$ = BASE LINE of the Background parameter list.
$b$ = Background fraction of γ quanta [0..1].
$\tau$ = Effective thickness of the absorber ( > 0 ).
$f_S$ = Mössbauer-Lamb factor of the source [0..1].
$\Gamma_S$ = Full width at half maximum (FWHM) of the Lorentzian peak function associated with the source. Note that in the case of the squared Lorentzian source line shape the FWHM of the source line can be expressed as $\Gamma_S\sqrt{\sqrt{2}-1} \approx 0.6436\,\Gamma_S$ . The fit parameter "Source Line Width" in the FIT menu of MossWinn refers to $\Gamma_S$ .

$T(\infty)$ – Note that due to the omission of the exponential factor—that would express non-resonant atomic absorption—in the above definition of $T(v)$, in the above case $T(\infty) = 1$.

The **effective thickness** of the absorber can be calculated on the basis of the formula $\tau = f_a n_a \sigma_0$, where $f_a$, $n_a$ and $\sigma_0$ denote, respectively, the probability of recoilless nuclear resonance absorption of resonant γ radiation by Mössbauer nuclei in the absorber (recoilless fraction), the surface density of the number of resonant nuclei (e.g. $^{57}$Fe) of the absorber in the path of the γ rays, and the maximum cross section for the resonant absorption per Mössbauer nucleus (e.g. $\sigma_0 \approx 256\times10^{-20}$ cm$^2$ for $^{57}$Fe).

When **hyperfine parameter distributions** are fitted in conjunction with the transmission integral, then MossWinn includes a parameter named "**Filter cutoff**" into the parameter list of the "Base Line". The value of this parameter determines the cutoff "frequency" of the noise filter function used to derive the distribution curve. Its value should remain in the range of 0…1. Fit this parameter together with the rest of the fit parameters in order to set its optimal value. Fitting of spectra with lower S/N ratio (i.e. with larger — relative — magnitude of the statistical noise) will in general result in a *Filter cutoff* value that is closer to zero.

The relative area fractions of subspectra modeling a hyperfine parameter distribution are automatically constrained with a percentage parameter when transmission integral is used to calculate the model.

Concerning the transmission integral analysis of spectra with hyperfine parameter distributions, see

Z. Klencsár: *AIP Conference Proceedings* **1622** (2014) 30.

Note that the above form of the transmission integral does not take into account effects related to the polarization of the absorber. MossWinn allows the use of corresponding models (including, among others, models for single crystals and samples with magnetic polarization) together with the above form of the transmission integral, but for polarized thick absorbers this approach may fail to reproduce the apparent spectral shape with good accuracy. In this regard, see

J.M. Williams, J.S. Brooks: *Nucl. Instr. Meth.* **128** (1975) 363-372.

and references therein.

**References**

G.K. Shenoy, J.M. Friedt, H. Maletta, S.L. Ruby: Curve Fitting and the Transmission Integral: Warnings and Suggestions, in *Mössbauer Effect Methodology*, Volume **9**, (Edited by I.J. Gruverman, C.W. Seidel, D.K. Dieterly) pp. 277

S.Margulies, J.R.Ehrman: *Nucl. Inst. Meth.* **12** (1961) 131.

S.Margulies, P.Debrunner, H.Frauenfelder: *Nucl. Inst. Meth.* **21** (1963) 217.

A. Vértes, D.L. Nagy (eds.): *Mössbauer Spectroscopy of Frozen Solutions*, Akadémiai Kiadó, Budapest (1990) pp. 34.

## 27.9. The Parameters page

The **Parameters Page** occupies the left side of the **FIT** menu. It displays the parameters of the fitted model grouped according to different schemes. To select a scheme, LMC the GROUP BOX in the left upper corner, and select the required scheme. Available schemes are the followings.

| | |
|---|---|
| **Group by Subspectra** | The parameters will be grouped by subspectra. After the parameter groups of the VELOCITY AXIS (present only when calibration is being performed) and the BACKGROUND, the subspectra are listed one after the other. For each subspectra first the amplitude type parameters, then the position type parameters, then the line width type parameters, and at last the extra parameters are displayed. Each subspectrum has its own color that corresponds to the color used to draw the subspectrum on the spectrum graph. In case of simultaneous fitting of spectra the color of the subspectra are determined individually for each spectrum. That is, shared subspectra do not have necessarily the same color in each of the spectra. However, shared subspectra have the same name in all of the spectra where they exist. |
| **Group by Parameter** | The parameters will be grouped by their type. First the amplitude type parameters, then the position type parameters, then the line width type parameters, and at last the extra parameters are displayed. In each of the type-groups the parameters belonging to the same subspectrum follow each other. |
| **Group by Name** | The parameters will be grouped by their type first, then they will be ordered according to their name. First the amplitude type parameters, then the position type parameters, then the line width type parameters, and at last the extra parameters are displayed. In each of the type-groups the parameters follow each other in alphabetical order. |

In addition, the option of '**Show/Hide Subspectrum Name**' enables the showing/hiding of the headlines of subspectra on the parameters page. The box, right beside the Group box, displays the number of the current spectrum and the number of the simultaneously fitted spectra in the following form:

**„S"** ***Serial number of the current spectrum displayed / Number of the spectra fitted simultaneously***

When simultaneous fit of several spectra are performed, press on this box to order the fitted spectra in accordance with the following options. Note that by default the spectra are ordered according to the value of the special parameter TEMPERATURE [K].

| | |
|---|---|
| **Order spectra according to file name** | The spectra will be ordered alphabetically according to their file name. |
| **Order spectra according to parameter** | The submenu of this menu item will list the parameters of shared subspectra. Select one of the parameters to have spectra ordered in an ascending manner with respect to the value of the selected parameter. |
| **Order spectra according to special parameter** | The submenu of this menu item will list the special parameters the spectra can be characterized with. Select one of the special parameters to have spectra ordered in an ascending manner with respect to the value of the special parameter in question. Special parameters can be defined via the **Special parameters...** submenu option of the **SET** menu box in the main menu (see page 28). |
| **Reset original spectrum order** | Select this option in order to reset the original order of spectra that was set automatically when the FIT menu was entered. |

The spectrum order set up via the above options will influence the order in which the spectra will follow each other when the **TAB** and **Backspace** keys are pressed, the order in which the spectra follow each other on the "All Spectra" tab, as well as the order in which spectra will appear on images printed to printer or copied to the clipboard.

The box right beside displays the number of fitted parameters in the following form:

**„P”** ***Number of fitted parameters***

Press on this box in order to access the following options related to the fixing/unfixing of fit parameters (see also section 27.10). (The fix status of nuclear and user-defined extra parameters—if any—will not be altered by selecting the options below.)

| | |
|---|---|
| **Fix all parameters for the current spectrum** | Turn to this option in order to ensure that all the fit parameters influencing the fit model set for the current spectrum becomes fixed to their current value. The status of the parameters will change as follows (see 27.10).<br><br>Free (darkgray) → Fixed (red)<br>Shared (blue) → Independently fixed shared (red)<br>Sharefixed (magenta) → Sharefixed (magenta) (i.e. no change) |
| **Unfix all parameters for the current spectrum** | Turn to this option in order to ensure that all the fit parameters influencing the fit model set for the current spectrum become unfixed, i.e. variable during a fit, with the exception of parameters that are either sharefixed (see 27.10) in case of simultaneous fitting, or are required to remain fixed inherently by the calculations (such as, e.g., the smoothing factor in the case of unrestricted hyperfine field distributions, see 27.17). The status of the parameters will change as follows.<br><br>Fixed (red) → Free (darkgray)<br>Independently fixed shared (red) → Shared (blue)<br>Independently fixed sharefixed (red) → Sharefixed (magenta)<br>Sharefixed (magenta) → Sharefixed (magenta) (i.e. no change) |
| **Reverse fix status of parameters for the current spectrum** | Turn to this option in order to reverse the fixed status of parameters contributing to the model set for the current spectrum. The status of the parameters will change as follows.<br><br>Free (darkgray) ↔ Fixed (red)<br>Shared (blue) ↔ Sharefixed (magenta)<br>Independently fixed shared (red) ↔ Independently fixed sharefixed (red) |

In the case of simultaneous fitting of multiple spectra, the following options are also available.

| | |
|---|---|
| **Fix all parameters for all of the spectra** | Turn to this option in order to fix all parameters for all of the simultaneously fitted spectra. The status of the parameters will change as follows.<br><br>Free (darkgray) → Fixed (red)<br>Shared (blue) → Sharefixed (magenta)<br>Independently fixed shared (red) → Independently fixed sharefixed (red) |
| **Unfix all parameters for all of the spectra** | Turn to this option in order to unfix all parameters for all of the simultaneously fitted spectra. The status of the parameters will change as follows.<br><br>Fixed (red) → Free (darkgray)<br>Independently fixed shared (red) → Shared (blue)<br>Independently fixed sharefixed (red) → Shared (blue)<br>Sharefixed (magenta) → Shared (blue) |
| **Reverse fix status of parameters for all of the spectra** | Turn to this option in order to reverse the fix status of all parameters for all of the simultaneously fitted spectra. It will result in the following status changes.<br><br>Free (darkgray) ↔ Fixed (red)<br>Shared (blue) ↔ Sharefixed (magenta)<br>Independently fixed shared (red) ↔ Independently fixed sharefixed (red) |

Further, rights beside there are two tabs for the following two tab pages:

| Bars | StD |
|---|---|
| After the parameters bars are displayed that can be used to set the values of parameters. LMC the bar and move the mouse left or right to change the value of the parameter inside the range defined by the constraints of the parameter in question, and monitor the changes in the corresponding subspectrum continuously on the Spectrum Page. **To increase the maximum of the parameter, draw the corresponding bar beyond its maximum and, without releasing the left mouse button, press the right mouse button until the required maximum is reached.** To modify the minimum, draw the bar beyond its minimum towards the left, and modify the minimum by pressing the right mouse button without releasing the left one. | *During fitting:*<br><br>When a parameter changes during fitting, the difference between its new value and old value is displayed after its new value.<br><br>*After CAL STD has been clicked:*<br><br>After the parameters their standard deviation values are displayed according to the current state of the fit. |

When parameters are grouped by subspectra with their headline enabled, each subspectrum starts with a headline showing its name and its relative area fraction (%). Press on this headline in order to access the options available also via the shapes before the corresponding parameters, as detailed below.

On the left of each parameter a colored rectangle or a colored circle is displayed. **Subspectra with rectangles** are non-shared subspectra that are present only in the current spectrum. **Subspectra with circles** are shared subspectra that are present in two or more of the simultaneously fitted spectra. Shared subspectra have always the same structure in all of the simultaneously fitted spectra that they exist in. That is, if the theory/interaction of a shared subspectrum is changed in the current spectrum, then it will also change for all of the corresponding shared subspectra in all other simultaneously fitted spectra. In contrast, the theory/interaction of unshared subspectra can be set independent from any other subspectra. Furthermore, shared subspectra can have shared parameters, whereas unshared ones cannot.

Click on a rectangle to choose one of the following options:

| | |
|---|---|
| **Rename subspectrum: #Subspectrum Name** | To rename the selected subspectrum. |
| **Add one more subspectrum of this type** | To add an identical (non-shared) subspectrum to the fit model. |
| **Add subspectrum to all other spectra** | The selected subspectrum will be added to all of the simultaneously fitted spectra, and all of them will be shared with the selected one. |
| **Rejoin subspectrum to existing sharing** | The selected subspectrum will be joined to similar shared subspectra in other simultaneously fitted spectra. Use this option for subspectra that were unshared via *"Unshare Subspectrum in this spectrum only"***.** |
| **Delete subspectrum: #Subspectrum Name** | To remove the selected subspectrum from the current model. |
| **Join #Spectrum Name . #Subspectrum Name to:** | To join the selected subspectrum to one of the similar subspectra (shared or yet unshared) in another simultaneously fitted spectrum. |

Click on a circle to choose one of the following options:

| | |
|---|---|
| **Rename subspectrum: #Subspectrum Name** | To rename the selected subspectrum. |
| **Add one more subspectrum of this type** | To add an identical shared subspectrum to the fit model. The new subspectrum will appear in the model of those spectra that include the subspectrum to be duplicated. |
| **Unshare subspectrum in all of the spectra** | The selected subspectrum, as well as all the subspectra that are shared with it in other spectra, will be disconnected from each other, so that they will be independent, i.e. "*Unshared*". |
| **Unshare subspectrum in this spectrum only** | The selected subspectrum will get unshared in the current spectrum, so that it can be changed independently of the subspectra it was earlier shared with. (Use *„Rejoin Subspectrum to existing sharing"* to rejoin the selected subspectrum to the shared subspectra it was shared with.) |
| **Delete subspectrum: #Subspectrum Name** | To remove the selected subspectrum from the model of one or more simultaneously fitted spectra. |
| **Share #Spectrum Name . #Subspectrum Name with:** | To share the selected subspectrum with one of the similar (yet unshared) subspectra in another simultaneously fitted spectrum. |

Independent of whether the subspectrum is shared or not, the following menu items may also be available.

| | |
|---|---|
| **Fix all subspectrum parameters** | Turn to this option in order to ensure that all the fit parameters influencing the corresponding subspectrum become fixed. In the case of simultaneous fitting of multiple spectra, the actual way the parameters become fixed will depend on whether the procedure is to be carried out only for the current spectrum or for all of the simultaneously fitted spectra. (The program will raise the corresponding question when applicable.)<br><br>When the procedure is carried out only for the current spectrum, the following status changes will take place.<br><br>Free (darkgray) → Fixed (red)<br>Shared (blue) → Independently fixed shared (red)<br><br>When the procedure is carried out for all the fitted spectra, the following status changes will take place.<br><br>Free (darkgray) → Fixed (red)<br>Shared (blue) → Sharefixed (magenta, see 27.10) |
| **Unfix all subspectrum parameters** | Turn to this option in order to set fit parameters influencing the corresponding subspectrum to unfixed. In the case of simultaneous fitting of multiple spectra, the actual effect of the function will depend on whether the procedure is to be carried out only for the current spectrum or for all of the simultaneously fitted spectra. (The program will raise the corresponding question when applicable.)<br><br>When the procedure is carried out only for the current spectrum, the following status changes will take place.<br><br>Fixed (red) → Free (darkgray)<br>Independently fixed shared (red) → Shared (blue)<br>Independently fixed sharefixed (red) → Sharefixed (magenta)<br>Sharefixed (magenta) → Sharefixed (magenta) (i.e. no change)<br><br>When the procedure is carried out for all the fitted spectra, the following status changes will take place.<br><br>Fixed (red) → Free (darkgray)<br>Independently fixed shared (red) → Shared (blue)<br>Independently fixed sharefixed (red) → Shared (blue)<br>Sharefixed (magenta) → Shared (blue) |
| **Constrain parameters to be equal to those of** | Select a subspectrum appearing as a subitem of this menu option in order to constrain parameter values of the subspectrum (whose headline was pressed) to be equal to those of corresponding parameters in the subspectrum selected as subitem. The constraints are also set up for associated shared subspectra (if any). |
| **Fit only this subspectrum** | Turn to this option in order to fit only those fit parameters that belong either to the corresponding subspectrum or (in case of simultaneous fit of spectra) to associated shared subspectra (if any). |
| **Fit all but this subspectrum** | Turn to this option in order to fit only those free fit parameters that belong neither to the corresponding subspectrum nor to associated shared subspectra (if any). |
| **Copy peak positions and areas to clipboard** | Turn to this option in order to copy to the Windows clipboard a list of comma-delimited numerical data regarding the positions and areas of the individual peaks contributing to the selected subspectrum. For each of the peaks the following information is included in a single row as simple text:<br><br>• Position of the center of the peak,<br>• Absolute area associated with the peak (skipped for transmission integral fits),<br>• Area fraction of the peak with respect to the area of the whole subspectrum,<br>• Relative area of the peak with respect to the peak with the lowest non-zero area.<br><br>In the case of transmission integral fits, after the peak position only the thin-absorber limit area fraction and relative area are included in the copied list. The menu option is not available for subspectra describing arbitrary-profile parameter distributions and for subspectra calculated according to relaxation theories or auxiliary libraries. |
| **including information on nuclear states** | Select this submenu option in order to include in the output information on nuclear states involved in the nuclear transitions leading to the peaks of the subspectrum. This option is available only for subspectra calculated according to static Hamiltonian models having “M+Q” or “Q+M” in their name. See http://www.mosswinn.hu/help/nsnt.gif for details. |

On the bottom of the Parameters Page there are the following boxes available.

| | |
|---|---|
| **DOWN / UP** | To scroll the parameter list by one parameter. |
| **PAGE DOWN / PAGE UP** | To scroll the parameter list by one subspectrum. |
| **CHI**<br>Weighted squared deviation (Chisquare)<br>Simple squared deviation<br>Absolute deviation<br><br>Do not ignore zero points for current spectrum<br><br>Ignore zero points for all fitted spectra | To select the fitness function that is minimized during the fitting process. To have the chi-square as fitness function, zero points must be ignored in all of the simultaneously fitted spectra.<br><br>For the current spectrum zero points will be considered when the fitness function is calculated.<br><br>For all of the simultaneously fitted spectra the zero valued data points will be ignored when the fitness function is calculated. |
| **LINFIT** | LMC to adjust the *amplitude type parameters of the current spectrum* to their optimal values.<br><br>RMC to adjust the *amplitude type parameters of all the simultaneously fitted spectra* to their optimal values. |
| **AREA / AMPLITUDE** | To change between Area and Amplitude modes. For linear models these modes influence the meaning of the amplitude type parameters via influencing the calculation of individual absorption lines. For details see page 103. |
| **TRANSMISSION / REFLECTION** | To select the geometry of the measurement. From the point of view of the calculations, it determines whether the absorption peaks of the calculated model are subtracted (transmission mode) or added (reflection mode) to the Background. |
| **EXIT** | LMC to leave the **FIT** menu and keep all distributions (if any).<br><br>RMC to leave the **FIT** menu and does not keep any distributions. |

Above these boxes the fitness function value is displayed, which value belongs to the group of the simultaneously fitted spectra as a whole. When this function is the chi-square, then the meaning of the numbers is the following:

**CHI:** CHISQUARE **(**NORMALIZED CHISQUARE**) [**GOODNESS OF FIT**]**

## 27.10. Fixing and releasing parameters, the meaning of different parameter colors

To fix the value of a parameter, click on its name with the left mouse button. Its color will change to red. To release it, click with the left mouse button on its name again. Its color will change to dark gray again. The following table explains the meaning of various parameter colors.

| Color of Parameter | Meaning |
|---|---|
| Dark gray | The parameter is free and it is fitted. |
| Red | The parameter is fixed, and it is not fitted. (It can be a fixed non-shared parameter, an independently fixed shared parameter or an independently fixed sharefixed parameter.) |
| Brown | The value of the parameter depends on that of another parameter(s). Click on its name to see how it depends on the other parameter(s). |
| Blue | The parameter shares a common value with corresponding parameters in other spectra. The common value is fitted. (So called **shared** parameter.) (To add a new spectrum to the current fit — in order to initiate simultaneous fitting of spectra — click on the **ADD** box and select **NEW SPECTRUM TO FIT...**) |
| Magenta | The parameter shares a common value with corresponding parameters in other spectra. The common value is fixed, not fitted. (So called **sharefixed** parameter.) |
| White | The parameter is subjected to a distribution: the corresponding subspectrum is calculated as the sum of several subspectra, each corresponding to a different value of the parameter in question. The corresponding distribution curve — whose X axis will display equally spaced values of the parameter in question, and whose Y axis will display the corresponding subspectrum weights — can be made to become displayed on one of the Insight pages. |

## 27.11. Simultaneous fitting of Mössbauer spectra

To perform simultaneous fitting of several Mössbauer spectra, proceed as follows.

- Load all the spectra — to be fitted simultaneously — onto the same project desk.
- Select one of them to be the (red-framed) master window and enter the FIT menu.
- Set the required fit model for the spectrum.
- Select **Add → New Spectrum to fit** and then one of the remaining spectra to be added to the simultaneous fit, or '**More at once...**' in order to add more spectra in one step.
- Use the **TAB** and the **BACKSPACE** keys to select the simultaneously fitted spectra successively one after the other, or press with the right mouse button on the spectrum image on the 'Spectrum' tab to select a spectrum directly.

Simultaneous fitting of Mössbauer spectra provides the advantage that one can fit several Mössbauer spectra at once, with a common set of fitting parameters. Consequently, parameters of models (belonging to different spectra) that are related to each other — for some physical reason — does not need to be fitted independently, but they can be cross referenced to reduce the number of fitting parameters and to obtain a result that is better balanced in the rest of the parameters.

In MossWinn one has the possibility to cross-reference — or in general to relate — any two fitting parameters to each other. This can be done in the following way. Select the parameter that should be related to another parameter that is, the value of the selected parameter should be influenced by the value of another parameter that is to be selected yet. (A parameter is THE SELECTED parameter, when it is selected in the Parameters List box on the Model Page.) Click on the CONSTRAIN POPUP box and select the type of constraint (e.g. **:= #PARAMETER**). From the list of parameters, appearing on the left, select the parameter that should be the basis of the constraint. If the required parameter is not among those listed, then select MORE PARAMETERS… that will bring up a form where one can select any parameter of any of the subspectra in any of the simultaneously fitted spectra.

The procedure of defining all the necessary cross-references, however, may be time consuming in this way when numerous Mössbauer spectra are fitted simultaneously. Therefore a more powerful concept has also been developed in MossWinn. This is **the concept of Shared and Unshared subspectra**.

Unshared subspectra are independent from any other subspectrum, and its parameters can be cross-referenced with other parameters only in the way described above.

In contrast, **Shared subspectra** are present in two or more spectra, always having the same structure (theory/interaction, line shape etc.) in all of the spectra that they exist in. Shared subspectra, at the same time, provide a very simple way to cross-reference its parameters to the corresponding parameters of the corresponding subspectrum in other spectra. The following cross-reference types are available.

| **Type of cross reference** | **How to ACTIVATE cross reference** |
|---|---|
| The parameter should have the same value in all of the spectra in which the corresponding shared subspectrum exists. This value should be fitted. | Click on the name of the parameter with the right mouse button. When its color gets blue then the cross reference has been activated, and the corresponding parameter — if the corresponding subspectrum exists — gets blue in all other spectra as well. |
| The parameter should have the same value in all of the spectra in which the corresponding shared subspectrum exists, and this value should be fixed. | Perform the step above to make the parameter cross referenced, and its color to get blue. Then click on its name with the left mouse button and select:<br><br>FIX THIS PARAMETER IN ALL OF THE SPECTRA |

| **Type of cross reference** | **How to DEACTIVATE** |
|---|---|
| The parameter should have the same value in all of the spectra in which the corresponding shared subspectrum exists. This value should be fitted. | Click on the name of the parameter with the right mouse button, and select one of the followings.<br><br>Select<br>UNSHARE PARAMETER IN THIS SPECTRUM ONLY<br>to decouple the selected parameter from the others which latter will remain shared/cross referenced.<br><br>Select<br>UNSHARE THIS PARAMETER IN ALL OF THE SPECTRA<br>to completely eliminate the activated cross reference among the corresponding parameters. |
| The parameter should have the same value in all of the spectra in which the corresponding shared subspectrum exists, and this value should be fixed. | Click on the parameter with the left mouse button and select<br><br>UNFIX THIS PARAMETER IN ALL OF THE SPECTRA<br>(The parameters will remain cross referenced, but fixing will be lifted.) |

In general, to change or lift a cross reference, click on the name of the cross-referenced parameter with the left or right mouse button, and select the required option.

To add an Unshared subspectrum to the current spectrum only, select ADD → NEW SUBSPECTRUM on the Model Page. To add a Shared subspectrum to all of the simultaneously fitted spectra, select ADD → NEW SHARED SUBSPECTRUM instead.

Shared and Unshared subspectra can be differentiated on the basis of the drawing before their parameters. Before the name of their parameters, UNSHARED subspectra are denoted by rectangles, and SHARED subspectra are denoted by circles. In each of the simultaneously fitted spectra the first subspectra after the background are the Shared subspectra in alphabetical order of their names. The Shared subspectra are then followed by the Unshared ones.

## *27.12. Fitness functions of the fit*

One can choose from three different fitness functions in the **FIT** menu of MossWinn by the help of the CHI menu box (see page 93). During fitting the program searches then for the parameter vector which minimizes the selected fitness function.

| | |
|---|---|
| **CHISQUARE** | Mössbauer spectra encountered in practice suffer from nearly normally distributed statistical noise. In this case the maximum likelihood estimator of a fit is the chi-square quantity:<br>$$\chi^2(\underline{v}) = \sum_{i=1}^{h} \frac{(W_i - f_i(\underline{v}))^2}{W_i}$$<br>Where $W_i$ denotes the counts in the *i*th channel of the Mössbauer spectrum, $h$ is the number of channels, and $f_i$ is the value of the fitting function (e.g. sum of Lorentzians subtracted from the *Base Line*) corresponding to the *i*th channel of the spectrum. MossWinn also displays the quantities called NORMALIZED CHISQUARE, and GOODNESS OF FIT.<br>**Normalized Chisquare = Chisquare / Degree of freedom**<br>**Degree of freedom = Fitted-channel number – Fitted-parameter number**<br>For **GOODNESS OF FIT** see:<br>W.H.PRESS, B.P. FLANNERY, S.A. TEUKOLSKY, W.T. VETTERLING:<br>*NUMERICAL RECIPES, THE ART OF SCIENTIFIC COMPUTING*<br>CAMBRIDGE UNIVERSITY PRESS, CAMBRIDGE, NEW YORK (1990) |
| **SQUARED DEVIATION** | $$\text{Squared deviation}(\underline{v}) = \sum_{i=1}^{h} (W_i - f_i(\underline{v}))^2$$<br>Where $W_i$ denotes the counts in the *i*th channel of the Mössbauer spectrum, $h$ is the number of channels and $f_i$ is the value of the fitting function corresponding to the *i*th channel of the spectrum. |
| **ABSOLUTE DEVIATION** | $$\text{Absolute deviation}(\underline{v}) = \sum_{i=1}^{h} \left|W_i - f_i(\underline{v})\right|$$<br>Where $W_i$ denotes the counts in the *i*th channel of the Mössbauer spectrum, $h$ is the number of channels and $f_i$ is the value of the fitting function corresponding to the *i*th channel of the spectrum. |

## 27.13. The Spectrum Page

In the right bottom corner of the FIT menu the **Spectrum Page** can be seen. The SPECTRUM TAB shows the current spectrum with the subspectra corresponding to the current model. Click on the spectrum graph with the right mouse button to select another simultaneously fitted spectrum (if any). Press TAB / BACKSPACE on the keyboard to make the next / previous spectrum displayed — even during fitting. To make the residual displayed above the spectrum, press R or SHIFT+R on the keyboard. Click on the RESIDUAL TAB to make the spectrum and the residual to be displayed below each other. They are separated with a stripe that can be moved to resize the two windows. Additionally three Insight pages are available on the Spectrum page (Insight A, B, C). To change between the tabs in the Spectrum page during fitting, position the mouse pointer above the Spectrum page, and press space on the keyboard.

In high resolution GUI mode two additional tabs appear on the Spectrum page. Select the **All Spectra** tab in order to display all the simultaneously fitted spectra. Press with the right mouse button on any of the displayed spectra for additional options. Select the **Insights** tab in order to display all the insight pages. Press with the right mouse button on any of the displayed insight pages for additional options.

At the bottom of the spectrum page the fitness function value for the current spectrum is displayed. When the fitness function is the chi-square, then the meaning of the numbers is the following:

**CHI:** CHISQUARE **(**NORMALIZED CHISQUARE**) [**GOODNESS OF FIT**]**

Above the fitness function values there is a light-gray stripe that displays information on the current spectrum. Click on this stripe to change the type of the displayed information or the attributes of the spectrum graphics via the menus of the appearing popup. The menu option of **OPEN HTML FITLOG** of the same popup can be used to open the HTML FitLog created previously for the current spectrum. The FitLog (if exists) is opened in the default web browser application.

## 27.14. The Insight Pages

The INSIGHT PAGES (A, B, C, D, E, F) can be used to display simultaneously fitted spectra, distribution curves, and the dependence of any parameter of a shared subspectrum on a special parameter or on another parameter of any other shared subspectrum. All the six insight pages have equivalent functionality in this regard. **Insight F** does not have its own separate page, but it can be visualized on the **Insights** tab, as well as on the extra screen area gained on the **Model page** in high resolution GUI modes.

To set the parameter whose values should serve as the X axis of the graph on the current insight page, click on the popup box after the letters „**X:**”, and select one of the options. If a spectrum or a distribution is selected, then the content of the other axis will be set automatically. Otherwise, click on the popup box after the letters „**Y:**”, and select the parameter that should serve as the Y values of the function to be displayed.

A typical application of insight pages is to display the isomer shift of a shared subspectrum as a function of temperature for several simultaneously fitted spectra that were measured on the same material but at different temperatures. (Turn to the option “Add => Extra Fit Parameter” in order to add the “Temperature [K]” parameter to the parameter list of the background.)

If a single spectrum is fitted, then the only meaningful functionality of an insight page is to display a distribution curve belonging to one of the distribution-based subspectra or cumulatively to all the VBF/xVBF subspectra of the fitted model.

The content of the insight pages can be saved as an ASCII data file via the menu option “Save => Save Insight Page...”. One can turn to this option in order to export cumulative VBF/xVBF distributions (see section 27.5) from MossWinn. Press with the right mouse button on any of the insight pages for additional options.

In order to have error bars — associated with fit parameter values — displayed on graphs set up for the insight pages, calculate the standard deviation (σ) of parameters by pressing on the **Cal StD** box on the **Functions page** (see page 98). The error bars extend ±1σ from the respective data points.

## 27.15. The Functions Page

In the center of the **FIT** menu the FUNCTIONS PAGE can be seen with blue colored menus. The table below lists the functionality of the various boxes on the Functions Page.

| | |
|---|---|
| **GLOBAL** | Click on the GLOBAL box to perform an infinite global search for the optimum solution using Evolution Algorithm. During this global search the values of parameters will remain in the range determined by their constraint list as displayed in the constraints list box on the Model Page. For simple models one can use global search to automatically set appropriate initial parameter values for the local search (fine tuning) procedure. For complicated models, however, it can be used to perform a long lasting search for a solution better than that already found. If it does not find a better solution, then with high probability there does not exists any better solution.<br>**Press the ESC key on the keyboard to finish the global search.** |

| | |
|---|---|
| **FIT** | LMC<br>Click with the left mouse button on the FIT box to initiate a local search (fine tuning) for the best set of fit parameters with high precision, using FITTING METHOD A. When the fit converges, the local search ends automatically. Press the ESC key on the keyboard to finish the local search any time before.<br><br>RMC<br>Click with the right mouse button on the FIT box to select one of the following options.<br><br>**FIT USING METHOD A** – Equivalent to the LMC of the FIT box.<br>**FIT USING METHOD B** – Method B performs a local search for the best parameter set just as Method A, but it displays interim results more frequently than Method A. Method B, at the same time, converges slower than Method A.<br>**LINEAR FIT AMPLITUDES –** The optimal value of Amplitude type parameters will be set for the current spectrum.<br>**FIT CURRENT SPECTRUM ONLY –** Fits only those fit parameters that belong to the current spectrum. (Uses Method A)<br>**FIT SPECTRA SEQUENTIALLY –** Fits spectra one after the other, sequentially. (Uses Method A) Shared parameters are fitted only for one of the spectra.<br>**FIT ONLY AMPLITUDES –** Fits only Amplitude type parameters. (Uses Method A)<br>**FIT ONLY POSITIONS –** Fits only position type parameters. (Uses Method A)<br>**FIT ONLY LINE WIDTHS –** Fits only Line Width type parameters. (Uses Method A)<br>**FIT ONLY EXTRA PARAMETERS –** Fits only extra parameters. (Uses Method A) |

| | |
|---|---|
| **CAL STD** | LMC<br>Click with the left mouse button on the Cal StD box to calculate the standard deviation of fit parameters via the inversion of the curvature matrix after a convergent fit was carried out. The matrix is approximated either via the 1st derivatives of the fit envelope or the 2nd derivatives of the chisquare depending on the option selected via the "Configuration settings..." submenu of the SET menu (in the main menu, see page 28). When **Weighted squared deviation (Chisquare)** is selected as fitness function (see page 93), the program takes the variance of individual counts to be equal to the value of the counts. In other cases a uniform variance of the counts is estimated on the basis of a hypothetical normal distribution of the counts around the fit envelope curve.<br><br>RMC<br>Click with the right mouse button on the CAL STD box to select one of the following options.<br><br>**Copy correlation matrix to clipboard** - Turn to this option in order to copy the correlation matrix of fit parameters into the clipboard. The correlation matrix becomes recalculated each time the StD of parameters is calculated via the inversion of the curvature matrix. As the output format of the correlation matrix the following options are available.<br>**As image (for all spectra)** - The correlation matrix will be copied into the clipboard as a grayscale bitmap. All the fitted spectra are considered.<br>**As image (for current spectrum)** - The correlation matrix will be copied into the clipboard as a grayscale bitmap. Only those fit parameters are considered, that belong to the fit model of the current spectrum.<br>**As image (value limited, for all spectra)** - The correlation matrix will be copied into the clipboard as a |

grayscale bitmap. Only those fit parameters are considered that display correlation values higher than or equal to the value set by the user on the appearing dialog box.

**As text (for all spectra)** - The correlation matrix will be copied into the clipboard as a table given as comma delimited text. All the fitted spectra are considered.

**As text (for current spectrum)** - The correlation matrix will be copied into the clipboard as a table given as comma delimited text. Only those fit parameters are considered, that belong to the fit model of the current spectrum.

**As text (value limited, for all spectra)** - The correlation matrix will be copied into the clipboard as a table given as comma delimited text. Only those fit parameters are considered that display correlation values higher than or equal to the value set by the user on the appearing dialog box.

**Save correlation matrix** - Turn to this option in order to save the correlation matrix of fit parameters as a GIF image file that is optimal for being inspected by the help of web browsers. As the output format of the correlation matrix the following options are available.

**As GIF image (for all spectra)** - The GIF image of the correlation matrix is saved by considering all the fitted spectra.

**As GIF image (for current spectrum)** - The GIF image of the correlation matrix is saved by considering only those fit parameters that belong to the fit model of the current spectrum.

**As GIF image (value limited, for all spectra)** - The GIF image of the correlation matrix is saved by considering only those fit parameters that display correlation values higher than or equal to the value set by the user.

**APPROXIMATE STD VIA 1ST DERIVATIVES** - Calculates standard deviation of the fit parameters via the approximation of the curvature matrix on the basis of the numerical approximation of the 1st derivatives of the fit model envelope with respect to the fit parameters. This method is in general faster and more reliable than the method based on the chisquare 2nd derivatives.

**APPROXIMATE STD VIA 2ND DERIVATIVES** - Calculates standard deviation of fit parameters via the approximation of the curvature matrix on the basis of the numerical approximation of the 2nd derivatives of the chisquare quantity with respect to the fit parameters. This method is susceptible to failure when the fit involves hyperfine parameter distributions.

**APPROXIMATE STD VIA MONTE CARLO ITERATIONS –** Standard deviation values will be estimated using Monte Carlo iterations. This procedure can be time consuming, but it provides the well balanced standard deviation values of any of the fit parameters as well as of corresponding derived parameters such as the $S_0$, $S_1$ and $S_2$ invariants (see page 53). The number of iterations to be taken can be selected in the appearing popup. To finish calculations, press ESC on the keyboard. This method calculates the reliability of distributions as well.

**CLEAR STD VALUES –** Select this option in order to clear the calculated standard deviation values of the fit parameters.

**APPROXIMATE RELIABILITY OF DISTRIBUTIONS –** Assuming all the fitting parameters to be fixed to their current value, this method calculates the reliability of distributions (if any) using a Monte Carlo procedure. It generates model spectra from the envelope of the current fit by simulating normal statistical noise, and adding it to the envelope. Then for the resulted model spectrum the distributions will be calculated. On any of the insight pages displaying a distribution one red and one blue curve will appear beside the black one. At any points of the distribution the red curve denotes the maximum probability value encountered by fitting the model spectra, while the blue curve denotes the minimum probability value encountered. At points where the blue curve displays zero probability, there could as well be zero probability in the original distribution curve if the measurement would be repeated. So that in all that points either the non-zero value of the distribution curve, or the position of the corresponding peak cannot be taken seriously. In this way one can avoid to interpret small peaks in the distribution curve, which peaks are only a consequence of the normal noise of the Mössbauer spectrum. Note, that while this method does not take into account the uncertainty in the fit parameters (as they are kept fixed during the calculations) it provides a valuable result in a short time. To calculate the blue and red curves more precisely, the APPROXIMATE STD VIA MONTE CARLO ITERATIONS method can be used.

**RESET DISTRIBUTION GRAPHS** – Select to remove the red and blue curves from the distributions.

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|---|---|
| **ACCEPT** | LMC<br>Click on the ACCEPT box with the left mouse button in order to save the current state of the fit of the spectra to the spectrum files. Accepting of the fit is important, as MossWinn will try to extract the fit results from the spectrum files in various situations. Such a situation can be for example the creation of a table of the fit results in the **TBL** menu, or the refitting of the spectrum later on. When the fit is accepted, fits that were accepted earlier for the same spectrum, will be overwritten. Provided that the corresponding functionality (AUTOMATIC HTML FITLOG CREATION ON ACCEPT) is enabled (see page 28), an LMC on the Accept box will also save a HTML FitLog according to the current state of the fit.<br><br>RMC<br>Click with the right mouse button on the ACCEPT box to select one of the following options.<br><br>**Revert to previously accepted fit parameter values** - Turn to this option in order to reload the value of those actually defined fit parameters that were also included in the fit accepted previously via an LMC on the ACCEPT box. (The fit model itself is not reloaded.)<br><br>**Save HTML FitLog according to the present state** - Select this option to save a HTML FitLog to the FitLog file of the current spectrum, according to the current state of the fit. (See page 36 for further details concerning the name and location of the FitLog file.)<br><br>**Reload previously logged fit model...** - Select one of the submenus of this menu option in order to reload and set the corresponding fit model from the FitLog file associated with the current spectrum. The currently set fit model will be overwritten.<br><br>**Delete FitLog from log file...** - Select one of the submenus of this menu option in order to remove the corresponding FitLog from the FitLog file associated with the current spectrum.<br><br>**Delete all FitLogs but the last** - Select this menu option in order to remove all but the last saved FitLog from the FitLog file(s) associated with the current spectrum, or with all the fitted spectra. |

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| **PRINT** | Press on the PRINT menu box with the left mouse button in order to carry out the default print operation assigned to the PRINT menu box in the corresponding submenu of the SET menu box. Press on the PRINT menu box with the right mouse button in order to access one of the following options.<br><br>**Print fit results as text** - Select this option in order to print the textual fit report associated with one or more of the fitted spectra to the default printer. In order to send the print job to a different printer, select the printer in question from the appearing list.<br>**Print current spectrum** - Select this option in order to print the graph of the current spectrum either to the default printer, or to the selected one.<br>**Print current spectrum + distributions** - Select this option in order to print the graph of the current spectrum and those of the fitted distributions (if any) either to the default printer, or to the selected one. The graphs are all printed on the same page.<br>**Print fit results + spectrum + distributions** - Select this option in order to print either to the default or to the selected printer the textual fit report(s), and then on separate page (pages) the graph (graphs) of the spectrum (spectra) and fitted distributions (if any).<br>**Print all spectra** - Select this option in order to print the graph of all of the simultaneously fitted spectra on a single page by using either the default printer, or the selected one.<br>**Copy to clipboard as text** - Select this option in order to copy the textual fit report associated with the current spectrum to the clipboard of Windows.<br>**Copy all to clipboard as text** - Select this option in order to copy the textual fit report of all the simultaneously fitted spectra to the clipboard of Windows.<br>**Copy to clipboard as table for graphics** - Select this option in order to copy the fit results to the clipboard as comma-delimited text forming a table in which the parameters characterizing a particular spectrum are all listed in a single row, whereas each parameter - as well as each StD value - has its own column. This arrangement is especially useful for drawing the value of some parameter (e.g. isomer shift) as a function of another one (e.g. temperature) by the help of an external grapher program.<br>**Copy to clipboard as table for presentation** - Select this option in order to copy the fit results to the clipboard as comma-delimited text forming a table in which the parameters characterizing a particular spectrum are all listed in a single column, whereas each parameter has its own row. This arrangement is considered to be useful when creating tables for a presentation. |

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| | **Copy current spectrum to clipboard** - Select this option in order to copy the graph of the current spectrum to the clipboard of Windows according to the default settings attributed to Clipboard - single spectrum on the Printer Setup Dialog.<br>**Copy current spectrum + distributions to clipboard** - Select this option in order to copy the graph of the current spectrum and those of the fitted distributions (if any) to the clipboard of Windows.<br>**Copy all Insight Pages to clipboard** - Select this option in order to copy the graphical content of non-empty insight pages (if any) to the clipboard of Windows.<br>**Copy all spectra to clipboard** - Select this option in order to copy the graph of all the simultaneously fitted spectra to the clipboard of Windows.<br>**Save and open as HTML FitLog** - Select this option in order to save and open a HTML FitLog for one or more of the fitted spectra according to the current state of the fit. The FitLog file is saved to the folder that contains also the corresponding spectrum data file, and it is opened in the default web browser application. See pages 28, 36, 97 and 100 for further details concerning the functionalities related to HTML FitLogs.<br>**Save as simple text** - Select this option in order to save the fit report of the current spectrum as text file.<br>**Save all as simple text** - Select this option in order to save the fit report of all the simultaneously fitted spectra in the same text file one after the other.<br>**Save as table for graphics** - Select this option in order to save the fit results as comma-delimited text into a text file forming a table in which the parameters characterizing a particular spectrum are all listed in a single row, whereas each parameter - as well as each standard deviation value - has its own column. This arrangement is especially useful for drawing the value of some parameter (e.g. isomer shift) as a function of another one (e.g. temperature) by the help of an external grapher program.<br>**Save as table for presentation** - Select this option in order to save the fit results as comma-delimited text into a text file forming a table in which the parameters characterizing a particular spectrum are all listed in a single column, whereas each parameter has its own row. This arrangement is considered to be useful when creating tables for a presentation. |

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| **SET** | Click with the left mouse button on the Set box to select one of the following options.<br>**SPECTRUM PARAMETERS** - Select this option in order to set/modify spectrum parameters associated with the current spectrum.<br>**ISOMER SHIFT REFERENCE** - Select this option in order to set/modify the isomer shift of the isomer shift reference material (associated with the current source nuclide) relative to the corresponding standard IS reference material. The value given here is considered when the fitness of MIDB records is evaluated (with respect to the current spectrum) for example when the **FIND AND APPLY BEST MATCH** submenu option of the **DB** menu is selected.<br>**LINE WIDTHS…**<br>**CONSTRAIN ALL TO BE THE SAME** - All Lorentzian line width parameters in the model of the current spectrum will be cross-referenced to be always the same.<br>**SET ALL TO BE INDEPENDENT** - Cross references that relate line width type parameters to each other will be removed.<br>**PARAMETER BOUNDARIES…**<br>**SHARE FOR THE SELECTED PARAMETER** - Parameter boundaries set for the actually selected parameter will be transferred to the corresponding parameter (if it exists) in all other spectra that are fitted simultaneously.<br>**SHARE FOR POSITION AND WIDTH PARAMETERS** - Parameter boundaries set for position and width type parameters *in the actually selected subspectrum* will be transferred to the corresponding parameters (if they exist) in all other spectra that are fitted simultaneously.<br>**SHARE FOR ALL POSITION AND WIDTH PARAMETERS** - Parameter boundaries set for position and width type parameters *in the model of the actually selected spectrum* will be transferred to the corresponding parameters (if they exist) in all other spectra that are fitted simultaneously.<br>**STRETCH TO MAKE CURRENT PARAMETER VALUES VALID** - Parameter boundaries, that do not contain the current value of the corresponding parameter, will be extended so that all current parameter values will be valid.<br>**TRY PARAMETERS OF CURRENT SOLUTION FOR ALL OTHER SPECTRA** - Parameter values of shared subspectra in the current spectrum will be tried for another spectra. If a better fit is obtained, the corresponding parameter values will be transferred from the current spectrum to the other simultaneously fitted spectra. |

**IF LORENTZIAN WITH DISPERSION IS SELECTED AS LINE SHAPE…**

**SET IT ONLY FOR THE SELECTED SUBSPECTRUM** - When the user selects "Lorentzian with dispersion" as the line shape for a subspectrum, then only the subspectrum in question will be altered.

**SET IT FOR ALL THE SUBSPECTRA** - When the user selects "Lorentzian with dispersion" as the line shape for a subspectrum, then this line shape will be set for all the existing subspectra (recommended option).

**DISABLE SUBSPECTRUM CALCULATION FOR TRANSMISSION INTEGRAL** - In Transmission Integral mode formal subspectra are calculated. Select this option to disable the calculation of these formal subspectra, and speed up the calculation process.

**DETERMINE PARAMETER VALUES WITH A RELATIVE PRECISION OF** - In the appearing popup select the relative precision required for the fitted parameters. When during a fit the relative change in the fit parameters is less than this set value, then the fit terminates.

**ENABLE NEGATIVE AMPLITUDE/AREA VALUES** - Set this option to enable the setting of negative area and amplitude values.

**ENABLE NEGATIVE LINE WIDTH VALUES** - Set this option to enable the setting of negative line width values.

**REMOVE CALIBRATION OF THE CURRENT SPECTRUM** - Set this option to discard the calibration of the current spectrum. After that the X axis of the spectrum will display channel numbers rather than velocity values.

**SET GUI RESOLUTION...** – to alter and check on the internal MossWinn GUI (graphical user interface) screen resolution. See page 41 for associated options.

**CONFIGURATION SETTINGS...** – to set various configuration options influencing the operation of MossWinn.

**LEFT MOUSE CLICK ON THE PRINT BOX SHOULD…** - Several options are available for the default function of the PRINT box for the case when it is clicked with the left mouse button.

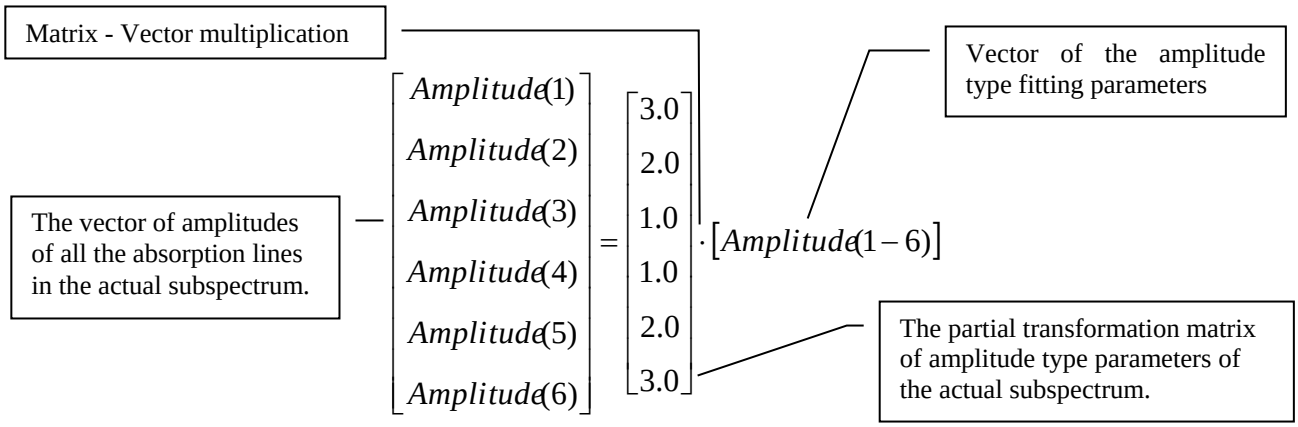
## *27.16. The Details Page*

Click on the **DETAILS** box on the MODEL PAGE to invoke the **DETAILS** page. This page can be used to fine tune linear models. Models based on Hamiltonian calculations cannot be modified in this way.

In the top of the DETAILS page there is a Subspectrum popup in which the current subspectrum can be selected. Below this popup there are three list boxes. The first one is a **PARAMETERS** list box in which the parameters of the current subspectrum are displayed, and the current parameter can be selected. Right beside there is the **AFFECTED LINES** list box which lists all the absorption lines belonging to the current subspectrum. The absorption lines that are influenced by the current parameter are selected blue; those not influenced by the current parameter are not selected. Further on the right there is the **MATRIX** list box that displays the matrix elements belonging to the partial transformation matrix of the current parameter in the current subspectrum. To each of the parameter types (Amplitude type, Position Type, Line Width type) there is an independent partial transformation matrix maintained. Whenever a zero value occurs among the matrix elements, the corresponding line will be deselected, as it is not influenced by the current parameter.

In the current subspectrum, the amplitudes of all the constituent absorption lines are calculated on the basis of the amplitude type parameters in the **PARAMETERS** list box. How this is done is explained in the followings.

To each of the amplitude type parameters belongs exactly one column in the partial transformation matrix of the Amplitude type parameters in the current subspectrum. The elements of this column can be seen in the **MATRIX** list box when the parameter is selected in the **PARAMETERS** list box. For the case of a sextet described by one amplitude type parameter for example, the partial transformation matrix has only one column, and the amplitudes of the absorption lines are calculated in the following way.

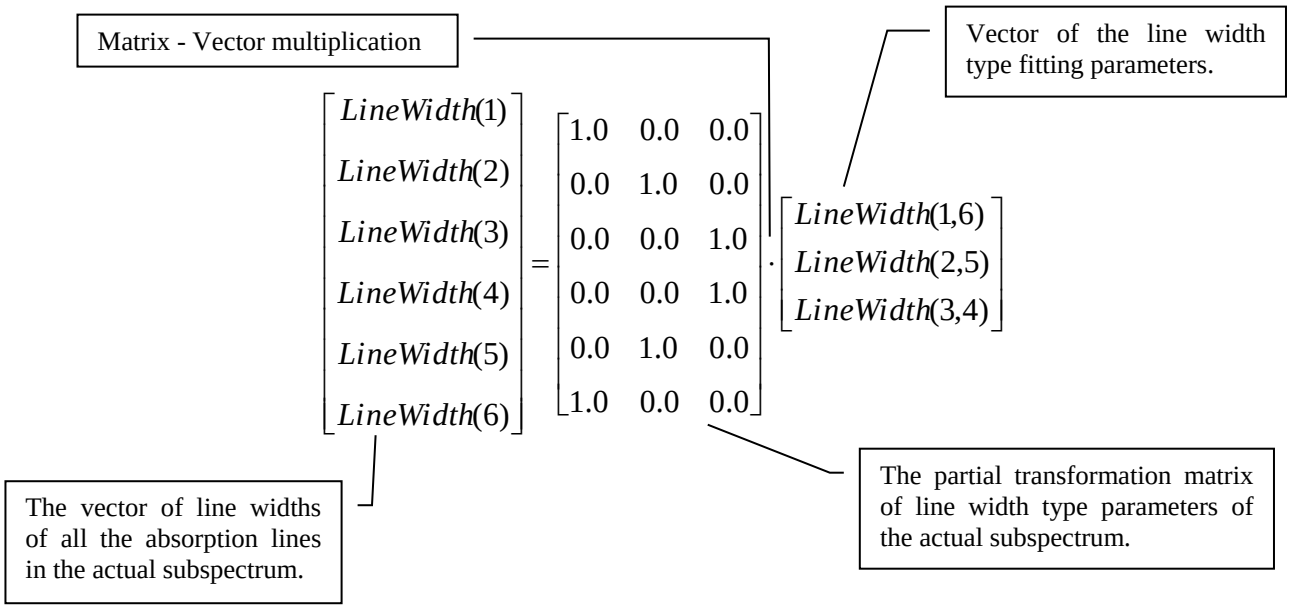


For the case of a sextet described by two amplitude type parameters (for single crystal) the multiplication looks like this:

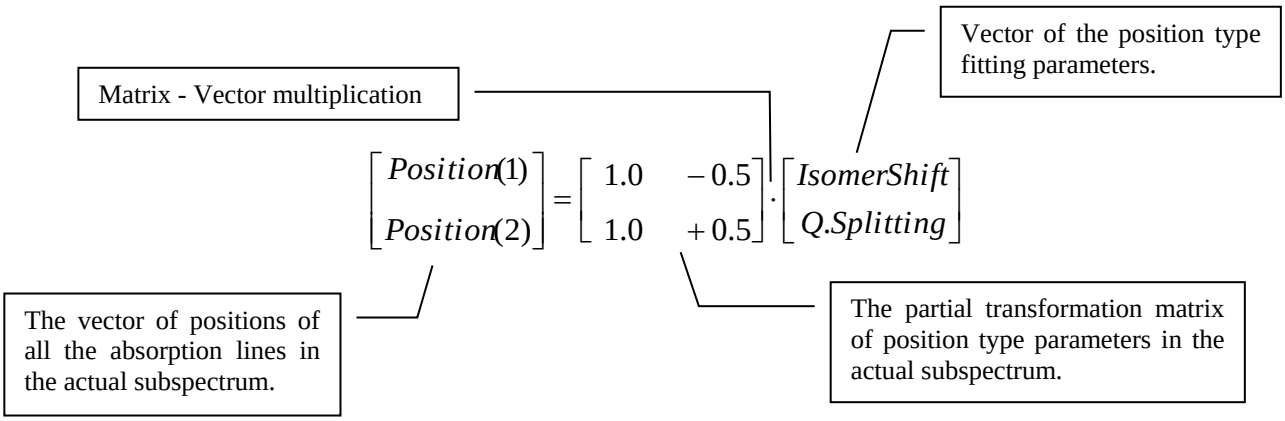
$$\begin{bmatrix} Amplitude(1) \\ Amplitude(2) \\ Amplitude(3) \\ Amplitude(4) \\ Amplitude(5) \\ Amplitude(6) \end{bmatrix} = \begin{bmatrix} 3.0 & 0.0 \\ 0.0 & 1.0 \\ 1.0 & 0.0 \\ 1.0 & 0.0 \\ 0.0 & 1.0 \\ 3.0 & 0.0 \end{bmatrix} \cdot \begin{bmatrix} Amplitude(1,3,4,6) \\ Amplitude(2,5) \end{bmatrix} = \begin{bmatrix} 3.0 \cdot Amplitude(1,3,4,6) \\ 1.0 \cdot Amplitude(2,5) \\ 1.0 \cdot Amplitude(1,3,4,6) \\ 1.0 \cdot Amplitude(1,3,4,6) \\ 1.0 \cdot Amplitude(2,5) \\ 3.0 \cdot Amplitude(1,3,4,6) \end{bmatrix}$$

In this latter case the ratio of the lines (1,6) and (3,4) is fixed to 3:1, and the amplitude of the lines (2,5) is independent from the amplitude of the lines (1,3,4,6).

The same works for position and line width type parameters as follows. For a sextet described with three different line width type parameters the partial transformation matrix and the corresponding multiplication looks like this:



The position of the lines in a quadrupole doublet is calculated from the position type parameters and the partial transformation matrix of position type parameters in the following way.




Readers familiar with the Transformation Matrix system of MossWinn version 2.0i may have already recognized that the system of partial transformation matrices works exactly like that of the Transformation matrix, but unlike Transformation matrices that describe a whole fit model with all of its subspectra, the sphere of operation of a partial transformation matrix is a certain type (amplitude, position or width) of parameters in a single subspectrum.

The elements of the partial transformation matrix can be changed in the **MATRIX** list box. To connect the amplitude of a certain absorption line to a certain amplitude type parameter, do the followings. Select the parameter in question in the **PARAMETERS** list box. The absorption line whose amplitude should be determined by the selected parameter is not selected yet in the **AFFECTED LINES** list box. To make the connection, click on the name of the absorption line in question with the left mouse button in the **AFFECTED LINES** box. As a result it will get selected blue, and at the same time it will be disconnected from the parameter that determined its amplitude earlier. The amplitude of the selected absorption line is now determined by the current amplitude type parameter. The very same procedure works for line width type parameters. MossWinn will change the name of parameters, and remove or add parameters automatically when it is required during these procedures.

To make an absorption line disconnected from a certain amplitude type / line width type parameter, click on its selected name in the **AFFECTED LINES** box. As a result a new amplitude type / line width type parameter will be added to the parameter list, which parameter will determine the amplitude / line width of the absorption line disconnected from the other parameter.

On the bottom of the **DETAILS PAGE** there are three boxes with the following options.

| | |
|---|---|
| HIDE | To hide the **DETAILS PAGE**. It can be invoked again by a LMC on the DETAILS box on the **MODEL PAGE**. |
| TOOLS | Further necessary tools to fine-tune linear models. |
| ADD POSITION TYPE PARAMETER | To add a new position type parameter to the current subspectrum. For example, to create the subspectrum of a doublet from the subspectrum of a singlet, one could add one absorption line to the subspectrum first, then add a new position type parameter (Q. Splitting) to the resulted subspectrum. After that the matrix elements belonging to the new position type parameter should be set to their correct values (−0.5 and +0.5 for the first and second lines, respectively). |
| REMOVE POSITION TYPE PARAMETER | To remove a position type parameter from the current subspectrum. |
| ADD ABSORPTION LINE | To add a new absorption line to the current subspectrum. |
| REMOVE ABSORPTION LINE | To remove an absorption line from the current subspectrum. |
| | These three options determine the content of the **DETAILS PAGE**. |
| SHOW MATRIX ELEMENTS | To show the **AFFECTED LINES** and **MATRIX** list boxes. |
| SHOW ENABLED INTERVALS | To show the enabled intervals for the current parameter. Here one can check how MossWinn compiled the constraints defined for the current parameter in the **CONSTRAINTS** list box on the **MODEL PAGE**. |
| SHOW INTERNAL VALUES | To show the values of internal variables belonging to the current subspectrum. It is intended to help the author to monitor the working of the program. Some notations are listed here, while others are not documented.<br><br>N - the number of the current parameter in the current subspectrum.<br>AN - The number of amplitude type parameters in the current subspectrum.<br>PN - The number of position type parameters in the current subspectrum.<br>WN - The number of width type parameters in the current subspectrum.<br>EN - The number of extra parameters in the current subspectrum.<br>DP - The serial number of the parameter that serves as the basis of a distribution.<br>P_LLW - The serial number of the extra parameter that determines the Lorentzian line width for PSEUDO-VOIGT line shapes.<br>P_VANGLE - The serial number of the extra parameter that determines the Visual Angle for LORENTZIAN WITH COSINE SMEARING line shapes.<br>CODE - Each subspectrum should have a different code number.<br>SHARED CODE - Subspectra with the same — nonzero — shared code are shared subspectra that are connected to each other. |

## *27.17. Fitting of hyperfine field distributions*

MossWinn is able to fit distributions of any position type parameter, of any subspectrum. Subspectra of distributions and subspectra of crystalline sites can be combined arbitrarily. The maximum number of distribution subspectra in one spectrum is 5. The maximum number of distribution data points altogether for five distributions is 360.

To fit a magnetic field distribution, for example, add a new subspectrum to the model. Then select the corresponding interaction — e.g. MAGNETIC (POWDER) in this case — in the **INTERACTIONS** popup box on the **MODEL PAGE**. Select the parameter named MAGNETIC FIELD [T] in the PARAMETERS LIST box on the **MODEL PAGE**. Then click on the popup box with the text CONSTRAIN, and select DISTRIBUTION / POSITIVE, ZERO LEFT & RIGHT BOUNDARIES (PZLRB). As a result, a magnetic field distribution becomes activated with an isomer shift independent from the magnetic field.

To activate correlations, select any of the position type parameters — in our case the ISOMER SHIFT parameter — in the PARAMETERS LIST box on the **MODEL PAGE**. Click again on the CONSTRAIN popup box, and go to the item **:= #PARAMETER * CONST1 + CONST2** , and select the parameter MAGNETIC (1) . MAGNETIC FIELD [T] from the appearing list of parameters. As a result, the ISOMER SHIFT parameter will depend linearly on the MAGNETIC FIELD [T] parameter, so that a distribution with linear correlation has been activated. The linear correlation coefficients are now added to the parameter list of the distribution subspectrum.

To see the distribution curve itself, go to one of the Insight pages, e.g. **INSIGHT D**, and select the activated distribution by clicking on the popup box after the **Y:** letters. The current state of the distribution curve will be displayed on the **INSIGHT PAGE D**. The displayed distribution curve will change continuously when the corresponding parameter values are changed.

The value of the distribution parameter — in our case MAGNETIC FIELD [T] — will be always equal to the weighted average of the corresponding distribution curve. For the parameters correlated with the distribution parameter a value will be displayed that is based on this weighted average of the distribution parameter.

When a model contains one or more distributions, and some of the subspectra are constrained by a percentage parameter, but there is at least one distribution that is not constrained by a percentage parameter, then MossWinn will add the parameter TOTAL AREA MULTIPLIER to the parameter list of the Background. The value of this parameter is used to derive the correct value of the total area under the spectrum from the total area estimated on the basis of the spectrum data points. This parameter can be fitted, but in normal situations its value should remain close to 1.0 . MossWinn estimates the total spectrum area in the following way in this case:

Total Spectrum Area = Total Area Multiplier * (Spectrum area estimated on the basis of the measured data points)

MossWinn calculates the distributions on the basis of a slightly modified version of the method of Hesse and Rübartsch [*]. This modification makes it possible to fit the SMOOTHING FACTOR when a strictly positive valued distribution is fitted. In the case of UNRESTRICTED distributions, which are derived exactly via the original method of Hesse and Rübartsch, the SMOOTHING FACTOR cannot be fitted.

When distributions are fitted in conjunction with the **transmission integral mode**, then distribution subspectra are automatically constrained by a percentage parameter, and a further parameter named "**Filter cutoff**" is added to the list of parameters. See page 87 for more details in this regard.

The data points of the distribution curves derived via the above described method constitute a **discrete probability distribution function**, and consequently the sum of their values is normalized to 1. Note that this is in contrast with the **VBF/xVBF** distribution curves (see page 63), which are presented by MossWinn via discrete samples of the corresponding (continuous) **probability density functions** having an *integral area* of 1.

[*] J. Hesse, A. Rübartsch: *J. Phys. E :Sci. Instr.* **7** (1974) 526.

## *27.18. How to complement MossWinn with user programmed functions*

One can add any function on the subspectrum level to the list of theories built into MossWinn by default. Thus, MossWinn's capabilities are not restricted to the built in theories, linear and Hamiltonian models, but it can fit any fitting function programmed and compiled by the user.

### *27.18.1.* How to compile a user written model function

To complement MossWinn with a custom model function, the source code of the function has to be written, and compiled to a library, by the user. It is recommended to use Borland/Inprise/CodeGear Delphi 2.0 or later 32 bit compilers to compile the written source code.

If the source code is written as outlined in this chapter, then the compiler will compile it as a Dynamic Link Library (DLL). This DLL should have a name corresponding to the mask **SUB*.DLL** . The file name of the library (without the path but including the extension) should not exceed 45 characters. (32 in versions released in 2020 or before.) When the compilation was successful, place the corresponding DLL library file in the folder **..\MossWinn 4.0\DLLs** . In order to access the functions of the new library, restart MossWinn or turn to the menu option **SET → Enable/disable libraries**.

One can fit a spectrum according to a model function included in a DLL by selecting the corresponding DLL function under the **EXTERNAL LIBRARIES** menu option of the **INTERACTIONS** popup box, on the **MODEL** page of the FIT menu. MossWinn identifies DLL code libraries on the basis of their file name. Consequently, if the code of a DLL with a given name is changed, models that contained a subspectrum taken from the old DLL will be changed as well.

Below an example is given for a library source code that can be compiled for example with Delphi 2007. The bold characters are in the file — named SUB_DLL_DEMO.PAS — itself, comments with non-bold characters are there only to explain the functionality of the procedures, they should not be included in the source file. The name of the procedures can start with **DLL** (as below) or, alternatively, with **DLL1, DLL2** or **DLL3**. It is important to use the variable type **ShortString** instead of string throughout the library.

```
library SUB_DLL_DEMO;

uses SysUtils,Classes;

{$R *.res}
```

The headline of the library.

```
procedure DLL_SET_INTERACTION_NAME(var s:ShortString;source:ShortString);export;
begin
 s:='Demo DLL';
end;
```

This is the first procedure in the library. Its job is to define the short name of the physical interaction, and to put it into the variable **s**. The name of the interaction can depend on the value of the **source** string variable, which contains the source string actually selected in MossWinn. It can have one of the following values:

57FE 119SN 151EU 125TE 121SB 129I 197AU 161DY 141PR 237NP M1/E1 M1+E2 E2

This procedure has the job to define a longer description for the interaction. It takes the **source** string as parameter, and returns the longer name of the interaction in the string **s**.

```
procedure DLL_SET_DESCRIPTION(var s:ShortString;source:ShortString);export;
var
  s2:ShortString;
begin
 DLL_SET_INTERACTION_NAME(s2,source);
 s:='1 SINGLET'+' ('+s2+')';
end;
```

This procedure has the job to set the following internal values of the subspectrum:

**AN** = Number of the amplitude type parameters.
**PN** = Number of the position type parameters.
**WN** = Number of the line width type parameters.
**NAME** = A descriptive name of the subspectrum.

Again, this procedure takes the **source** parameter, and the action taken may depend on it. Also a **P** pointer is passed to this routine, but this pointer should not be referenced, as in the present version its value is set to **NIL**.

```
procedure DLL_SET_SUBSPECTRUM_INTERNAL_VALUES(var AN,PN,WN:byte;var Name:ShortString;
                                              Source:ShortString;p:pointer);export;
begin
   AN:=1;
   PN:=1;
   WN:=1;
   Name:='DLL Singlet (1)';
end;
```

This procedure has the job to initialize parameters of the subspectrum. Its action again may depend on the value of the **source** passed to it. The **P** pointer should not be referenced; its value is **NIL**. The procedure takes the following input parameters:

**n** = The serial number of the parameter that should be initialized.
**Cmin** = The absolute minimum of the spectrum.
**Cmax** = The absolute maximum of the spectrum.
**Vmin** = The minimum of the velocity axis.
**Vmax** = The maximum of the velocity axis.

The procedure has to set the value of four variables:

**Name** = The name of the parameter.
**Minimum_Value** = A value which the parameter should exceed.
**Maximum_Value** = A value which the parameter should not exceed.
**Initial_Value** = A valid value for the parameter.

```
procedure DLL_SET_PARAMETERS_INTERNAL_VALUES(n:longint;Cmin,Cmax,Vmin,Vmax:double;
                                             var Name:ShortString;
                                             var Minimum_Value,Maximum_Value,
                                             Initial_Value:double;
                                             Source:ShortString; p:pointer);export;
begin
   Case n of
        1:begin
            Name:='Amplitude';
            Minimum_Value:=0.0;
            Maximum_Value:=abs(Cmax-Cmin)+2.0*sqrt(abs(Cmax));
            Initial_Value:=abs(Cmax-Cmin);
          end;
        2:begin
            Name:='Isomer Shift (T=300K)';
            Minimum_Value:=Vmin;
            Maximum_Value:=Vmax;
            Initial_Value:=(Vmin+Vmax)/2.0;
          end;
        3:begin
            Name:='Line Width';
            Minimum_Value:=0.2;
            Maximum_Value:=0.6;
            Initial_Value:=0.2;
          end;
   end;
end;
```

This procedure has the job to determine whether or not the individual parameters of the subspectrum are initialized in a fixed state. (Parameters that are initialized in a fixed state won't be fitted during spectrum fitting unless they are unfixed in advance manually by applying a left mouse button click on the parameter's name.) The action of the procedure may depend on the value of the **source** parameter passed to it. The procedure takes the following input parameters:

**n** = The serial number of the parameter for which the value of the fixed property should be set (in consistency with the procedure **DLL_SET_PARAMETERS_INTERNAL_VALUES**).
**Source** = the source string actually selected in MossWinn, with the possible values given further above.

The function can return the following values in the parameter **Result**:

**True**: Indicates that the parameter with index **n** should be initialized as a fixed parameter.
**False**: Indicates that the parameter with index **n** should be initialized as a free/fitted parameter.

```
function DLL_SET_PARAMETER_FIXED(n:longint;Source:ShortString):boolean;
begin
   Case n of
        1:Result:=False;
        2:Result:=False;
        3:Result:=False;
     else Result:=False;
   end;
end;
```

This procedure has the job to determine whether or not the individual parameters of the subspectrum are initialized in a hard-constrained state. (Parameters initialized as being hard-constrained cannot take on values outside of the enabled [**Minimum_Value,Maximum_Value**] interval set in the procedure **DLL_SET_PARAMETERS_INTERNAL_VALUES** above.) The action of the procedure may depend on the value of the **source** parameter passed to it. The procedure takes the following input parameters:

**n** = The serial number of the parameter for which the value of the hard-constrained property should be set (in consistency with the procedure **DLL_SET_PARAMETERS_INTERNAL_VALUES**).
**Source** = the source string actually selected in MossWinn, with the possible values given further above.

The function can return the following values in the parameter **Result**:

**True**: Indicates that the parameter with index **n** should be initialized as a hard-constrained parameter.
**False**: Indicates that the parameter with index **n** should not be initialized as a hard-constrained parameter.

```
function DLL_SET_PARAMETER_HARD_CONSTRAINED(n:longint;Source:ShortString):boolean;
begin
   Case n of
        1:Result:=False;
        2:Result:=False;
        3:Result:=False;
     else Result:=False;
   end;
end;
```

In the case when the subspectrum represented by the present DLL is chosen in place of another existing subspectrum (overwriting the model of the latter existing subspectrum with the one of the present DLL function, as opposed to the creation of a new, additional subspectrum), this procedure has the job to determine whether or not the individual parameters of the present DLL subspectrum may take the value and other attributes of the corresponding parameters of the original subspectrum. (For example, when replacing a doublet subspectrum with the present DLL singlet, one may want to copy the value and other attributes of the isomer shift parameter of the doublet as the corresponding attributes of the **'Isomer Shift'** parameter of the present DLL singlet.

The action of the procedure may depend on the value of the **source** parameter passed to it. The procedure takes the following input parameters:

**n** = The serial number of the parameter for which the value of the transfer property should be set (in consistency with the procedure **DLL_SET_PARAMETERS_INTERNAL_VALUES**).
**Source** = the source string actually selected in MossWinn, with the possible values given further above.

The function can return the following values in the parameter **Result**:

**True**: Indicates that the parameter with index **n** should take the value and other attributes of the corresponding parameter of the original subspectrum (which is replaced with the present DLL model).
**False**: Indicates that the parameter with index **n** should not take the value and other attributes of the corresponding parameter of the original subspectrum (which is replaced with the present DLL model).

MossWinn also considers the parameter names when deciding which parameter of the original subspectrum corresponds to the individual parameters of the present DLL subspectrum. It is therefore recommended to use parameter names—associated with the same physical meaning in different DLL subspectra—consistently.

```
function DLL_ALLOW_PARAMETER_VALUE_TRANSFER(n:longint;Source:ShortString):boolean;
begin
   Case n of
        1:Result:=False;
        2:Result:=True;
        3:Result:=True;
     else Result:=False;
   end;
end;
```

This function has the job to inform MossWinn about special parameters that should be appended to the parameter list of the baseline in order to be available to multiple DLL functions. Turn to this function if multiple DLL-based subspectra should depend on the value of a common fit parameter. MossWinn calls this function for **pcode** values of 1..32 (allowing to request up to 32 common special parameters) unless **Result** is set to **False**, after which no more calls are made. The action of the function may depend on the value of the **source** string passed to it.

The function takes the following parameters:

**pcode** = the index of the parameter whose name is to be returned. In the first call the value of **pcode** is 1, in the second call it is 2, and increasing so on up either until 32 or until the first index for which **Result** is set to **False**. The value of **pcode** determines the index of the given parameter in the double array whose address is passed as the value of the p pointer when calling the procedures **DLL_SET_SUBSPECTRUM** and **DLL_SET_AREA_OF_SUBSPECTRUM** (see below).
**source** = the source string actually selected in MossWinn, with the possible values given further above.

The function has to set the value of the following variable:

**aparname** = The name of the special parameter, to be set by the function as being associated with the index **pcode**, that needs to be appended to the parameter list of the baseline for common use by multiple DLL-based subspectra.

The function can return the following values in the parameter **Result**:

**True**: Indicates that the function was called successfully for the index **pcode**.
**False**: Indicates that the function did not succeed for the index **pcode**, and therefore it does not need to be called again, because there are not any more common special parameters requested.

```
function DLL_REQUEST_PARAMETER(pcode:longint;
                               var aparname:ShortString;
                               source:ShortString):boolean;
begin
   Result:=True;
   case pcode of
        1:aparname:='Temperature [K]';
        2:aparname:='dIS/dT [mm/s/K]';
     else Result:=False; {Important: This will stop the calling of this function.}
   end;
end;
```

One can use the above function in the following form if the DLL does not require common special parameters:

```
function DLL_REQUEST_PARAMETER(pcode:longint;
                               var aparname:ShortString;
                               source:ShortString):boolean;
begin
  Result:=False;
end;
```

This function has the job to set attributes of the common special parameters requested in the function **DLL_REQUEST_PARAMETER** above. These attributes are considered only when the requested parameter does not exist yet when the subspectrum associated with the present DLL is added to the fit model. MossWinn calls this function for **pcode** values of 1..32 (allowing to set corresponding attributes for up to 32 common special parameters) unless **Result** is set to **False**, after which no more calls are made. The action of the function may depend on the value of the **source** string passed to it.

The function takes the following parameters:

**pcode** = the index of the parameter whose attributes are to be set. The indexes associated with the requested parameters are determined by the **DLL_REQUEST_PARAMETER** function above. (In the present example **pcode** = 1 for **'Temperature [K]'** and **pcode** = 2 for **'dIS/dT [mm/s/K]'**.)
**source** = the source string actually selected in MossWinn, with the possible values given further above.

The function has to set the value of the following variables:

**pstartval** = The value of this parameter should be set to the requested starting value of the parameter having the index **pcode**.
**pmin** = The value of this parameter should be set to the requested minimum value of the parameter having the index **pcode**.
**pmax** = The value of this parameter should be set to the requested maximum value of the parameter having the index **pcode**.
**hardconstraint** = The value of this parameter should be set to **True** in order to make the [**pmin,pmax**] interval to be treated as a hard constraint (see page 38) for the parameter having the index **pcode**, or it should be set to **False** otherwise.

The function can return the following values in the parameter **Result**:

**True**: Indicates that the function was called successfully for the index **pcode**.
**False**: Indicates that the function did not succeed for the index **pcode**, and therefore it does not need to be called again, because there are not any more common special parameter attributes requested to be set.

```
function DLL_REQUEST_PARAMETER_ATTRIBUTES(pcode:longint;
                                          var pstartval,pmin,pmax:double;
                                          var hardconstraint:boolean;
                                          source:ShortString):boolean;
begin
   Result:=True;
   case pcode of
        1:begin pstartval:=300;pmin:=0.01;pmax:=1000;hardconstraint:=True;end;
        2:begin pstartval:=0.0;pmin:=-0.002;pmax:=0.0;hardconstraint:=True;end;
    else Result:=False;
   end;
end;
```

One can use the above function in the following form if the DLL does not require common special parameters:

```
function DLL_REQUEST_PARAMETER_ATTRIBUTES(pcode:longint;
                                          var pstartval,pmin,pmax:double;
                                          var hardconstraint:boolean;
                                          source:ShortString):boolean;
begin
  Result:=False;
end;
```

This procedure has the job to calculate the subspectrum. Its action again may depend on the value of the **source** string passed to it.

The procedure takes the following input parameters:

**AreaMode** = TRUE if the actual mode in MossWinn is the AREA mode. FALSE if the actual mode in MossWinn is the AMPLITUDE mode. The calculations may depend on the value of this Boolean variable.
**n** = The number of channels in the spectrum. The subspectrum has to be calculated for all the **n** channels.
**pPARAMETERS** = Pointer that points to the start address of a vector of floating point numbers of the type **DOUBLE**. Reference it as in the example below. It contains the values of the subspectrum parameters one after the other.
**pDATA** = Pointer that points to the start address of a vector of exactly **n** floating point numbers of the type **DOUBLE**. This is the data array, where the results of the calculations should be – not placed but – added. The subspectrum should be calculated and added with the absorption peaks pointing 'upwards', that is in positive direction. Do not change the content of this vector in any other way, because it may already contain the contribution of other subspectra.
**pVELOCITY** = Pointer that points to the start address of a vector of exactly **n** floating point numbers of the type **DOUBLE**. This is the data array that lists the velocity value for each channel one after the other.
**p** = Pointer that points to the start address of a vector of floating point numbers of the type **DOUBLE**. This is the data array that lists the actual values of the parameters requested in the function **DLL_REQUEST_PARAMETER** , with the parameter order being the same as given there.

```
procedure DLL_SET_SUBSPECTRUM(n:longint;
                              pPARAMETERS,pDATA,pVELOCITY:pointer;
                              AreaMode:boolean;Source:ShortString;p:pointer);export;
Type
 TARRAY = ARRAY[1..8191] of DOUBLE;
var
 PARAMETERS,DATA,VELOCITY:^TARRAY;
 RPA:^TARRAY;
 i:longint;
 x,y,v,A,ISH,IS300,LW,RPA_T,RPA_DISPDT:double;
begin

  PARAMETERS:=pPARAMETERS;DATA:=pDATA;VELOCITY:=pVELOCITY;RPA:=p;

  RPA_T:=RPA^[1]; {Temperature [K]}
  RPA_DISPDT:=RPA^[2]; {dIS/dT [mm/s/K]}

  A:=PARAMETERS^[1];if A<0.0 then A:=0.0;

  IS300:=PARAMETERS^[2];
  ISH:=IS300+RPA_DISPDT*(RPA_T-300);

  LW:=PARAMETERS^[3];if LW<=0.0 then LW:=0.001;
  y:=LW*LW/4.0;

  if AreaMode then
   begin
     for i:=1 to n do
      begin
         v:=Velocity^[i];
         x:=(v-ISH)*(v-ISH)+y;
         DATA^[i]:=DATA^[i]+(LW/(Pi+Pi))*A/x;
      end;
   end
   else
   begin
     for i:=1 to n do
      begin
         v:=Velocity^[i];
         x:=(v-ISH)*(v-ISH)+y;
         DATA^[i]:=DATA^[i]+y*A/x;
      end;
   end;
end;
```

This procedure has the job to calculate the area of the subspectrum solely on the basis of the subspectrum parameters and the requested parameters (if any). Its action again may depend on the value of the **source** string passed to it. The procedure takes the following input parameters:

**AreaMode** = TRUE if the actual mode in MossWinn is the AREA mode. FALSE if the actual mode in MossWinn is the AMPLITUDE mode. The calculations may depend on the value of this boolean variable.
**pPARAMETERS** = Pointer that points to the start address of a vector of floating point numbers of the type **DOUBLE**. Reference it as in the example below. It contains the values of the subspectrum parameters one after the other.
**p** = Pointer that points to the start address of a vector of floating point numbers of the type **DOUBLE**. This is the data array that lists the actual values of the parameters requested in the function **DLL_REQUEST_PARAMETER** , with the parameter order being the same as given there.

The procedure should set the value of the following variables:

**AREA** = This should be set equal to the subspectrum area that was calculated.
**CanDO** = Set it to TRUE if you can do the calculation of the subspectrum area on the basis of the subspectrum parameters. Set it to FALSE, and proceed like in the alternative solution below, if you cannot calculate the area of the subspectrum. The latter solution is much simpler, but results in a slower execution, because in this case MossWinn will calculate the subspectrum area by numerical integration.

```
procedure DLL_SET_AREA_OF_SUBSPECTRUM(var AREA:double;
                                      var CanDO:boolean;
                                      pPARAMETERS:pointer;
                                      AreaMode:boolean;Source:ShortString;
                                      p:pointer);export;
Type
 TARRAY = ARRAY[1..8191] of DOUBLE;

var
 PARAMETERS:^TARRAY;
 A,LW:double;
begin
  CanDO:=True;

  PARAMETERS:=pPARAMETERS;

  A:=PARAMETERS^[1];if A<0.0 then A:=0.0;

  if AreaMode then AREA:=A else
   begin
     LW:=PARAMETERS^[3];if LW<=0.0 then LW:=0.001;
     AREA:=A*LW*Pi/2.0;
   end;
end;

{An alternative solution:

procedure DLL_SET_AREA_OF_SUBSPECTRUM(var AREA:double;
                                      var CanDO:boolean;
                                      pPARAMETERS:pointer;
                                      AreaMode:boolean;Source:ShortString;
                                      p:pointer);export;
begin
   CanDo:=False;
end;

}
```

```
exports

  DLL_SET_INTERACTION_NAME,
  DLL_SET_DESCRIPTION,
  DLL_SET_SUBSPECTRUM_INTERNAL_VALUES,
  DLL_SET_PARAMETERS_INTERNAL_VALUES,
  DLL_SET_PARAMETER_FIXED,
  DLL_SET_PARAMETER_HARD_CONSTRAINED,
  DLL_ALLOW_PARAMETER_VALUE_TRANSFER,
  DLL_REQUEST_PARAMETER,
  DLL_REQUEST_PARAMETER_ATTRIBUTES,
  DLL_SET_SUBSPECTRUM,
  DLL_SET_AREA_OF_SUBSPECTRUM;

begin
end.
```

### *27.18.2.* How to complement MossWinn with an arbitrary cross-reference function

There is a possibility to complement the cross-reference options available in MossWinn with an arbitrary function programmed by the user. With the help of this option arbitrary functional dependence can be defined between parameters. That is, one parameter can be made to depend on one or more parameters via an arbitrary function. To define this custom functional dependence, the source file DEP_DLL1.PAS has to be modified and compiled by using a Borland/Inprise/CodeGear Delphi 2.0 or later 32 bit compiler. The resulted new file (named DEP_DLL1.DLL) should replace then the old DEP_DLL1.DLL . The default content of DEP_DLL1.PAS is listed below with notes explaining the job of the procedures. The source code below can be compiled, e.g., with Delphi 2007.

```
library DEP_DLL1;

uses SysUtils, Classes;

{$R *.res}
```

This procedure has the job to define a short name for the function.

```
Procedure DEPDLL1_SET_SHORT_NAME(var s:ShortString);export;
begin
  s:='Cubic';
end;
```

This procedure has the job to define a longer name for the function.

```
Procedure DEPDLL1_SET_LONG_NAME(var s:ShortString);export;
begin
  s:=':= User Programmed Function [ Cubic ]';
end;
```

This procedure has the job to define the number of extra parameters that are necessary to add to the list of parameters to make the function work.

```
Procedure DEPDLL1_SET_NUMBER_OF_EXTRA_PARAMETERS(var n:longint);export;
begin
  n:=4;
end;
```

This procedure has the job to define a short name for each of the extra parameters. The serial number of the extra parameter whose name should be put into the string **s** is given by the variable **n**.

```
Procedure DEPDLL1_SET_PARAMETER_NAME(var s:ShortString;n:longint);export;
begin
  Case n of
       1:s:='Constant';
       2:s:='Linear';
       3:s:='Quadratic';
       4:s:='Cubic';
  end;
end;
```

This procedure has the job to initialize each of the extra parameters, and to define their minimum and maximum values. The serial number of the extra parameter that should be initialized is given by the variable **n**.

```
Procedure DEPDLL1_INITIALIZE_PARAMETER(var value,min,max:double;n:longint);export;
begin
  Case n of

       1:begin
           Value:=0.0;
           min:=0.0;
           max:=1.0;
         end;

       2:begin
           Value:=0.0;
           min:=-1.0;
           max:=1.0;
         end;

       3:begin
           Value:=0.0;
           min:=0.0;
           max:=1.0;
         end;

       4:begin
           Value:=0.0;
           min:=0.0;
           max:=1.0;
         end;

  end;
end;
```

This procedure has the job to calculate the value of the parameter for which the cross reference was activated in MossWinn.

**pPARAMETERS** = pointer that points to the start address of (n+1) floating point numbers of the type **DOUBLE**, where n equals to the number of the extra parameters that was set by the procedure **DEPDLL1_SET_NUMBER_OF_EXTRA_PARAMETERS** . The (n+1)th parameter is the parameter that serves as the base of the cross reference (this is the parameter that was selected from the appearing sub-popup list of the **CONSTRAIN** popup).

The calculated value should be placed in the variable **x** .

```
Procedure DEPDLL1_SET_PARAMETER_VALUE(var x:double;pPARAMETERS:pointer);export;
Type
 TARRAY = ARRAY[1..8191] of DOUBLE;
var
 PARAMETERS:^TARRAY;
begin
PARAMETERS:=pPARAMETERS;
x:=PARAMETERS^[1]+PARAMETERS^[5]*(PARAMETERS^[2]+PARAMETERS^[5]*(PARAMETERS^[3]+Parame
ters^[5]*Parameters^[4]))
end;
```

The library should end like this.

```
exports

  DEPDLL1_SET_SHORT_NAME,
  DEPDLL1_SET_LONG_NAME,
  DEPDLL1_SET_NUMBER_OF_EXTRA_PARAMETERS,
  DEPDLL1_SET_PARAMETER_NAME,
  DEPDLL1_INITIALIZE_PARAMETER,
  DEPDLL1_SET_PARAMETER_VALUE;

begin
end.
```

# 28. The Mössbauer Line Sharpening menu

The nature of the fit model suitable for the analysis of a given Mössbauer spectrum is sometimes not obvious. In some cases we may not even be able to determine the number of the resonance lines contributing to the spectrum. To establish a proper fit model in the thin absorber approximation, a model-independent analysis can be performed provided that the spectrum, $y(v)$, can be considered as to be the convolution of the distribution function of hyperfine energies, $p(v)$, with a Lorentzian curve, $l(v)$:

$$y(v) = \int_{-\infty}^{+\infty} p(w) \cdot l(v-w) \cdot dw \,.$$

The relevant information about the spectrum is contained in $p(v)$ that consists of sharper peaks than $y(v)$ does. In the case of overlapped Mössbauer spectra, the knowledge of $p(v)$ can therefore facilitate the spectrum decomposition by revealing the pattern of individual spectral lines, which can help to establish the appropriate model for the spectrum decomposition. According to the previous equation, $y(v)$ is a convolution of $p(v)$ and $l(v)$. Hence

$$p(v) = \boldsymbol{F}^{-1} \frac{\boldsymbol{F}y(v)}{\boldsymbol{F}l(v)} = \boldsymbol{F}^{-1} \frac{Y(k)}{L(k)}$$

where $\boldsymbol{F}$ and $\boldsymbol{F}^{-1}$ denote, respectively, the Fourier transformation and its inverse operation, while $Y(k)$ and $L(k)$ are the Fourier transforms of $y(v)$ and $l(v)$, respectively. In applications of the Fourier transform methods for deconvolution, *a filter function* is needed to avoid unwanted enhancement of statistical noise. The choice of the filter function is crucial from the point of view of the results obtained. In the case of Mössbauer spectroscopy different filter functions, $D(k)$, have been tried in order to reduce the high-frequency oscillations in $p(v)$ arising from statistical noise. In principle, every spectrum would require its own unique filter function. (See, e.g., D.L. Nagy, U. Röhlich: *Hyperfine Interactions* **66** (1991) 105.)

The Mössbauer Line Sharpening (**MLS**) menu allows the deconvolution of a Lorentzian line shape with a given line width from the normalized Mössbauer spectrum.

In this menu the following windows can be seen on the screen.

1, The original spectrum after normalization (Left Upper corner).
2, The filtered frequency spectrum of the normalized spectrum (Right Upper corner).
3, The filtered frequency spectrum of the deconvoluted spectrum (Center).
4, The deconvoluted spectrum. (Left Bottom corner).

The functions of the various visual elements are as follows.

**The original spectrum** - This spectrum window shows either the original spectrum that was in the red-framed window when the MLS menu was entered, or its normalized version. (If the red-framed spectrum is not normalized when the MLS menu is entered, then the program offers to carry out normalization of the spectrum.) The MLS menu works properly only if this original spectrum has a baseline equal or close to zero.

**The filtered frequency spectrum** - This window shows the **frequency spectrum** (under which we mean the absolute value of the Fourier spectrum) of the original spectrum filtered according to one of the built in filter functions as selected by the user. If there is not any filter function selected, then the content of the window simply shows the frequency spectrum of the original spectrum. (Manual filtering does not affect the content of this window: this is because manual filtering is applied *after* the deconvolution process.)

**The frequency spectrum after deconvolution** - This window shows the frequency spectrum of the original spectrum after noise filtering via one of the built in filter functions (if selected), the deconvolution of the Lorentzian line shape, as well as manual filtering (if any) has taken place. The window also shows the shape of the selected filter function by red line provided that the show filter check box is checked. Move the mouse over this window in order to carry out manual filtering: press the left mouse button in order to increase / decrease the amplitude of a selected frequency component, or press the right mouse button to limit the amplitude of the frequency spectrum right hand side of the cross (which follows the movement of the mouse) according to the actual height of the cross.

**The spectrum after deconvolution** - This window shows the resulted, sharpened counterpart of the original spectrum, after noise filtering and deconvolution of the Lorantzian peak shape has taken place. It is calculated as the inverse Fourier transform of the frequency domain function underlying the deconvoluted frequency spectrum shown in the middle of the menu screen. This is the result that is preserved when the menu is left via pressing the **EXIT** menu box.

**The filter selector popup** - Press on this box to select one of the built in filter functions from the appearing list. The shape of the filter functions may depend on the cutoff frequency and - in the case of the Fermi-Dirac filter - Lorentz width parameters. It is also possible to use a custom filter function loaded from the data window that was the green-framed one when the MLS menu was entered. Selecting a built in filter function will undo any manual filtering carried out previously.

**Show filter check box** - Check / uncheck this check box in order to show / hide the selected built in filter function overlaid by red line on the graph of the deconvoluted frequency spectrum. The filter function corresponding to the effects of manual filtering (if any) is not included in the curve.

**Filter cutoff frequency** - This is the frequency (as measured on the frequency scale of the frequency spectrum after deconvolution) beyond which built in filter functions strongly suppress frequency components. The actual meaning of the cutoff frequency depends on the type of the built in filter function selected. Click on the number part of this box in order to set the cutoff frequency value. If the value is set higher than the maximum value achievable by the filter cutoff frequency slide, then the latter maximum will be extended such that the newly set value will be set as the new maximum value. Set here a negative value for the filter cutoff frequency in order to set the maximum of the cutoff frequency slide (to the corresponding absolute value) irrespective of whether the newly set value is higher or lower than the former maximum.

**Filter cutoff frequency slide** - Press on this slide to change the filter cutoff frequency continuously with the movement of the mouse. The filtered frequency spectrum and the sharpened end result will be updated continuously, too. In order to set the maximum cutoff frequency achievable by this slide, turn to the edit box of the cutoff frequency.

**Lorentz width** - This is the width (FWHM) of the Lorentzian peak shape that is deconvoluted from the original normalized spectrum. This is usually set to the minimum experimental line width value (e.g. 0.28 mm/s) achievable via the applied radioactive source and experimental setup. As a result of deconvolution high frequency statistical noise becomes intensified as an exponential function of the product of frequency and line width, such that the application of higher line widths will generally require the setting of a lower filter cutoff frequency. Click on the number part of the box in order to edit the Lorentzian width value. If the value is set higher than the maximum value achievable by the Lorentzian width slide, then the latter maximum will be extended such that the newly set value will be set as the new maximum value. Set here a negative value for the Lorentzian width in order to set the maximum of the Lorentzian width slide (to the corresponding absolute value) irrespective of whether the newly set value is higher or lower than the former maximum.

**Lorentzian width slide** - Press on this slide to change the Lorentzian width continuously with the movement of the mouse. The filtered frequency spectrum and the sharpened end result will be updated continuously, too. In order to set the maximum Lorentzian width achievable by this slide, turn to the Lorentz width edit box.

**Reset all** - Press on this box to undo all filter operations.

**Adjust Y scale** - Press on this box to recalibrate the Y axis of the deconvoluted frequency spectrum shown in the middle of the menu screen. This is useful when the maximum of the deconvoluted frequency spectrum is reduced by manual filtering, because in such a case the Y-axis range is not adjusted automatically.

**Exit & Keep** - to leave the MLS menu by previously selecting the set of windows (e.g. the applied filter function) that is preserved as result.

**Exit** - to leave the MLS menu instantly by preserving only the sharpened spectrum as result.

**Cancel** - to leave the MLS menu instantly without preserving any result.

# 29. The noise FiLTering menu

With the help of the **FLT** menu statistical noise can be filtered out from data files. The windows in this menu have similar functionality to those described in the previous section in the case of the **MLS** menu. The only difference is that in the **FLT** menu the step of the deconvolution of the Lorentzian line shape is omitted. The following windows can be seen on the screen in this menu.

1, The original spectrum after normalization (Left Upper corner).
2, The frequency spectrum of the normalized spectrum (Right Upper corner).
3, The filtered frequency spectrum (Center).
4, The filtered spectrum. (Left Bottom corner).

The functions of the various visual elements are as follows.

**The original spectrum** - This spectrum window shows either the original spectrum that was in the red-framed window when the FLT menu was entered, or its normalized version. (If the red-framed spectrum is not normalized when the FLT menu is entered, then the program offers to carry out normalization of the spectrum.) The FLT menu works properly only if this original spectrum has a baseline equal or close to zero.

**The frequency spectrum** - This window shows the **frequency spectrum** (under which we mean the absolute value of the Fourier spectrum) of the original spectrum.

**The filtered frequency spectrum** - This window shows the frequency spectrum of the original spectrum after noise filtering via one of the built in filter functions (if selected) and manual filtering (if any) has taken place. The window also shows the shape of the selected filter function by red line provided that the show filter check box is checked. Move the mouse over this window in order to carry out manual filtering: press the left mouse button in order to increase / decrease the amplitude of a selected frequency component, or press the right mouse button to limit the amplitude of the frequency spectrum right hand side of the cross (which follows the movement of the mouse) according to the actual height of the cross.

**The filtered spectrum** - This window shows the resulted, filtered counterpart of the original spectrum, after noise filtering has taken place. It is calculated as the inverse Fourier transform of the frequency domain function underlying the filtered frequency spectrum shown in the middle of the menu screen. This is the result that is preserved when the menu is left via pressing the **EXIT** menu box.

**The filter selector popup** - Press on this box to select one of the built in filter functions from the appearing list. The shape of the filter functions may depend on the cutoff frequency and - in the case of the Fermi-Dirac filter - steepness parameters. It is also possible to use a custom filter function loaded from the data window that was the green-framed one when the FLT menu was entered. Selecting a built in filter function will undo any manual filtering carried out previously.

**Show filter check box** - Check / uncheck this check box in order to show / hide the selected built in filter function overlaid by red line on the graph of the filtered frequency spectrum. The filter function corresponding to the effects of manual filtering (if any) is not included in the curve.

**Filter cutoff frequency** - This is the frequency (as measured on the frequency scale of the filtered frequency spectrum) beyond which built in filter functions strongly suppress frequency components. The actual meaning of the cutoff frequency depends on the type of the built in filter function selected. Click on the number part of this box in order to set the cutoff frequency value. If the value is set higher than the maximum value achievable by the filter cutoff frequency slide, then the latter maximum will be extended such that the newly set value will be set as the new maximum value. Set here a negative value for the filter cutoff frequency in order to set the maximum of the cutoff frequency slide (to the corresponding absolute value) irrespective of whether the newly set value is higher or lower than the former maximum.

**Filter cutoff frequency slide** - Press on this slide to change the filter cutoff frequency continuously with the movement of the mouse. The filtered frequency spectrum and the filtered end result will be updated continuously, too. In order to set the maximum cutoff frequency achievable by this slide, turn to the edit box of the cutoff frequency.

**Steepness** - This parameter determines the steepness of the Fermi-Dirac filter function. Click on the number part of the box in order to edit the steepness value. If the value is set higher than the maximum value achievable by the steepness slide, then the latter maximum will be extended such that the newly set value will be set as the new maximum value. Set here a negative value for the steepness in order to set the maximum of the steepness slide (to the corresponding absolute value) irrespective of whether the newly set value is higher or lower than the former maximum. The steepness edit box is shown only when the Fermi-Dirac function is selected as filter.

**Steepness slide** - Press on this slide to change the steepness of the Fermi-Dirac filter continuously with the movement of the mouse. The filtered frequency spectrum and the filtered end result will be updated continuously, too. In order to set the maximum steepness achievable by this slide, turn to the steepness edit box. The steepness slide is shown only when the Fermi-Dirac function is selected as filter.

**Reset all** - Press on this box to undo all filter operations.

**Adjust Y scale** - Press on this box to recalibrate the Y axis of the filtered frequency spectrum shown in the middle of the menu screen. This is useful when the maximum of the filtered frequency spectrum is reduced by manual filtering, because in such a case the Y-axis range is not adjusted automatically.

**Exit & Keep** - to leave the FLT menu by previously selecting the set of windows (e.g. the applied filter function) that is preserved as result.

**Exit** - to leave the FLT menu instantly by preserving only the filtered spectrum as result.

**Cancel** - to leave the FLT menu instantly without preserving any result.

# 30. The TaBLe Maker menu

The TBL menu provides the possibility to create tables of fit parameters participating in the fit accepted previously in the FIT menu for the red-framed spectrum. While the names of possible fit parameters are extracted exclusively from the file associated with the red-framed window, values of the fit parameters are extracted from all (or some, depending on the choice of the user) of the files associated with the spectrum windows on the current project desk. The extracted parameter names are shown in the **ITEMS FOUND** box: a parameter will be included in the table if the corresponding check box is checked. In the table to be created parameters appear with shorter names which are displayed in the **NAME IN TABLE** box. The box entitled **FORMAT** displays whether the value of a parameter is to be treated as a numeric value or as a string. The extracted parameter values will appear in the table with the number of decimals shown in the **DEC** box. The title of the table will be displayed in the upper left corner cell of the table. The table will be ordered according to the value of the **master item**.

Tables can be created with two different arrangements: either with the parameters or with the file names listed downwards. Press on the corresponding grid shown on the right side of the screen in order to choose between the two options.
The functions of the various visual elements are as follows.

**Items found (list of parameter items)** - The items found box contains the names of parameters extracted from fits accepted previously for the red-framed spectrum. Check the check box before those parameters that should be present in the table to be built. Press on the magenta colored headline of the box in order to select/deselect more parameters at once. If there are more parameters than the box allows to see, scroll down/up the parameter list either by using the mouse wheel, or by pressing on the lower/upper part of the box. In order to select the master parameter, i.e. the parameter according to which the table should be ordered, press with the right mouse button on the corresponding check box. The master parameter will be shown by red color, and its name will also appear in the **MASTER ITEM (X)** info box. To add a new, custom parameter to the list, press on the **ADD NEW ITEM** box.

**Name in table** - This box displays the names by which the selected parameters will appear in the table to be built. Press on the names in order to edit them.

**Format** - This box displays the way parameter values are handled when the table is built. Whereas for numeric values only a single number will be present in the table, in string values any character (e.g. %) as well as multiple numbers can be present. Press on the magenta colored headline of the box in order to set whether standard deviation values should be included in the table or not.

**DEC** - This box displays the maximum number of decimals that the parameter values can have when they appear in the table. Click on the numbers to edit them one by one, or press on the magenta colored headline of the box in order to limit the number of decimals for all the selected parameters. The limit set here will also influence the appearance of numbers inside string values.

**Title of Table** - The string set here will appear in the upper left corner cell of the table.

**Master item (X)** - This box displays the master item on the basis of which the table will be ordered. In the **ITEMS FOUND** box press on a check box with the right mouse button in order to make the corresponding parameter to be the master item. The master item/parameter also provides the abscissa (x) values of tables saved as X,Y[x] data.

**Include files** - Press on this box in order to set which spectrum files should participate in the table among those being on the current project desk.

**Add new item** - Press on this box in order to add a custom parameter item to the list of items extracted from the file of the red-framed spectrum window. If the newly added parameter item can be found in the remaining spectra on the current project desk, then the corresponding parameter values will appear in the table to be created.

**Save** - Press on this box to save the table as a comma-delimited text file.

**Copy** - Press on this box to copy the table to the Windows clipboard as comma-delimited text.

**Print table** - Press on this box to print the table to the default printer.

**Print to file** - Press on this box to print the table to a bitmap image file.

**X,Y[x]** - Press on this box to save the table to file as X,Y[x] data intended for grapher programs.

**Exit** - to leave the TBL menu.

# 31. The MTX menu

In MossWinn 2.0i, and in earlier versions as well, the so-called transformation matrices served as models to fit Mössbauer spectra. Such transformation matrices can be managed in the **MTX** menu. Beginning with the version of MossWinn 3.0, a new system has been used for the description of Mössbauer models (this new system can be managed in the **FIT** menu itself), and the system based on transformation matrices can be considered as obsolete. To preserve compatibility with earlier versions, in MossWinn 4.0 the transformation matrices remained applicable. However, whenever a transformation matrix is selected as fit model and the FIT menu is entered, MossWinn will compile the transformation matrix to a model of the new system.

The menu of MTX allows to load, modify and build together existing transformation matrices being in the Transformation Matrix Directory (**..\MOSSWINN 4.0\USERS\PUBLIC\TMATRIX**) and having the extension: **.MAT** . Transformation Matrices describe linear fit models. How this is done, is described in the followings.

## *31.1. The job of the Transformation Matrix*

An individual Lorentzian line can be described by 3 parameters: Amplitude, Position, and Line Width. A spectrum containing only one Lorentzian can be described by 4 parameters: Base Line + The parameters describing the Lorentzian line itself. If we have, however, a symmetrical quadrupole doublet (consisting of two Lorentzians with the same amplitude) to fit, then we won't need 1+3+3 = 7 parameters to describe the two lines because the amplitudes of them are the same. How to tell an information like this to the fitting program ? This is what a Transformation Matrix can do.

A Transformation Matrix is a matrix of dimension $\boldsymbol{N \times M}$ ($N$ rows, $M$ columns). $N$ is always equal to $\mathbf{3}\boldsymbol{L}$ **+ The number of parameters describing the Background** (usually only the Base Line parameter, but slope and curvature parameters are also possible), where $L$ denotes the number of Lorentzians being present in the spectrum. $M$ is equal to the number of parameters actually fitted in the **FIT** menu. The transformation matrix has always a block diagonal form in the case of the MossWinn program.

If **V** denotes the vector built from the parameters describing the background and the Lorentzian lines (usually **V** has $3L+1 = N$ elements) and **W** denotes the vector built from the independent parameters actually fitted (**W** has $M$ elements) and **T** denotes the Transformation Matrix then

$$\mathbf{V} = \mathbf{T} \cdot \mathbf{W}$$

In the case of fitting only one Lorentzian line the matrix **T** is diagonal and the multiplication above has the rather trivial form:

$$\begin{bmatrix} BASELINE \\ AMPLITUDE \\ POSITION \\ LINEWIDTH \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} BASELINE \\ AMPLITUDE \\ ISOMERSHIFT \\ LINEWIDTH \end{bmatrix}$$

In the case of the fitting of a symmetrical quadrupole doublet, the multiplication can be written in the following form:

$$\begin{bmatrix} BASELINE \\ AMPLITUDE-(1) \\ AMPLITUDE-(2) \\ POSITION-(1) \\ POSITION-(2) \\ LINEWIDTH-(1) \\ LINEWIDTH-(2) \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & +0.5 & 0 \\ 0 & 0 & 1 & -0.5 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} BASELINE \\ AMPLITUDE \\ ISOMERSHIFT \\ Q.SPLITTING \\ LINEWIDTH \end{bmatrix}$$

If the Lorentzians of the quadrupole doublet do not have necessarily the same line width then the multiplication looks like this:

$$\begin{bmatrix} BASELINE \\ AMPLITUDE-(1) \\ AMPLITUDE-(2) \\ POSITION-(1) \\ POSITION-(2) \\ LINEWIDTH-(1) \\ LINEWIDTH-(2) \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & +0.5 & 0 & 0 \\ 0 & 0 & 1 & -0.5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} BASELINE \\ AMPLITUDE \\ ISOMERSHIFT \\ Q.SPLITTING \\ LINEWIDTH-(1) \\ LINEWIDTH-(2) \end{bmatrix}$$

## *31.2. Examples for transformation matrices stored as text files*

The MossWinn program uses the following coding system to store transformation matrices in the form of text files on the hard disk. Transformation matrices are stored in the form of text files thus they can be edited with any text editor program. A matrix of **one singlet** should look like this (characters between the signs {} are not in the file.)

**1** {The first row of the text file. The number of Lorentzians ( *L* )}
**0** {The number of curvature type parameters.([0,1])}
**0** {The number of slope type parameters.([0,1])}
**1** {The number of base line parameters. (Always 1)}
**1** {The number of Amplitude type parameters }
**1** {The number of Position type parameters (IS,QS,MS)}
**1** {The number of Width type parameters }
**[1 Singlet]** {Name of the matrix}
**BASE LINE:** {Name of the Base Line type parameter}
**1** { T[1,1] }
**AMPLITUDE:** {Name of the Amplitude type parameter}
**1** { T[2,2] }
**ISOMER SHIFT:** {Name of the Position type parameter}
**1** { T[3,3] }
**LINE WIDTH:** {Name of the Width type parameter}
**1** { T[4,4] }
**ETM** {Indicates the end of the matrix definition}

A text file of a matrix describing a **symmetrical quadrupole doublet** is the following.

**2** {The first row of the text file. The number of Lorentzians ( *L* )}
**0** {The number of curvature type parameters.([0,1])}
**0** {The number of slope type parameters.([0,1])}
**1** {The number of base line parameters. (Always 1)}
**1** {The number of Amplitude type parameters }
**2** {The number of Position type parameters (IS,QS,MS)}
**1** {The number of Width type parameters }
**[1 Doublet]** {Name of the matrix}
**BASE LINE:** {Name of the Base Line type parameter}
**1** { T[1,1] }
**AMPLITUDE:** {Name of the Amplitude type parameter}
**1** { T[2,2] }
**1** { T[3,2] }
**ISOMER SHIFT:** {Name of the first Position type parameter}
**1** { T[4,3] }
**1** { T[5,3] }
**Q. SPLITTING:** {Name of the second Position type parameter}
**+0.5** { T[4,4] }
**-0.5** { T[5,4] }
**LINE WIDTH:** {Name of the Width type parameter}
**1** { T[6,5] }
**1** { T[7,5] }
**ETM** {Indicates the end of the matrix definition}

A text file of a matrix describing **1 doublet + 1 singlet** can be the following:

**3** {The first row of the text file. The Number of Lorentzians ( *L* )}
**0** {The number of curvature type parameters.([0,1])}
**0** {The number of slope type parameters.([0,1])}
**1** {The number of base line parameters. (Always 1)}
**2** {The number of Amplitude type parameters }
**3** {The number of Position type parameters (IS,QS,MS)}
**2** {The number of Width type parameters }
**[1 D + 1 S]** {Name of the matrix}
**BASE LINE:** {Name of the Base Line type parameter}
**1** { T[1,1] }
**A (Doublet):** {Name of the first Amplitude type parameter}
**1** { T[2,2] }
**1** { T[3,2] }
**0** { T[4,2] }
**A (Singlet):** {Name of the second Amplitude type parameter}
**0** { T[2,3] }
**0** { T[3,3] }
**1** { T[4,3] }
**IS (Doublet):** {Name of the first Position type parameter}
**1** { T[5,4] }
**1** { T[6,4] }
**0** { T[7,4] }
**Q.S.(D):** {Name of the second Position type parameter}
**+0.5** { T[5,5] }
**-0.5** { T[6,5] }
**0.0** { T[7,5] }
**IS (Singlet):** {Name of the third Position type parameter}
**0** { T[5,6] }
**0** { T[6,6] }
**1** { T[7,6] }
**LW (Doublet):** {Name of the first Width type parameter}
**1** { T[8,7] }
**1** { T[9,7] }
**0** { T[10,7] }
**LW (Singlet):** {Name of the second Width type parameter}
**0** { T[8,8] }
**0** { T[9,8] }
**1** { T[10,8] }
**ETM** {Indicates the end of the matrix definition}

The next matrix-file can be used to analyze an **α-iron calibration** spectrum.

**6**
**0**
**0**
**1**
**3**
**2**
**1**
**IRON CALIBRATION (SIX LINES ; 3 AMPLITUDES ; EQUAL LINE WIDTHS)**
**BASE LINE:**
**1**
**AMPLITUDE (1-6):**
**1**
**0**
**0**
**0**
**0**
**1**
**AMPLITUDE (2-5):**
**0**
**1**
**0**
**0**
**1**
**0**
**AMPLITUDE (3-4):**
**0**
**0**
**1**
**1**
**0**
**0**
**CENTER:**
**1**
**1**
**1**
**1**
**1**
**1**
**REC.CAL.FACT.:**
**-5.32128** {Position of the 1st line of the α-Fe sextet relative to its center.}
**-3.08079** {Position of the 2nd line of the α-Fe sextet relative to its center.}
**-0.84029** {Position of the 3rd line of the α-Fe sextet relative to its center.}
**0.84029** {Position of the 4th line of the α-Fe sextet relative to its center.}
**3.08079** {Position of the 5th line of the α-Fe sextet relative to its center.}
**5.32128** {Position of the 6th line of the α-Fe sextet relative to its center.}
**LINE WIDTHS:**
**1**
**1**
**1**
**1**
**1**
**1**
**ETM**

## 31.3. Options available in the MTX menu

In the menu of **MTX** there is the possibility to modify existing Transformation Matrices and to build new Transformation Matrices by merging existing matrices together. The functions of the various visual elements are as follows.

**Transformation matrices found** - This box lists the transformation matrices (with extension MAT) found in the transformation matrix directory of MossWinn. A transformation matrix can be selected for modifications by pressing with the right mouse button on the check box before its name. As a result, the name of the matrix will become red (it will be the **red-selected matrix**) and the parameters included in the corresponding fit model will appear in the PARAMETERS FOUND box. In order to build together existing transformation matrices (for example with the aim to create the model of [1 singlet + 1 doublet] from the individual models of [1 singlet] and [1 doublet]) select them by pressing with the left mouse button on the check box before their name. If there are more matrices than the box allows to see, scroll down/up the matrix list either by using the mouse wheel, or by pressing on the lower/upper part of the box. Press on the magenta colored headline of the box in order to edit the file name or the headline of the red-selected matrix.

**Parameters found** - This box displays the fit parameters included in the fit model represented by the red-selected matrix (if any being highlighted in the TRANSFORMATION MATRICES FOUND box). Press on the name of one of the fit parameters with the right mouse button in order to select it (its name will be highlighted in red color). The matrix elements associated with the selected parameter will be shown in the ELEMENTS box. In order to edit a parameter name, press on it with the left mouse button. Whether in this box a parameter is selected or not influences the effect of the ADD, DEL, INSERT, UNGROUP and GROUP menu boxes.

**Elements** - This box displays the matrix elements belonging to the parameter selected in the PARAMETERS FOUND box. In order to edit the displayed matrix elements, press on them with the mouse. There will be as many matrix elements (i.e. as many rows in the box) as the number of Lorentzians (or in general: absorption peaks) contributing to the corresponding fit model. A given amplitude-, position- or width-type fit parameter can influence the amplitude/position/width of a Lorentzian peak only if it has a nonzero matrix element in the row associated with the peak in question. If there are more than 6 rows/Lorentzians, use the mouse wheel or press on the magenta colored top/bottom edges of the box to scroll the elements up or down.

**Add** - This menu box has multiple functions depending on whether a parameter in the Parameters found box is selected or not:

> If a parameter is selected, then press on the ADD menu box in order to set the minimum and maximum of the selected fit parameter, which information is automatically loaded when the corresponding transformation matrix is invoked for fitting.
>
> If there is not any parameter selected, then press on the ADD menu box to add a new parameter to the parameter list, or to add a new Lorentzian/peak to the fit model corresponding to the red-selected matrix.

**Del** - This menu box has multiple functions depending on whether a parameter in the Parameters found box is selected or not:

> If a parameter is selected, then press on the DEL menu box in order to delete the selected parameter from the fit model corresponding to the red-selected transformation matrix.
>
> If there is not any parameter selected, then press on the DEL menu box to delete the last Lorentzian/peak from the fit model corresponding to the red-selected transformation matrix.

**Insert** - By the help of this menu box one can reorder the parameters in the PARAMETERS FOUND box. First select one of the parameters, then press on this box to have the text INSERT become highlighted in yellow. Then press on one of the parameters by the left mouse button in order to insert the selected parameter before or after the parameter that was pressed on.

**Ungroup** - This menu box can be used to ungroup the Lorentzians/peaks from the viewpoint of the selected parameter. First select one of the parameters in the PARAMETERS FOUND box, then press on this menu box. If the selected parameter has influenced the amplitude/position/width of more than one

Lorentzians/peaks, then new parameters of the same type will be created and added to the list in order to have each of the associated parameters influence only one of the Lorentzians/peaks. The effect of this menu box can be undone by the application of the GROUP menu box in conjunction with the newly created parameters.

**Group** - This menu box can be used to group together the Lorentzians/peaks influenced by two parameters of the same (amplitude/position/width) type. First select one of the parameters, then press on this box to have the text GROUP become highlighted in yellow, then press on one of the remaining parameters with the left mouse button. As a result, the two parameters will be merged into a single parameter that influences all the Lorentzians/peaks influenced earlier by the two independent parameters.

**Build** - This menu box can be used to merge the selected/checked (blue-colored) matrices. The result is a new transformation matrix that includes all the subspectra and associated parameters that take place in the selected matrices that were built together. The newly created matrix will appear in the TRANSFORMATION MATRICES FOUND box if it is saved with the extension MAT.

**Exit** - Press on this box to leave the MTX menu and load in the red-selected transformation matrix (if any).

# 32. The Mössbauer Project Desks menu

The Mössbauer Project Desks (**MPD**) menu serves for the organization of Mössbauer spectra in different project desks. Projects are organized in project groups. To add a spectrum to the actually selected project, simply load the spectrum via the **LOAD** menu. The program updates the content of the project desks automatically when the program is exited. Any project and all the spectra belonging to it can then be reloaded easily any time later on. LMC the MPD box to access the following options.

- **List of project groups and associated projects** - click to display the selected project desk on the screen.
- **Add new Project...** - to create a new project desk either in one of the existing project groups or in a newly created project group. MossWinn can handle around 800 project desks distributed in around 25 project groups.
- **Import Project...** - to import a project desk - or a whole project group with multiple project desks - from a *.TPF file (Transfer Project File), that was exported previously via the EXPORT CURRENT PROJECT... or EXPORT PROJECT GROUP.... menu options. The imported project(s) will be added to the project structure of MossWinn: they will contain all the spectrum- and text windows that were present on the corresponding project desks when the latter were exported. The imported windows will refer to newly created physical data files. Exporting/importing transfer project files is the recommended way to exchange data between different copies of MossWinn, as well as to archive projects/project groups.
- **Export Current Project...** - to export the current project desk with all of its associated data and text windows into a standalone transfer project file (*.TPF) that can be imported via the IMPORT PROJECT... menu option. **This is the best way to exchange data with another researcher using MossWinn.**
- **Export Project Group...** - to export the selected project group with all of its project desks and associated data and text windows into a standalone transfer project file (*.TPF) that can be imported via the IMPORT PROJECT... menu option. **This is the best way to archive the corresponding data.**
- **Update Current Project** - to update the current project desk according to its current state. Normally, active project desks become updated when the program is closed. (Entering the ORGANIZE MOSSBAUER PROJECTS menu will cause the active project desks to become updated, too.)
- **Rename Current Project** - to change the name of the current project.
- **Rename Project Group...** - to change the name of the selected project group.
- **Organize Projects...** - to enter the ORGANIZE MOSSBAUER PROJECTS menu (equivalent to the action of the right mouse button).

# 33. How to organize Mössbauer Projects

To organize existing Mössbauer projects, RMC the **MPD** box. On the appearing form the screen is divided into two equivalent sides, one on the left, and one on the right of the screen. In this menu there is the possibility

**1. TO EXPORT A PROJECT OR A WHOLE PROJECT GROUP TO A STANDALONE FILE.**

**To export a whole project group:**

- Select the project group in the left or right cyan colored popup box.

- Click on **EXPORT PROJECT GROUP** on the corresponding side (left or right) and follow the instructions.

**To export a project:**
- Select the project group that contains the required project.
- Select the required project in the corresponding list box.
- Click on **EXPORT PROJECT** on the corresponding side (left or right) and follow the instructions.

**2. TO MOVE OR COPY PROJECTS BETWEEN PROJECT GROUPS.**

**To copy a project to an another project group:**
- Select the source project group in the popup box on the left side.
- Select the project to be copied in the list box on the left side.
- Select the target project group in the popup box on the right side.
- Click on the **COPY PROJECT** box on the left side.

**To move a project to an another project group:**
- Select the source project group in the popup box on the left side.
- Select the target project group in the popup box on the right side.
- DRAG AND DROP the required project from the list box on the left to the list box on the right.

**3. TO MOVE OR COPY SPECTRA BETWEEN PROJECTS.**

**To copy a spectrum to an another project:**
- Select the source project in the list box on the left side.
- Select the spectrum to be copied in the list box on the left side.
- Select the target project in the list box on the right side.
- Click on the **COPY FILE** box on the left side.

**To move a spectrum to an another project:**
- Select the source project in the list box on the left side.
- Select the target project in the list box on the right side.
- DRAG AND DROP the required spectrum file from the list box on the left to the list box on the right.

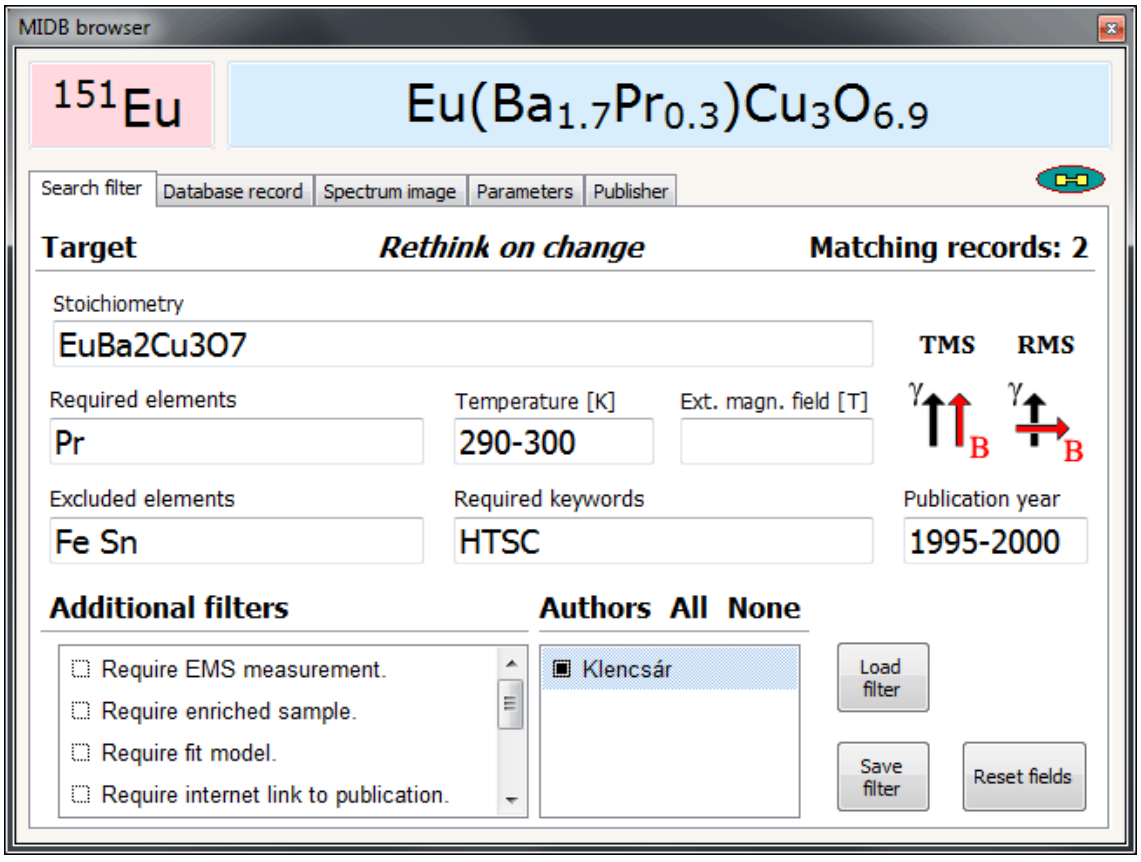
**4. TO REMOVE PROJECTS OR WHOLE PROJECT GROUPS FROM THE PROJECT DESK SYSTEM.**
- Select the project to be removed on the left side.
- Click on the **DELETE PROJECT** box on the left side.
- To remove a project group remove all of its projects.

**5. TO REMOVE SPECTRA FROM PROJECTS.**
- Select the spectrum to be removed in the list box on the left side.
- Click on the **REMOVE FILE** box on the left side. (The spectrum file on the hard disk won't be altered.)

# 34. The DaTaBase functions menu

The DTB menu box provides access to a subset of the functions of the MossWinn Internet Database directly from the main menu. (The complete set of functions is available via the DB menu box of the FIT menu, see page 37). To preserve compatibility with earlier versions, this menu box also provides access to the data operations (DTA) menu (see section 34.1). The available submenu options are the followings:

- **Browse the MossWinn Internet Database (MIDB)** – Select this option to query and browse the records of the MossWinn Internet Database by the means of a database browser form that offers a major subset of the functionality of the MIDB browser. This is a **free service to MossWinn licencees**, i.e. subscription to the MIDB is not required to access this function. Note that internet access to the MossWinn Internet Database needs to be enabled (via the SET menu box) in order to be able to browse the database records. RMC the DTB box in order to access this menu option directly.
- **Edit MIDB record** – Select this option to edit one of the own MIDB records by changing the record parameters that can be set on the Database record input form. (The fit model and the resampled spectrum associated with the record cannot be edited in this way.) The own record that is to be edited can be selected on the appearing form. In order to be able to edit a database record, one needs to be subscribed to the database service.
- **Withdraw MIDB record** – Select this option to withdraw one of the own MIDB records from the MossWinn Internet Database. The own record that is to be withdrawn can be selected on the appearing form. Own records can be withdrawn from the database even without subscription to the database service.
- **DTA menu** – Select this option to access the data operations menu (see section 34.1).




The database browser form accessible via the DTB menu box.

## 34.1. The DaTA operations menu

The DTA menu provides the possibility to edit measured spectrum data, delete selected subspectrum envelops, copy data series (e.g. subspectra) from one spectrum window to the other, as well as to examine and edit parameters associated with the spectrum data. Although these functions can also be invoked by other means in MossWinn (spectrum data can be edited in the SRE menu, subspectra can be deleted and grouped/ungrouped via the DEL menu and the PLT menu, respectively, and finally spectrum parameters can be edited via the EDT menu), the DTA menu provides a useful and convenient collection of them. When the DTA menu is invoked, the menu screen becomes divided into two panels of equivalent function, one on the left and one on the right side. Any of the data windows being present on the actual project desk can be selected for processing via the data window list popup box, one being situated on the top of each panel. The functions of the various visual elements are as follows.

**Data window list** - Press on this popup box to select the spectrum window whose data are to be displayed in the corresponding panel.

**Data series list** - This list box shows the data series (measured data, fit envelope and subspectra - if any) of the data window selected for the corresponding panel. Click on the items to select/deselect one or more of them. Selected items will be displayed by white background color, and they will vanish from the graph of the spectrum. Press on the DELETE SELECTED menu box in the corresponding panel in order to delete the selected subspectrum items. In order to add one of the displayed data series to those of the spectrum window displayed in the right panel, drag & drop the corresponding item either to the data series list or to the spectrum window of the right panel.

**Velocities - X data** - This list box shows the velocities attributed to the channels of the spectrum displayed in the corresponding panel. The corresponding measured data can be seen/edited in the list box beside it. The velocities themselves cannot be edited. Use the mouse wheel or press on the arrows to scroll the data up or down.

**Measured data series - Y data** - This list box shows the measured data of the spectrum displayed in the corresponding panel. Press on the list box to edit the data. Use the mouse wheel or press on the arrows to scroll the data up or down.

**Delete selected** - Press on this box to delete the selected data series (subspectra or the envelope) from the spectrum window shown in the corresponding panel. The data series belonging to the measured data cannot be deleted. Press on the UPDATE box to finalize the operation by updating the physical file associated with the spectrum window.

**Update** - Press on this box to update the physical file associated with the spectrum window of the corresponding panel according to the current state of the window. When the spectrum parameters are edited, the update procedure is carried out automatically.

**Spectrum window** - This is the spectrum window selected via the DATA WINDOW LIST in the corresponding panel. In order to add a subspectrum to the corresponding data, drag & drop to this window one of the data series shown in the other panel.

**Spectrum parameters** - Press on this box to edit the shown spectrum parameters. Use the mouse wheel or press on the arrows to scroll the parameter list up or down. When the spectrum parameters are edited, the corresponding spectrum window becomes automatically updated.

# 35. The menu of Hard Disk Operations

LMC the **HDO** box to access the following options.

- **Rename red window** - to rename the file associated with the red-framed window.
- **Update red window** - to update the content of the file associated with the red-framed window according to the actual state of the window. If the window does not have an associated file (i.e. it has not been saved yet), then it will be saved as a temporary file.
- **Update all windows** - to update all windows (i.e. the files associated with them) on the current project desk according to their actual state. Windows that have not been saved yet will be saved as a temporary file.
- **Update current project** - to update the current project desk according to its actual state. Normally, active project desks are automatically updated when MossWinn is closed.
- **Compile HTML FitLog summary of folder** - to display the HTML FitLog Summary Dialog (see section 35.1) that allows the creation of FitLog summary files on the basis of fitted Mössbauer spectra situated in a certain folder/drive (or its subfolders) and satisfying certain criteria set by the user. This tool can also be used effectively to locate certain type of Mossbauer spectrum files on a drive or in a folder and its subfolders.
- **Save all shown temporary files into a single folder** - to save all temporary files (shown as gray-framed windows) associated with the current project desk into a single folder to be created or entered on the appearing dialog form. The program also offers the option to make the current project refer to the newly saved files. This option can be used, e.g., to convert hyperfine field distributions — derived in the FIT menu as temporary files — to normal (i.e. not temporary) files.
- **Save all files of the project into a single folder** - to save a copy of all files associated with the current project desk into a single folder to be created or entered on the appearing dialog form. The program also offers the option to make the current project refer to the newly saved files. This option can be used, e.g., to store a project based on files loaded from removable media on a local fixed disk, or to duplicate the files referenced by the current project.
- **Save all files of the project group into a single folder** - to save a copy of all files associated with the projects of the selected project group into subfolders of a single folder to be created or entered on the appearing dialog form. The subfolders store the files and bear the name associated with the individual projects of the project group. The program also offers the option to make the projects of the selected project group refer to the newly saved files. This option can also be used to duplicate the files associated with the selected project group.
- **Reload red window** - to reload the content of the red-framed window from the file associated with it.
- **Reload current project** - to reload the current project desk. Changes applied to the project desk (e.g. new windows created or loaded) since its last update will be abandoned.
- **Create new directory...** - to display the file explorer dialog of MossWinn in *create new directory* mode, which allows the creation of a new directory on a storage medium.

## 35.1. The HTML FitLog Summary dialog

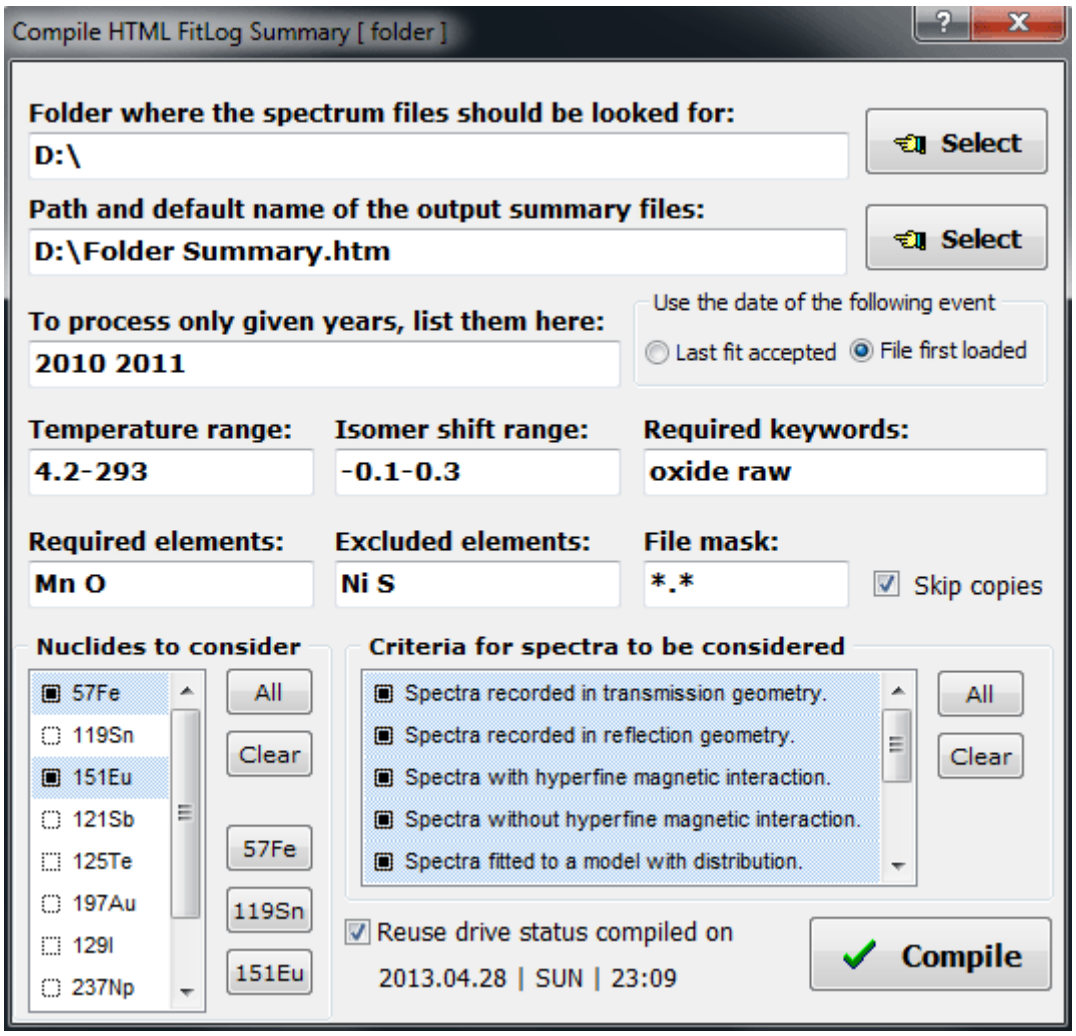
The HTML FitLog Summary dialog provides the possibility to compile a summary of Mossbauer spectra fitted by MossWinn and satisfying criteria set via this dialog. MossWinn will search through folders (or whole drives) including subfolders (recursively), and will collect spectra and their analysis details into HTML FitLog files. Spectra associated with different years (concerning either of their last accepted fit or of their first load) are collected into different files whose name includes the year in question. The compilation process, initiated by pressing on the COMPILE button, can take a considerable amount of time (depending on the number of files encountered inside the source folder) during which MossWinn displays the found suitable spectra consecutively in the FIT menu. To break the process before its completion, press ESC on the keyboard. The dialog offers the following options.

**Folder where the spectrum files should be looked for** (edit box) - Source folder where MossWinn will look for the spectrum files recursively (including subfolders). When a whole drive is searched through, as in the example below, MossWinn will also save the current status of the drive, i.e. the list of the path & name of the spectrum files available on the drive in question. This status can then be used during follow-up searches to speed up the compilation process.

**Select** (source folder) (button) - Press to select the source folder where the spectrum files are looked for.

**Path and default name of the output summary files** (edit box) - This will be the path and the basis of the name of the output FitLog summary files. The final name of the created FitLog files will include the year information, associated with the corresponding spectrum files, between parentheses.

**Select** (path of the output files) (button) - Press to select the path of the output FitLog summary files.



**To process only given years, list them here** (edit box) - MossWinn associates a certain year with each of the fitted spectra it encounters during the search. Depending on the corresponding setting (see below), this can be the year when a fit was last accepted for the given spectrum, or the year when the spectrum was first loaded with MossWinn. Spectra associated with different years are included in different FitLog files whose name reflects the year in question. When this edit box is left empty, then spectra become processed from all the years. In order to process spectra only from given years, list the years here.

**Last fit accepted** (radio button) - Select this option to associate spectra with the year when last time a fit was accepted for them.
**File first loaded** (radio button) - Select this option to associate spectra with the year when they were first loaded with MossWinn.

**Temperature range** (edit box) - Only those spectra will be considered whose associated temperature parameter (set via the EDT menu) lies in the range given here. Leave the edit box empty in order to consider spectra irrespective of their temperature.

**Isomer shift range** (edit box) - Only those spectra will be considered whose accepted fit model includes at least one subspectrum whose associated isomer shift parameter lies in the range given here. Leave the box empty in order to consider spectra irrespective of the isomer shift of the corresponding subspectra.

**Required keywords** (edit box) - Only those spectra will be considered whose keyword list (see page 24) or headline (i.e. the first line of the corresponding file) include all the words listed here. Multiple words should be separated by space character. Leave the edit box empty in order to consider spectra irrespective of their headline and keyword list.

**Required elements** (edit box) - Only those spectra will be considered whose stoichiometry (set via the EDT menu) includes all the elements listed here. Leave the edit box empty in order to consider spectra withour requiring specific elements to be present in the stoichiometry.

**Excluded elements** (edit box) - Only those spectra will be considered whose stoichiometry (set via the EDT menu) does not include the elements listed here. Leave the edit box empty in order to consider spectra without requiring specific elements to be absent in the stoichiometry.

**File mask** (edit box) - Only those spectrum files will be considered whose name matches the mask given here. Leave the edit box empty in order to consider spectrum files irrespective of their file name.

**Skip copies** (check box) - Check to skip spectrum file copies that have the same name and fit date associated with them as another spectrum already considered.

**Nuclides to consider** (list box) - Only those spectra will be considered that were measured by the use of source nuclides selected here.
**All** (button) - Press to select all source nuclides.
**Clear** (button) - Press to deselect all source nuclides.
**57Fe** (button) - Press to select $^{57}$Fe only.
**119Sn** (button) - Press to select $^{119}$Sn only.
**151Eu** (button) - Press to select $^{151}$Eu only.

**Criteria for spectra to be considered** (list box) - Spectra that match criteria not selected here, will not be included in the compiled FitLog files. Note that deselecting, e.g., a pair of mutually exclusive criteria will prevent MossWinn to find suitable spectrum files.
**All** (button) - Press to select all criteria.
**Clear** (button) - Press to deselect all criteria.

**Reuse drive status compiled on** (check box) - Check to reuse drive status information compiled on the date given below. The status of a drive is compiled whenever the whole drive is searched through for spectrum files irrespective of the file name, i.e. when the source folder refers to a whole drive (as in the example shown), and the file mask edit box is left empty or is set to ***.***. The compiled status file includes path and name information about spectrum files (on the given drive) that were fitted with MossWinn. Reusing the status information in subsequent compilations related to the same drive can speed up the compilation process, but will exclude from the search those spectrum files (if any) that were renamed, relocated or were added to the drive after the available status was compiled.

**Date & time (of drive status last compiled)** (label) - Shows the date when the selected drive was last time thoroughly searched for spectrum files, i.e. when the status file for the given drive was compiled.

**Compile** (button) - Press to start the compilation of the HTML FitLog summary files. In order to break the process before its completion, press ESC on the keyboard.

# 36. PRiNting graphics, copying spectrum data

- **Save RED as...** - to save the graphical content of the red-framed window (via the file explorer dialog) as an image having the selected format: **GIF image**, **JPEG image**, **Color bitmap** or **B&W bitmap**. If an attempt is made to save the image file with a file name that already exists, then - without prompting - the program will save the image file with a name that differs from the given name (e.g. IMAGE.JPG) by numbering: IMAGE_(1).JPG. (The attributed number is increased until a file name is reached that does not exist yet.) The created image will obey the options set as default for CLIPBOARD - SINGLE SPECTRUM on the PRINTER SETUP DIALOG.
- **Save ALL as...** - to save the graphical content (i.e. all the windows) of the current project desk (via the file explorer dialog) as an image having the selected format: GIF image, JPEG image, Color bitmap or B&W bitmap. The created image will obey the options set as default for CLIPBOARD - MULTIPLE SPECTRA on the PRINTER SETUP DIALOG.
- **Print RED (ctrl-p)** - to print the graphical content of the red-framed window to the default printer. (Equivalent to the keystroke ctrl-P.) In order to send the print job to a different printer, select the printer in question from the appearing list.
- **Print ALL (ctrlshift-p)** - to print the graphical content (i.e. all the windows) of the current project desk to the default printer. (Equivalent to the keystroke CTRL+SHIFT-P.) In order to send the print job to a different printer, select the printer in question from the appearing list.
- **Copy RED to clipboard (ctrl-c)** - to copy the graphical content of the red-framed window to the clipboard of Windows. (Equivalent to the keystroke CTRL-C.) The options influencing the appearance of the resulting image can be set on the PRINTER SETUP DIALOG.
- **Copy ALL to clipboard (ctrlshift-c)** - to copy the graphical content (i.e. all the windows) of the current project desk to the clipboard of Windows. (Equivalent to the keystroke CTRL+SHIFT-C.) The options influencing the appearance of the resulting image can be set on the PRINTER SETUP DIALOG.
- **Copy RED to clipboard (as text)** - To copy the red-framed spectrum to the clipboard as text, with the velocity values, the measured data, the fit envelope and the subspectra included as comma delimited columns. This option may be used to export numerical data from MossWinn for use in external data processing & graphics software.
- **Copy ALL to clipboard (as text)** - To copy all spectra on the current desk to the clipboard as text, placed one after the other, in a single step.
- **Copy RED as xls** - to make a copy of the spectrum data in the red-framed window in the form of an XLS spreadsheet file. Once created, MossWinn attempts to open the XLS file with an associated software application. *This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.*
- **Copy ALL spectra as xls** - to make a copy of all the spectrum data on the current desk in the form of a single XLS spreadsheet file, in which the different spectra appear on separate worksheet pages. Once created, MossWinn attempts to open the XLS file with an associated software application. *This option requires either the **DBM version** of MossWinn or subscription to the **MossWinn services**.*
- **Print / Copy / Set defaults...** - to display the **PRINTER SETUP DIALOG** that allows the setting of options influencing the appearance of spectrum images printed to printer, copied into the clipboard or saved to a file.

## *36.1. The printer setup dialog*

The printer setup dialog provides the possibility to set the default attributes of the graphs printed / copied by MossWinn. **For the different available printers/clipboard functions the default attributes can be set independently.** (The *copy to clipboard* functions are also formally treated here as printers: CLIPBOARD - SINGLE SPECTRUM and CLIPBOARD - MULTIPLE SPECTRA). The menu can also be used to print / copy graphs with attributes different from the default ones. Some of the default attributes set here (such as, e.g., the drawing of the residual or the connection of the data points) may become overridden by the actual state of the spectrum window printed or copied. The functions of the various visual elements are as follows.

**File name** (popup box) - This popup box enables the selection of the red-framed spectrum window directly on the printer setup dialog. The red-framed window is the one whose parameters are displayed in the spectrum parameters list box, and whose content becomes printed / copied when the PRINT RED or COPY RED TO CLIPBOARD buttons are pressed.

**Show Caption** (check box) - Put a check on this box in order to have the caption - shown on the right - to be displayed on the bottom of the spectrum graph printed / copied. By default, the caption is equal to the headline of the red-framed spectrum.

**Caption** (edit box) - This is the (editable) caption that is displayed on the bottom of the printed / copied spectrum graph provided that the corresponding check box is checked. Note that the caption is set equal to the headline of the red-framed spectrum whenever the latter is changed.

**Set X Axis Decimals** (check box) - Put a check on this box in order to enforce the number of decimals displayed by the numeric labels of the X axis of the printed / copied graph. If the box is checked, then the number of decimals is determined by the number in the edit box on the right. Otherwise, the applied number of decimals is determined automatically.

**Set X Axis Decimals** (edit box) - This is the decimal number of the numeric labels of the X axis that is enforced if the corresponding check box is checked.

**Set Y Axis Decimals** (check box) - Put a check on this box in order to enforce the number of decimals displayed by the numeric labels of the Y axis of the printed / copied graph. If the box is checked, then the number of decimals is determined by the number in the edit box on the right. Otherwise, the applied number of decimals is determined automatically.

**Set Y Axis Decimals** (edit box) - This is the decimal number of the numeric labels of the Y axis that is enforced if the corresponding check box is checked.

**Set Font Size** (check box) - Put a check on this box in order to enforce the font size of the numeric / textual labels of the graph printed / copied. If the box is checked, then the font size is determined by the number in the edit box on the right. Otherwise, it is determined automatically.

**Set Font Size** (edit box) - This is the font size of the labels of the printed / copied graph that is enforced if the corresponding check box is checked. The possible values are 1 (small), 2 (medium) and 3 (big).

**Left Margin** (edit box) - This is the left margin applied to the printed graph, i.e. on the printed page the graph is shifted to the right by an amount of points given by this value. (One full page is usually equivalent to a few thousands of image points.) Graphs copied to the clipboard are not affected by this parameter.

**Top Margin** (edit box) - This is the top margin applied to the printed graph, i.e. on the printed page the graph is shifted downwards by an amount of points given by this value. (One full page is usually equivalent to a few thousands of image points.) Graphs copied to the clipboard are not affected by this parameter.

**Horizontal size** (edit box) - This is the horizontal resolution (i.e. resolution in the direction of the X axis) of the printed / copied image in pixels. (Depending on the resolution of the applied printer, one pixel can be equivalent to several printed image points.)

**Vertical size** (edit box) - This is the vertical resolution (i.e. resolution in the direction of the Y axis) of the printed / copied image in pixels. (Depending on the resolution of the applied printer, one pixel can be equivalent to several printed image points.)

**Point size** (check boxes) - These check boxes enable the selection of the size of the individual data points on the printed / copied image. For high resolution printout or for low amounts of data BIG, whereas for lower resolutions or for higher amounts of data MEDIUM or SMALL data point size is recommended.

**Line** (check boxes) - These check boxes enable the selection of THIN, MEDIUM or THICK line width for the fitting curve(s) drawn on the printed / copied image.

**YL** (Y label) (check box) - If this check box is checked, then all the printed / copied spectrum graphs will display the text on the right as Y-axis title label. Otherwise the Y-axis title label is set individually for each spectrum according to the Y-AXIS TITLE spectrum parameter (see the EDT menu).

**YL** (Y label) (edit box) - This is the text that is displayed as Y-axis title label for each of the printed / copied spectrum graphs provided that the corresponding check box is checked.

**XL** (X label) (check box) - If this check box is checked, then all the printed / copied spectrum graphs will display the text on the right as X-axis title label. Otherwise the X-axis title label is set individually for each spectrum according to the X-AXIS TITLE spectrum parameter (see the EDT menu).

**XL** (X label) (edit box) - This is the text that is displayed as X-axis title label for each of the printed / copied spectrum graphs provided that the corresponding check box is checked.

**Show Value of** (special parameters) (list box) - The value of special spectrum parameters (see the EDT menu) selected in this list box will be displayed on the top of the printed / copied spectrum data.

**Show Residual** (check box) - Put a check on this box in order to have the residual displayed above the spectrum data on the printed / copied spectrum graph.

**Print in color** (check box) - Uncheck this box in order to have the spectrum graph printed / copied in grayscale instead of in color.

**Econo Mode** (check box) - Put a check on this box in order to have the spectrum graph printed / copied in econo mode, i.e. with lighter colors that consume less ink when printed.

**Connect** (check box) - Put a check on this box in order to have the neighboring spectrum data points connected by a straight line on the printed / copied spectrum graph.

**StD bars** (check box) - Put a check on this box in order to have a vertical line segment drawn over each of the spectrum data points on the printed / copied spectrum graph. The line segments extend ±σ around the data points where σ is the square root of the data count value.

**Portrait** (check box) - Put a check on this box to set printout orientation to Portrait, and to reload the default settings for the portrait mode of the current printer. For a given printer different default settings can be attributed to the portrait and landscape modes. This option does not affect clipboard functions.

**Landscape** (check box) - Put a check on this box to set printout orientation to Landscape, and to reload the default settings for the landscape mode of the current printer. For a given printer different default settings can be attributed to the portrait and landscape modes. This option does not affect clipboard functions.

**Print Red** (button) - Press on this box in order to print the red-framed spectrum to the currently selected printer. If the currently selected printer is one of the clipboard functions (Clipboard - single spectrum or Clipboard - multiple spectra), then the graph is printed to the default printer (see the SET menu). Printing is performed by considering the currently set attributes.

**Print All** (button) - Press on this box in order to print all spectra on the current desk to the currently selected printer. If the currently selected printer is one of the clipboard functions (Clipboard - single spectrum or Clipboard - multiple spectra), then the graph is printed to the default printer (see the SET menu). Printing is performed by considering the currently set attributes.

**Copy Red To Clipboard** (button) - Press on this box in order to copy the graph of the red-framed spectrum to the clipboard of Windows by considering the current attributes set on the printer setup dialog.

**Copy All To Clipboard** (button) - Press on this box in order to copy the graph of all the spectra on the current desk to the clipboard of Windows by considering the current attributes set on the printer setup dialog.

**Printer** (popup box) - Press on this popup box in order to select another available printer / clipboard function, and to reload the default attributes of the newly selected printer / function.

**Load Defaults** (button) - Press on this box in order to reload the default attributes of the currently selected printer / clipboard function.

**Save as default** (button) - Press on this box in order to save the currently set printing attributes as the default attributes of the currently selected printer / clipboard function.

**Spectrum parameters** (list box) - This box shows the parameters of the red-framed spectrum window.

**Quit** - Press on this box in order to close the Printer Setup dialog.

# 37. The EXEcute menu

Press with the left mouse button on the EXE box in order to access the following options:

- **List of user-selected executables** - to execute the selected program (*.EXE) or the program associated with the selected file (e.g. the PDF reader for *.PDF files).
- **Add new executable...** - to display the file explorer dialog of MossWinn in *file selection* mode, in order to add a new file entry to the user-selected list of executables.
- **Remove from the list of executables** - to remove the selected file entry from the list of executables.
- **Select Editor Program...** - to display the file explorer dialog of MossWinn in *file selection* mode, in order to select the text editor program invoked by MossWinn when configuration files are to be edited (via the SET menu), or when the file belonging to the red-framed window needs to be edited (on pressing key 'E').

- **Run SCANFIT.EXE** - to execute the SCANFIT.EXE program that allows the creation of ASCII spectrum data from bitmap images of Mossbauer spectra. This program is located inside the directory **..\MossWinn 4.0\EXEs**

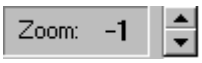
Press with the right mouse button on the EXE box in order to execute the program in the list of executables, that has the code word RMC written after its path+name in the configuration file **execute.cfg** (see section 8). Turn to the option EDIT CONFIGURATION FILE... in the menu list of the SET menu in order to add the code word after the file name of one of the executables.

# 38. The ScanFit.exe program

The ScanFit program can be started from the EXE menu of MossWinn. With the aid of ScanFit one can create ASCII data from bitmap images of Mössbauer spectra. Next follows the description of the available menus of the ScanFit program.

- To load the Bitmap containing the picture of the Mössbauer spectrum. In the latest version this item can be found in the File menu.

- To save the Bitmap in its actual state. In the latest version this item can be found in the File menu.



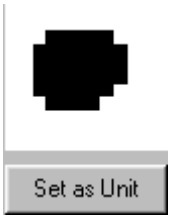

- Click to zoom in or out the Bitmap image on the screen.

- Set GREY LIMIT to a lower value to make noisy gray background to appear as white. Any Bitmap point that is lighter than the given value will be treated as white. (255 = White , 0 = Black)

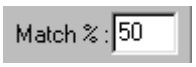
The area of the Bitmap picture *outside* of the selected rectangle will be *cut away*.

The area *inside* the selected rectangle will be filled with white.

The area *outside* of the selected rectangle will be filled with white.



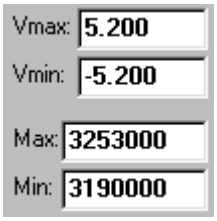

To create the ASCII data from the Bitmap image one has to select an area of the Bitmap that will serve as the unit of the identification procedure. In the case of Mössbauer spectra the unit should be one point of the spectrum (cross-, rectangle-, circle-, triangle-, or another type). The program does not require that all the points are exactly the same as the unit, but the unit should bear a basic resemblance to other points, at least considering its approximate size. To set the unit, select a single spectrum point on the Bitmap, and press the "Set as Unit" button. Before selection, zoom in the picture if necessary. A large unit with a large number of pixels (>100) may result in slower execution. In such a case reduce the number of pixels (via "Reduce Size", see later) if necessary.



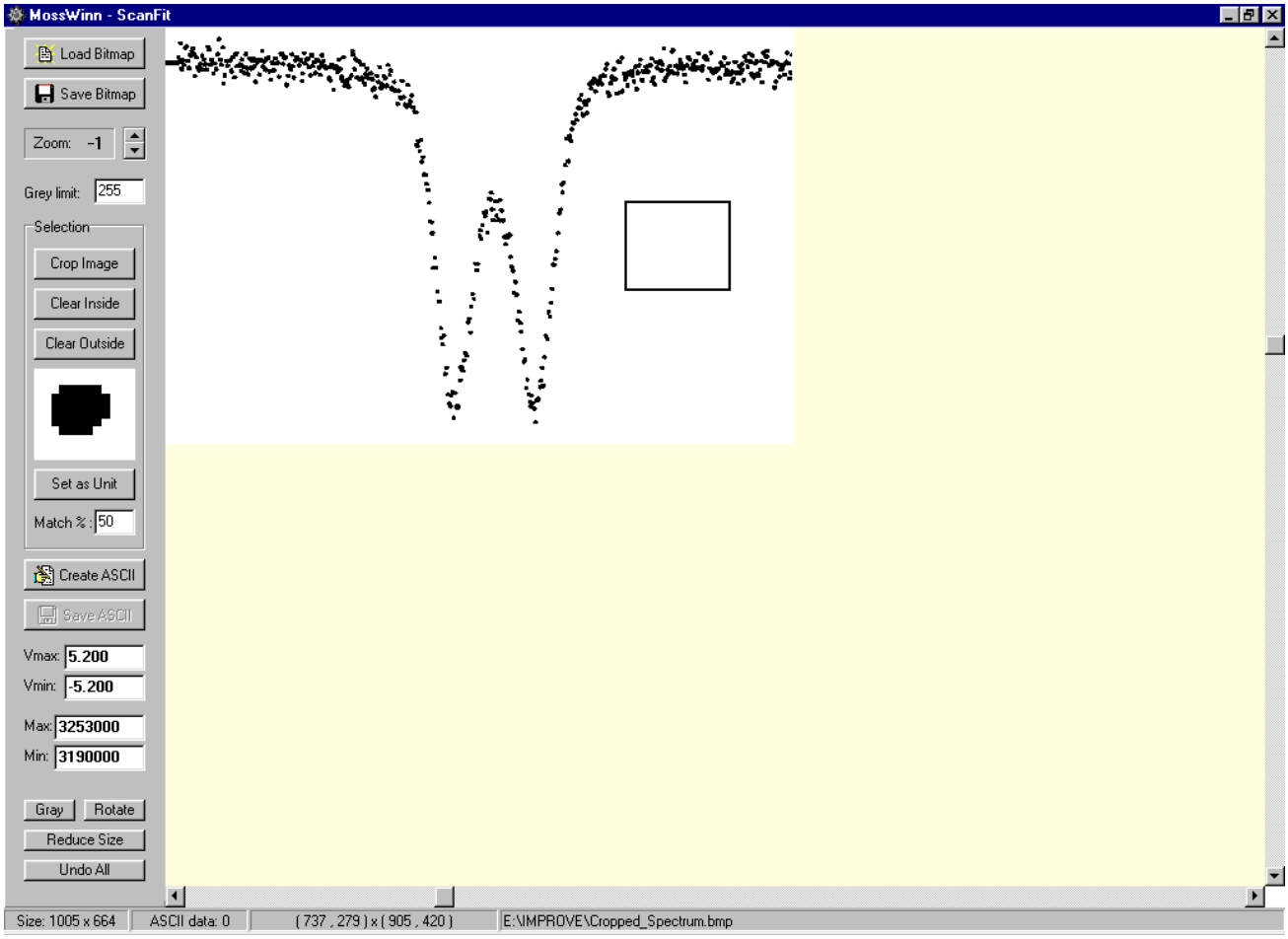

If the match between a specific area of the Bitmap and the selected Unit exceeds the given value, then that area will be identified as a spectrum point. Set it to a lower value if ScanFit did not identify all the Mössbauer data points.

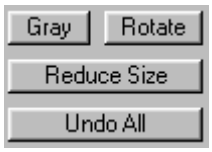
Click this button to start the ASCII data creation procedure.

Click the "Save ASCII" button to save the ASCII data that was created by the CREATE ASCII procedure. In the latest version this item can be found in the File menu.




Before starting the CREATE ASCII process, in order to create the correct ASCII data, set the minimum and maximum of the velocity axis — approximated on the basis of the Bitmap picture of the Mössbauer spectrum. The minimum and maximum of the spectrum — also approximated on the basis of the Bitmap image — can be set here as well. **These values will be attributed to the leftmost (Vmin), rightmost (Vmax), bottommost (Min) and topmost (Max) pixel of the Bitmap image when the ASCII data are created.** Therefore, before pressing "Create ASCII", use the "Crop Image" button to make the Bitmap look like it is illustrated on the next page, that is, the bitmap should contain only the spectrum data without the axes.




In the latest version these items can be found in the Edit menu.

- Click the “Gray” button to turn color images into grayscale. (Discard color information)

- Click the “Rotate” button to rotate the Bitmap image in order to make the velocity axis to be horizontal on the screen. This procedure introduces a slight distortion into the image therefore the number of rotations applied should be kept at a minimum.

- Click the “Reduce Size” button to reduce the number of pixels the Bitmap image consists of. Turn to this option if the image is too big to handle appropriately by your computer.

- Click on the “Undo All” button to restore the Bitmap image to the form it had when it was loaded.

The ASCII data file created and saved by the ScanFit program will have the appropriate form to get loaded and fitted by MossWinn.

# 39. The HELP menu

Press on the HELP menu box with the left mouse button in order to access the following options.

- **Licence code of the attached key: XXXX** - this line shows the licence code associated with the attached hardware key.
- **Request MossWinn Services subscription for the attached key... -** to request / renew subscription to the MossWinn Services for the attached hardware key by opening a subscription request E-mail in the default E-mail client.
- **Request abbreviation code for use in stoichiometry expressions...** - to request a new molecular formula abbreviation code to be used in stoichiometry expressions. Details of the abbreviation can be set on the appearing form that can also compose and open a corresponding E-mail in the default E-mail client. The E-mail is to be sent to the author of MossWinn.
- **Look up abbreviation codes for use in stoichiometry expressions...** - to look up abbreviation codes that have already been defined by opening the corresponding web page in the default browser.
- **Read release notes on the web...** - to open the web page displaying the release notes associated with the released MossWinn versions.
- **Check for updates of MossWinn executables...** - to download and install the latest version of the MossWinn program from the web.
- **Download and install latest help from the web** - to update the local help files to the latest version published on the web.
- **Download and open latest MossWinn manual from the web** - to download and open the latest version of the MossWinn manual as published on the web. The download operation is performed only when the version available for download is more recent than the version previously downloaded.
- **Load demo spectra** - to load the demo spectra of MossWinn on a separate project desk.
- **Video tutorials on the web...** - to open the web page showing video tutorials concerning MossWinn.
- **Help on the main menu** - to bring up the html help of MossWinn.
- **Help on the left side menus...** - to bring up the help information as included in the html help concerning the selected left side menu box.
- **Help on the right side menus...** - to bring up the help information as included in the html help concerning the selected right side menu box.
- **Help on the MossWinn Internet Database (MIDB)** - to bring up the help information as included in the html help concerning the MossWinn Internet Database.
- **Turn help mode ON/OFF** - to turn MossWinn's help mode ON/OFF. Equivalent to the function of the right mouse button.

Press on the HELP menu box with the right mouse button in order to turn MossWinn's help mode ON/OFF. If help mode is ON, then a mouse click on the menu boxes will bring up the corresponding help information in the html help. Help mode is ON when the HELP menu text is highlighted in red color. Help mode can also be turned off by a press on the ESC key.

# 40. The EXIT menu

LMC the EXIT box to leave the MossWinn program. The project desks loaded into the program will get updated automatically. If the number of windows decreased on a desk then MossWinn will ask for confirmation. An exception is the GENERAL DESK in the GENERAL PROJECTS project group, which desk gets updated automatically even if it is empty.

# 41. Keystrokes applicable in MossWinn

- **F1** - Set application window such that its size (in pixels) corresponds to 1× the internal MossWinn screen resolution.
- **F2** - Set application window such that its size (in pixels) corresponds to 2× the internal MossWinn screen resolution.
- **F3** - Set application window such that its size (in pixels) corresponds to 3× the internal MossWinn screen resolution.
- **F4** - Toggle between full screen and windowed modes.
- **F5** - Toggle between ***always on top*** and normal window modes.
- **F8** - To show or hide the Edit Spectrum Parameters Dialog (see page 24).
- **F12** - Invoke the html help.
- **TAB** - Go to the next active project desk.
- **Backspace** - Go to the previous active project desk.
- **E** - Edit the text file associated with the red-framed window by executing the user-defined editor program (see the EXE menu).
- **ESC** - Show/hide the blue side menus. (Rearranges the spectrum windows.)
- **ctrl-C** - Copy image of the red-framed spectrum into the clipboard of Windows.
- **ctrl+shift-C** - Copy image of all the spectra on the screen into the clipboard of Windows.
- **ctrl-P** - Print image of the red-framed spectrum to the default Windows printer.
- **ctrl+shift-P** - Print image of all the spectra on the screen to the default Windows printer.
- **J** - Save image of the red-framed spectrum as a JPEG image file.
- **shift-J** - Save image of all the spectra on the screen as a JPEG image file.
- **C** - Save image of the red-framed spectrum as a 24 bit color bitmap.
- **shift-C** - Save image of all the spectra on the screen as a 24 bit color bitmap.
- **B** - Save image of the red-framed spectrum as a 1 bit B&W bitmap.
- **shift-B** - Save image of all the spectra on the screen as a 1 bit B&W bitmap.
- **R** - to show/hide the residual for the red-framed spectrum window.
- **shift-R** - to show/hide the residual for all the spectrum windows.
- **shift-M** - Display the amount of physical memory available to MossWinn.
- **shift-A** - Display the 'About' page of MossWinn.

# 42. Nuclear constants as used in MossWinn 4.0

In practice it may happen to be necessary to analyze Mössbauer spectra using nuclear constants different from those used in the MossWinn program by default. Nuclear data default in MossWinn are based on the following references (note that some of the nuclear constants default in the MossWinn 4.0 series are very different from the corresponding constants default in the 3.0 series):


E.R. Cohen, B.N. Taylor: *Rev. Mod. Phys.* **59** (1987) 1121.

P. Raghavan: *Atomic Data and Nuclear Data Tables* **42** (1989) 189.

*P. Dufek, P. Blaha, K. Schwarz: *Phys. Rev. Lett.* **75** (1995) 3545.

**A.A. Moolenaar: A $^{141}$Pr Mössbauer study of Praseodymium Compounds, PhD Thesis (1994), Interfaculty Reactor Institute, Delft University of Technology, ISBN 90-73861-20-9

**AA. Moolenaar, P.C.M. Gubbens, J.J. van Loef, M.J.V. Menken, A.A. Menovsky: *Physica C* **267** (1996) 279.

P. Pyykkö: *Molecular Physics* **99** (2001) 1617.

P. Pyykkö: *Molecular Physics* **106** (2008) 1965.

NUDAT2: HTTP://WWW.NNDC.BNL.GOV/NUDAT2/


In order to override the default nuclear constants of MossWinn, create a text file named **nuclear.cfg** , and place it inside the directory: **..\MOSSWINN 4.0\USERS\PUBLIC\STATUS**

In the file **nuclear.cfg** the new values of nuclear constants can be defined as it is illustrated in the following table.

| SYNTAX (In the file **NUCLEAR.CFG**) | EXAMPLE (Default in MossWinn) | MEANING |
|---|---|---|
| **gFe32:** *newvalue* | **gFe32: -0.103267** | Gyromagnetic factor of the excited state of $^{57}$Fe |
| **gFe12:** *newvalue* | **gFe12: +0.18088** | Gyromagnetic factor of the ground state of $^{57}$Fe |
| **QFe32:** *newvalue* | **QFe32: +0.16E-28 {m2}** | Quadrupole moment of the excited state of $^{57}$Fe * |
| **EgammaFe:** *newvalue* | **EgammaFe: 14.4129 {keV}** | Energy of the gamma ray of the $^{57}$Fe Mössbauer transition |
| **gSn32:** *newvalue* | **gSn32: +0.422** | Gyromagnetic factor of the excited state of $^{119}$Sn |
| **gSn12:** *newvalue* | **gSn12: -2.09456** | Gyromagnetic factor of the ground state of $^{119}$Sn |
| **QSn32:** *newvalue* | **QSn32: -0.132E-28 {m2}** | Quadrupole moment of the excited state of $^{119}$Sn |
| **EgammaSn:** *newvalue* | **EgammaSn: 23.871 {keV}** | Energy of the gamma ray of the $^{119}$Sn Mössbauer transition |
| **gTe32:** *newvalue* | **gTe32: +0.403333** | Gyromagnetic factor of the excited state of $^{125}$Te |
| **gTe12:** *newvalue* | **gTe12: -1.77702** | Gyromagnetic factor of the ground state of $^{125}$Te |
| **QTe32:** *newvalue* | **QTe32: -0.31E-28 {m2}** | Quadrupole moment of the excited state of $^{125}$Te |
| **EgammaTe:** *newvalue* | **EgammaTe: 35.4919 {keV}** | Energy of the gamma ray of the $^{125}$Te Mössbauer transition |
| **gEu72:** *newvalue* | **gEu72: +0.740286** | Gyromagnetic factor of the excited state of $^{151}$Eu |
| **gEu52:** *newvalue* | **gEu52: +1.38868** | Gyromagnetic factor of the ground state of $^{151}$Eu |
| **QEu72:** *newvalue* | **QEu72: +1.28E-28 {m2}** | Quadrupole moment of the excited state of $^{151}$Eu |
| **QEu52:** *newvalue* | **QEu52: +0.903E-28 {m2}** | Quadrupole moment of the ground state of $^{151}$Eu |
| **EgammaEu:** *newvalue* | **EgammaEu: 21.541 {keV}** | Energy of the gamma ray of the $^{151}$Eu Mössbauer transition |
| **gSb72:** *newvalue* | **gSb72: +0.7194286** | Gyromagnetic factor of the excited state of $^{121}$Sb |
| **gSb52:** *newvalue* | **gSb52: +1.34536** | Gyromagnetic factor of the ground state of $^{121}$Sb |
| **QSb72:** *newvalue* | **QSb72: -0.728E-28 {m2}** | Quadrupole moment of the excited state of $^{121}$Sb |
| **QSb52:** *newvalue* | **QSb52: -0.543E-28 {m2}** | Quadrupole moment of the ground state of $^{121}$Sb |
| **EgammaSb:** *newvalue* | **EgammaSb: 37.133 {keV}** | Energy of the gamma ray of the $^{121}$Sb Mössbauer transition |
| **gPr72:** *newvalue* | **gPr72: +0.8** | Gyromagnetic factor of the excited state of $^{141}$Pr ** |
| **gPr52:** *newvalue* | **gPr52: +1.71016** | Gyromagnetic factor of the ground state of $^{141}$Pr ** |
| **QPr72:** *newvalue* | **QPr72: +0.28E-28 {m2}** | Quadrupole moment of the excited state of $^{141}$Pr ** |
| **QPr52:** *newvalue* | **QPr52: -0.0589E-28 {m2}** | Quadrupole moment of the ground state of $^{141}$Pr ** |
| **EgammaPr:** *newvalue* | **EgammaPr: 145.44 {keV}** | Energy of the gamma ray of the $^{141}$Pr Mössbauer transition ** |

| SYNTAX<br>(In the file NUCLEAR.CFG) | EXAMPLE<br>(Default in MossWinn) | MEANING |
|---|---|---|
| **g129I72:** *newvalue* | **g129I72: +0.748857** | Gyromagnetic factor of the ground state of $^{129}$I |
| **g129I52:** *newvalue* | **g129I52: +1.1218** | Gyromagnetic factor of the excited state of $^{129}$I |
| **Q129I72:** *newvalue* | **Q129I72: -0.498E-28 {m2}** | Quadrupole moment of the ground state of $^{129}$I |
| **Q129I52:** *newvalue* | **Q129I52: -0.604E-28 {m2}** | Quadrupole moment of the excited state of $^{129}$I |
| **Egamma129I:** *newvalue* | **Egamma129I: 27.8 {keV}** | Energy of the gamma ray of the $^{129}$I Mössbauer transition |
| **gNp52g:** *newvalue* | **gNp52g: +1.256** | Gyromagnetic factor of the ground state of $^{237}$Np |
| **gNp52e:** *newvalue* | **gNp52e: +0.672** | Gyromagnetic factor of the excited state of $^{237}$Np |
| **QNp52g:** *newvalue* | **QNp52g: +3.886E-28 {m2}** | Quadrupole moment of the ground state of $^{237}$Np |
| **QNp52e:** *newvalue* | **QNp52e: +3.85E-28 {m2}** | Quadrupole moment of the excited state of $^{237}$Np |
| **EgammaNp:** *newvalue* | **EgammaNp: 59.541 {keV}** | Energy of the gamma ray of the $^{237}$Np Mössbauer transition |
| **gAu32:** *newvalue* | **gAu32: +0.097167** | Gyromagnetic factor of the ground state of $^{197}$Au |
| **gAu12:** *newvalue* | **gAu12: +0.84** | Gyromagnetic factor of the excited state of $^{197}$Au |
| **QAu32:** *newvalue* | **QAu32: +0.547E-28 {m2}** | Quadrupole moment of the ground state of $^{197}$Au |
| **AE2pM1AU:** *newvalue* | **AE2pM1AU: +0.3317** | AMPLITUDE ( $\delta$ ) of the E2/M1 mixing ratio in the Mössbauer transition of $^{197}$Au. |
| **PE2pM1AU:** *newvalue* | **PE2pM1AU: 180.0 {deg}** | PHASE difference between the E2 and M1 radiations in the Mössbauer transition of $^{197}$Au.<br>MEASURED IN DEGREES.<br>($180 \cdot \frac{\zeta}{\pi}$ where $\zeta$ appears as $\delta \cdot e^{i \cdot \zeta}$ ) |
| **EgammaAu:** *newvalue* | **EgammaAu: 77.351 {keV}** | Energy of the gamma ray of the $^{197}$Au Mössbauer transition |
| **g161Dy52g:** *newvalue* | **g161Dy52g: -0.19212** | Gyromagnetic factor of the ground state of $^{161}$Dy |
| **g161Dy52e:** *newvalue* | **g161Dy52e: +0.2376** | Gyromagnetic factor of the 5/2− excited state of $^{161}$Dy |
| **Q161Dy52g:** *newvalue* | **Q161Dy52g: +2.507E-28 {m2}** | Quadrupole moment of the ground state of $^{161}$Dy |
| **Q161Dy52e:** *newvalue* | **Q161Dy52e: +2.506E-28 {m2}** | Quadrupole moment of the 5/2− excited state of $^{161}$Dy |
| **Egamma161Dy52:** *newvalue* | **Egamma161Dy52: 25.6514 {keV}** | Energy of the gamma ray of the $^{161}$Dy [excited 5/2−] → [ground 5/2+] Mössbauer transition |

To check whether the override of the above nuclear parameters is in effect in MossWinn, examine the file STARTUP.TXT that informs about any parameter override that took place when MossWinn started. The override of any parameter is in effect only if there is a clear indication in the file STARTUP.TXT about.

The following table informs about the value of some further physical constants used in MossWinn:

| *Constant and its value as used in MossWinn* | *Explanation* |
|---|---|
| $c = 2.99792458\times10^{8}$ m/s | Speed of light in vacuum |
| $e = 1.6021766208\times10^{-19}$ C | Elementary charge |
| $k_B = 1.38064852\times10^{-23}$ J/K | Boltzmann constant |
| $h/2\pi = 1.054571800\times10^{-34}$ Js | Planck constant / $2\pi$ |
| $\mu_N = 5.050783699\times10^{-27}$ J/T | Nuclear magneton |
| IS (SNP) = −0.26 mm/s | Isomer shift of Sodium Nitroprusside relative to α-Iron |
| IS ( Fe(Cr) ) = −0.154 mm/s | Isomer shift of Fe in Chromium matrix relative to α-Iron |
| IS (SS) = −0.09 mm/s | Isomer shift of Stainless Steel relative to α-Iron |
| IS (α-Fe) = 0.0 mm/s | Isomer shift of α-Iron (reference) |
| IS ( Fe(Rh) ) = +0.114 mm/s | Isomer shift of Fe in Rhodium matrix relative to α-Iron |
| IS ( Fe(Pd) ) = +0.177 mm/s | Isomer shift of Fe in Palladium matrix relative to α-Iron |

| | |
|---|---|
| NLW ( $^{57}$Fe ) = 0.194 mm/s | (Experimental) Natural line width of $^{57}$Fe (3/2 → 1/2) |
| NLW ( $^{119}$Sn ) = 0.646 mm/s | (Experimental) Natural line width of $^{119}$Sn (3/2 → 1/2) |
| NLW ( $^{125}$Te ) = 5.209 mm/s | (Experimental) Natural line width of $^{125}$Te (3/2 → 1/2) |
| NLW ( $^{151}$Eu ) = 1.31 mm/s | (Experimental) Natural line width of $^{151}$Eu (7/2 → 5/2) |
| NLW ( $^{121}$Sb ) = 2.10 mm/s | (Experimental) Natural line width of $^{121}$Sb (7/2 → 5/2) |
| NLW ( $^{141}$Pr ) = 1.017 mm/s | (Experimental) Natural line width of $^{141}$Pr (7/2 → 5/2) |
| NLW ( $^{129}$I ) = 0.586 mm/s | (Experimental) Natural line width of $^{129}$I (5/2 → 7/2) |
| NLW ( $^{237}$Np ) = 0.06727 mm/s | (Experimental) Natural line width of $^{237}$Np (5/2 → 5/2) |
| NLW ( $^{197}$Au ) = 1.882 mm/s | (Experimental) Natural line width of $^{197}$Au (1/2 → 3/2) |
| NLW ( $^{161}$Dy ) = 0.378 mm/s | (Experimental) Natural line width of $^{161}$Dy (5/2 → 5/2) |

# 43. Quadrupole splitting conversion constants

The following table can be used to derive the value of $eQ_{ground}V_{zz}$ in units of mm/s and MHz from the value of $V_{zz}$ measured in units of $10^{21}$ V/m$^2$ as displayed in MossWinn.

For example, if $V_{zz}$ = +3.0 [$10^{21}$ V/m$^2$] for $^{151}$Eu, then $eQ_{ground}V_{zz}$ [mm/s] can be obtained by multiplying 3.0 by 1.257(14), the end result being 3.77(4) mm/s, where the numbers in parentheses refer to the uncertainties in the last digits of the preceding values.

The constants in the table below were calculated by assuming the validity of the built in nuclear constants of MossWinn (see previous chapter). If the user has overridden the corresponding nuclear constants, then the conversion constants below are not valid anymore (in such a case use the corresponding constants **QSCe** and **QSCg** written on the fit reports – see section **Error! Reference source not found.**).

For some of the nuclear transitions, the electric quadrupole moment of the ground state equals to zero. In those cases ($^{57}$Fe, $^{119}$Sn, $^{125}$Te) $Q_{excited}$ is used instead of $Q_{ground}$.

In general 1 mm/s is equivalent to 0.806554486 × ($E_\gamma$ / keV) MHz, where $E_\gamma$ is the energy of the Mossbauer transition.

| Nuclear transition | In order to obtain $eQ_{ground}V_{zz}$ [**mm/s**], $V_{zz}$ [$10^{21}$ V/m$^2$] should be multiplied by: | In order to obtain $eQ_{ground}V_{zz}$ [**MHz**], $V_{zz}$ [$10^{21}$ V/m$^2$] should be multiplied by: |
|---|---|---|
| $^{57}$Fe (3/2 → 1/2) ( $eQ_{excited}V_{zz}$ ) | +0.333(2) | +3.87(2) |
| $^{119}$Sn (3/2 → 1/2) ( $eQ_{excited}V_{zz}$ ) | −0.166(1) | −3.19(2) |
| $^{125}$Te (3/2 → 1/2) ( $eQ_{excited}V_{zz}$ ) | −0.262(17) | −7.5(5) |
| $^{151}$Eu (7/2 → 5/2) | +1.257(14) | +21.83(24) |
| $^{121}$Sb (7/2 → 5/2) | −0.438(9) | −13.13(27) |
| $^{141}$Pr (7/2 → 5/2) | −0.0121(8) | −1.42(10) |
| $^{129}$I (5/2 → 7/2) | −0.537(8) | −12.04(17) |
| $^{237}$Np (5/2 → 5/2) | +1.957(3) | +93.96(15) |
| $^{161}$Dy (5/2 → 5/2) | +2.930(23) | +60.62(48) |
| $^{197}$Au (1/2 → 3/2) | +0.212(6) | +13.23(39) |

# 44. PHS model unit conversion constants

The crystal field parameters *D*, *a*, *F* and the elements of the hyperfine interaction tensor **A** are given in the literature in various units. The tables below inform about the conversion constants that can be used to obtain the corresponding values in units used in the MossWinn program.

| If the value of *D*, *a* or *F* is given in this unit, | multiply it with this factor to obtain its value in 1/cm. |
|---|---|
| **kelvin [K]** | 0.6950345704 |

| If the value of *A* is given in this unit, | multiply it with this factor to obtain its value in Tesla for the case of $^{57}$Fe. |
|---|---|
| **mm/s** (for the $I_e$ = 3/2 nuclear level of $^{57}$Fe) | −14.768 |
| **mm/s** (for the $I_g$ = 1/2 nuclear level of $^{57}$Fe) | +8.43125 |
| **MHz** (for the $I_e$ = 3/2 nuclear level of $^{57}$Fe) | −1.27039 |
| **MHz** (for the $I_g$ = 1/2 nuclear level of $^{57}$Fe) | +0.725282 |

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