

# **Recoil**

## **Mössbauer Spectral Analysis Software for Windows**

*version 1.0*

code and documentation written by Ken Lagarec  
software produced by the Mössbauer Group  
under the direction of Prof. Denis G. Rancourt

Department of Physics  
University of Ottawa

©1998 Ken Lagarec and D.G. Rancourt

# Table of Contents

## Chapter 1. Getting Started

1.1 Using This Document .....	1
1.2 Program Requirements and Installation .....	1
1.2.1 Minimum Program Requirements .....	1
1.2.2 Program Installation .....	1
1.2.3 Uninstalling Recoil .....	2
1.3 How to Reach the Authors .....	2
1.4 Recoil Design .....	3
1.5 Mössbauer Spectroscopy Parameters: Names and Symbols used in Recoil .....	4
1.5.1 General Analysis .....	4
1.5.2 Paramagnetic Materials .....	5
1.5.3 Magnetic Materials - the First-Order Perturbation Theory Results .....	5

## Chapter 2. Analysis Models

2.1 Voigt Peak Fit .....	6
2.1.1 Domains of Applicability .....	6
2.1.2 Model Parameters .....	6
2.1.3 References .....	7
2.1.4 File Format .....	7
2.2 Lorentzian Multiplet Analysis .....	8
2.2.1 Domains of Applicability .....	8
2.2.2 Model Parameters .....	8
2.2.3 References .....	9
2.2.4 File Format .....	9
2.3 Voigt-based Fitting (VBF) Analysis .....	10
2.3.1 Domains of Applicability .....	10
2.3.2 Model Parameters .....	11
2.3.3 References .....	11
2.3.4 File Format .....	12
2.4 Extended Voigt-based Fitting (xVBF) Analysis .....	13
2.4.1 Domains of Applicability .....	13
2.4.2 Model Parameters .....	14
2.4.3 References .....	15
2.4.4 File Format .....	15
2.5 Full Static Hamiltonian Site Analysis .....	16
2.5.1 Domains of Applicability .....	17
2.5.2 Model Parameters .....	17
2.5.3 References .....	19
2.5.4 File Format .....	19
2.6 Dynamic Line Shape Site Analysis .....	21
2.6.1 Domains of Applicability .....	21
2.6.2 Model Parameters .....	22
2.6.3 Parameter Constraints and Implementation Details .....	22
2.6.4 References .....	22
2.6.5 File Format .....	23
2.7 Source HWHM Extraction .....	24
2.7.1 Domains of Applicability .....	24
2.7.2 Model Parameters .....	24

Recoil Reference	iii
2.7.3 Cross-section file	24
2.7.4 References	25
2.7.5 File Format	25
<b>Chapter 3. Utilities</b>	
3.1 Debye Model Calculations	26
3.2 Ideal Thickness Calculations	27
3.3 The Mössbauer Thickness	28
3.4 References	28
<b>Chapter 4. How Do I</b>	
4.1 Analyse a spectrum ?	29
4.2 Create a calibration file ?	29
4.3 Fold a spectrum ?	30
4.4 Calculate the ideal thickness for a sample ?	30
4.5 Calculate the Mössbauer thickness of a sample ?	30
<b>Chapter 5. Configuring Recoil</b>	
5.1 The isotopes.ini File	31
5.2 The calibrat.ini File	31
5.3 General Program Options	31
5.3.1 Units of the Magnetic Hyperfine Field	31
5.3.2 Fitting Options	32
5.3.3 Mössbauer Source	32
<b>Chapter 6. Error Calculations</b>	
6.1 $\chi^2$ Topology Methods	33
6.1.1 Using the Covariance Matrix	33
6.1.2 Using the Constant $\chi^2$ Boundary	34
6.2 Monte Carlo Methods	34
6.2.1 Using the Bootstrap Method	34
6.2.2 Using Counting Statistics	35
<b>Chapter 7. Differences Between Recoil and MOSMOD</b>	
7.1 Using Isotopes Other Than $^{57}\text{Fe}$	36
7.2 Differences in the Implementations of the Analyses	36
7.2.1 N-line fitting with Voigts or Lorentzians (MOSMOD 3)	36
7.2.2 Thickness Correction (MOSMOD 4)	37
7.2.3 Lorentzian Site Analysis (MOSMOD 5)	37
7.2.4 Full Static Hamiltonian Site Analysis (MOSMOD 6)	37
7.2.5 Blume and Tjon Dynamic Line Shape Site Analysis (MOSMOD 7)	38
7.2.6 Voigt-based Fitting (MOSMOD 8, 9 and 10)	38
7.2.7 Differences in the Utilities (MOSMOD 0, 1 and 2)	38
<b>Chapter 8. File Formats</b>	
8.1 Folded Mössbauer Data Files	39
8.2 Raw Mössbauer Data Files	39
8.3 Analysis Documents	39
8.4 Fit Spectrum Files	40
8.5 Probability Density Distribution Files	40

# Chapter 1

## Getting Started



### 1.1 Using This Document

This document is provided as a guide to explain the functionality of Recoil, but it is not an exhaustive reference of all of its capabilities. Many of Recoil's data input and formatting options are not explicitly described in this manual, but the author has tried to make them as consistent as possible with standard Windows's behaviour.

In general, clicking an item with the right mouse button (a "right click") activates a popup menu showing the possible actions available on that item. Double-clicking an item with the left mouse button will perform the default action (open or display properties). The user is encouraged to experiment with the program in order to discover its extended capabilities: Try everything you think should be available and it might be!

In terms of organization, this document's chapters correspond to the basic elements needed to use this software: an introduction (chapter 1) which describes its use and the philosophy behind its design, a detailed description of the analyses that can be performed (chapter 2), a How To guide for performing basic and essential tasks (chapter 3), a reference to the utilities available to help the Mössbauer user in some everyday tasks (chapter 4), and a description of the configuration options which are available to the user (chapter 5).

### 1.2 Program Requirements and Installation

#### 1.2.1 *Minimum Program Requirements*

Recoil is a 32-bit program designed to run on Windows<sup>®</sup> 95 or Windows NT<sup>®</sup> on the Intel platform. Here are the minimum program requirements:

- ▶ Windows<sup>®</sup> 95 or Windows NT<sup>®</sup> 4.0
- ▶ 486 PC (Pentium or higher recommended)
- ▶ 4 MB of hard disk space (installation)
- ▶ 8 MB RAM (16 MB recommended)
- ▶ VGA adapter and monitor (256 colour SVGA recommended)
- ▶ Pointing device (mouse or equivalent) required for some operations
- ▶ Windows-compatible printer for hard copy output

## 2 Chapter 1. Introduction

### 1.2.2 Program Installation

If you are installing over an existing version of Recoil, it is recommended that you backup the settings files (recoil.ini, isotopes.ini and calibrat.ini) if you have manually modified them for your purposes and uninstall the version of Recoil you already have. You can then edit the new settings files to reflect your modifications.

Recoil is supplied with a Windows95<sup>®</sup>-compatible install and uninstall process. To install Recoil, double-click on the setup.exe program on your diskette from within Windows Explorer. Follow the simple instructions to proceed with the installation. If you received a single self-extracting file, double-click on the file and follow the instructions.

During the install process, Recoil will register several icons for the file extensions it uses. Should these settings be erased, you can reregister them by running Recoil from the command prompt with the -register option:

```
C:\Program Files\Recoil> Recoil -register
```

If you do not want these extensions registered, run Recoil from the command prompt with the -unregister option:

```
C:\Program Files\Recoil> Recoil -unregister
```

Should you encounter any problems, feel free to consult the web page or contact the authors for assistance.

### 1.2.3 Uninstalling Recoil

Should you desire to uninstall Recoil, open the Add/Remove Programs applets of the Control Panel (Start | Settings | Control Panel), select Recoil and press the Uninstall button. The uninstall program might not be able to erase everything in the installation directory if new files were created there, so you might have to do this manually.

## 1.3 How to Reach the Authors

This guide was written to explain how the program works and what you can do with it. It is not, however, complete and you may have reasons to contact the authors if you have problems or if you have found a bug you wish to report. The published articles describing the analysis methods should be consulted and understood before using this software: all of the methods require the intervention of a user who knows what he's doing.

Should you need to contact us, we can be reached by email at

[recoil@physics.uottawa.ca](mailto:recoil@physics.uottawa.ca).

If you do not have access to an e-mail account, you may also write, phone or fax us:

For technical support and the reporting of bugs,

Ken Lagarec  
Department of Physics

University of Ottawa  
150 Louis Pasteur, Ottawa, ON  
CANADA K1N 6N5  
tel: (613) 562-5800 x6743  
fax: (613) 562-5190

For general enquires and sales information,

*Dr. Denis Rancourt*  
Department of Physics  
University of Ottawa  
150 Louis Pasteur, Ottawa, ON  
CANADA K1N 6N5  
tel: (613) 562-5800 x6774  
fax: (613) 562-5190

In addition, product information, frequently asked questions (FAQ) and patches will be posted on the web at

<http://www.physics.uottawa.ca/~recoil/>

## 1.4 Recoil Design

Recoil is built around a document/view architecture: each analysis corresponds to a different “analysis document”. The parameters and some other information are *stored* in the file, but it is up to the views to *display* the information.

By default, two views are opened when an analysis is started: the *Parameters View*, which is the primary view, lists the model parameters as well as some fitting parameters (number of data points, number of parameters, reduce  $\chi^2$ , etc.). In addition, the *Plot View* displays the observed and fitted spectra, including sub-spectral site contributions and the residuals. Every document can also have a *Report View* which is a text account of the model and fitting parameters which can be printed or saved to an ASCII or Rich Text Format (keeps formatting and can be imported in any word processor) file. In some situations, a *Distribution View* is also available to display the distributions of parameters obtained from the model.

When a document is open, new views can be created by using the **Views|New View...** menu command, which displays the list of available views in a popup menu or by pressing the speed button associated with that view type on the control bar. Views can be opened and closed at will, except for the Parameters View, which, when closed will prompt the user to save or discard the information, if it has changed. The other views can be saved independently: the plot and distribution views save their spectra (observed and calculated) or their distributions to a file, and the report view saves its content to a word processor readable file for further editing.

Another useful concept used in Recoil is the project. A project document is the parent of any document created, and can be used to manage groups of files that are related to each other. The Project View lists all the files in the project in a TreeView control (hierarchical display of dependancies). Data files occur as parent nodes to the various analysis documents which correspond to each data file. In this way, it is easy to keep track of which analyses were performed. When a document is open, its node’s text appears in bold type for easy identification. All menu commands on the project must be executed through the right click popup menu.

## 1.5 Mössbauer Spectroscopy Parameters: Names and Symbols used in Recoil

In general, only three types of interactions are considered to affect the probe nucleus in a Mössbauer experiment (we only consider  $I = 1/2$  to  $3/2$  transitions):

the **electric monopole interaction**. It is characterized by a shift of the complete spectrum relative to the reference (calibration) material. This shift is known as the *isomer shift*. In addition, the spectrum is shifted by a temperature and sample dependent quantity, the *second-order Doppler shift* (SOD), resulting in a net shift relative to a calibration material known as the *center shift*.

the **electric quadrupole interaction**. It occurs when (1) the nucleus has a quadrupole moment and (2) the electronic density produces an electric field gradient (EFG) at the nucleus. This causes a splitting of the excited ( $I = 3/2$ ) nuclear state into the  $m = \pm 3/2$  and  $m = \pm 1/2$  branches, resulting in two distinct spectral lines (since the  $I = 1/2$  state has no quadrupole moment).

the **magnetic dipole interaction**. It occurs between an effective magnetic hyperfine field at the nucleus and the magnetic moment of the nucleus. This interaction lifts all degeneracy between nuclear levels and thus possibly results in 8 spectral lines (however, only 6 transitions are allowed for a purely magnetic dipole interaction, the other two only occur in the presence of mixed interactions).

Higher order interactions occur but they are negligible compared to these three. Also, in the following description we consider effectively static behaviour modelled by a static Hamiltonian having only time-independent interactions. A special type of analysis available in **Recoil** is used to treat dynamic effects.

### 1.5.1 General Analysis

For a single given electronic environment of the probe nucleus, the static interactions are characterized by the following set of hyperfine parameters, which, in general produce a set of eight Lorentzian lines:

$CS$ or $\delta$	the center shift
$eq$ or $V_{zz}$	the principal component of the EFG tensor (it defines the $\mathbf{z}$ axis of the EFG tensor system)
$Q$	the nuclear quadrupole moment of the excited ( $I = 3/2$ ) state
$\eta$	the asymmetry parameter of the EFG. $\eta = ( V_{xx}  -  V_{yy} ) /  V_{zz} $ such that $0 \leq \eta \leq 1$
$z$ (or $H_{hf}$ )	the hyperfine Zeeman splitting of the first excited state: $z = g^* \mu_N H_{hf}$ where $H_{hf}$ is the effective magnetic hyperfine field
$\phi_{H_{hf}}, \theta_{H_{hf}}$	the azimuthal and polar angles of the magnetic hyperfine field in the EFG tensor principal axes coordinate system
$\phi_{\gamma}, \theta_{\gamma}$	the azimuthal and polar angles of the $\gamma$ -ray in the EFG tensor principal axes coordinate system

### 1.5.2 Paramagnetic Materials

In the case of paramagnetic substances, when the hyperfine magnetic field is nil — or effectively nil, the spectrum is either a singlet or a doublet and only the following parameters are needed:

CS or $\delta$	the center shift
QS or $\Delta$	the quadrupole splitting, $\Delta = \frac{e^2qQ}{2} \sqrt{1 + \frac{1}{3}\eta^2}$ . When this parameter is nil, the spectrum is a singlet.
$\phi_{\gamma q}, \theta_{\gamma q}$	the azimuthal and polar angles of the incident $\gamma$ -ray in the EFG coordinate system. This only affects the relative intensities of the two peaks. In practice, the peak area ratios are used to characterize such effects. For a perfectly randomly oriented absorber, the ratio is 1 (neglecting the Goldanskii-Karyagin effect).

### 1.5.3 Magnetic Materials - the First-Order Perturbation Theory Results

If a hyperfine magnetic field produces the dominant interaction, when the *first order perturbation* assumption is respected ( $(e^2qQ)/4 \ll z$ ) the spectrum is a sextet with peaks numbered 1 through 6 with increasing velocity. The required parameters are then limited to:

CS or $\delta$	the center shift
$z$ (or $H_{hf}$ )	the hyperfine Zeeman splitting of the excited state (or the magnetic hyperfine field)
$\varepsilon$	the quadrupole shift ( $\varepsilon = \frac{e^2qQ}{8} [2 - (3 - \eta \cos 2\phi_{Hq}) \sin^2\theta_{Hq}]$ )
$\theta_{\gamma H}$	the angle between the incident $\gamma$ -ray and $\mathbf{H}_{hf}$ . One effect of this angle is to vary the relative intensities of peaks 2 and 5 with respect to the others. When a powder average is performed ( $\theta_{\gamma H}$ is averaged), the peak area ratios become 3:2:1:1:2:3. In general, the the relative intensities of the lines, as a function of $\theta_{\gamma H}$ are $3:4 \sin^2\theta_{\gamma H}/(1 + \cos^2\theta_{\gamma H}):1:1:4 \sin^2\theta_{\gamma H}/(1 + \cos^2\theta_{\gamma H}):3$ (neglecting the Goldanskii-Karyagin effect).

This result is also valid outside of the first-order perturbation limit if  $\eta=0$  (the EFG has an axial symmetry) and  $\theta_{Hq}=0$  (the  $\mathbf{H}_{hf}$  direction is along the  $z$  axis of the EFG tensor coordinate system).



# Chapter 2

## Analysis Models

---

Recoil is primarily a program used to analyse Mössbauer spectra using various models. This chapter is dedicated to briefly describing and explaining the analysis methods. The file formats are also explained for reference purposes, the published scientific articles relevant to each method are listed.

### 2.1 Voigt Peak Fit

In certain cases, a specific full spectrum analysis is either unwanted or unnecessary. Instead, it can be useful to fit individual peaks to Voigt line shapes to get their individual characteristics. That is the purpose of this analysis model. In addition, the algorithm to perform corrections of thickness effects requires the spectrum to be represented by a sum of Voigt peaks and therefore requires that the Voigt peak model be applied to the raw folded data as a first step.

Since the Voigt line shape is the convolution of a Gaussian and a Lorentzian function, a pure Lorentzian line shape can be modelled by setting the Gaussian width to 0. This is the procedure if fits using individual Lorentzians are required.

#### 2.1.1 Domains of Applicability

- This model makes no assumption on the peak parameters, except that the Lorentzian HWHM must be larger than the Heisenberg HWHM of the source (for physical reasons, this is always true in a real spectrum). This restriction is purely mathematical and is due to the fact that a Lorentzian of HWHM equal to the Heisenberg HWHM must be deconvoluted from the fitted spectrum.

#### 2.1.2 Model Parameters

##### Global Parameters

<i>Background</i> (in counts per channel)	the intercept of the off-resonance background of the spectrum (constant term)
<i>bkg slope</i> (in counts per channel/(mm/s))	the slope of the off-resonance background with respect to the Doppler velocity (linear term)
<i>bkg curvature</i> (in counts per channel / $(\text{mm/s})^2$ )	the curvature of the off-resonance background with respect to the Doppler velocity (quadratic term)

**Peak Parameters** (parameters for each site)

$x0$ (in mm/s)	the peak position
$hwhm$ (in mm/s)	the HWHM of the Lorentzian contribution to the peak
$\sigma$ (in mm/s)	the width of the Gaussian contribution to the peak
Area (in count mm/s)	spectral area of the peak

**2.1.3 References**

- ☞ Puerta, J. and Martin, P. Three and four generalized Lorentzian approximations for the Voigt lineshape. *Appl. Opt.* **20** (1981) 3923.

This article describes the numerical approximation used in Recoil to generate a Voigt lineshape. Several typographical errors were reported in Rancourt, D.G., J.Y. *Nucl. Instrum. Meth. Phys. Res.* **B44** (1989) 199.

- ☞ Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).

This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15). Read this reference for a discussion on error analysis.

**2.1.4 File Format**

Recoil uses the .vof extension to denote files from this type of analysis. Though it can read MOSMOD .pav files, the new format is quite different due to the implementation differences.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil Voigt Peak Fit v1.0
Docname
Dataname
bkg sig_bkg fit_bkg
bkg1 sig_bkg1 fit_bkg1
bkgq sig_bkgq fit_bkgq
chisq
uncertainties_method

[Peak List]
num_peaks
peak_1
...

[Comment]
comment
...
--end comment--
```

Each peak is formatted as follows:

```
x0 sig_x0 fit_x0
hwhm sig_hwhm fit_hwhm
sigma sig_sigma fit_sigma
Area sig_Area fit_Area
```

## 8 Chapter 2. Analysis Models

In all cases, `sig_p` represents the 95% confidence interval on parameter `p` and `fit_p` its fitting status (0 if frozen, 1 if adjusted).

## 2.2 Lorentzian Multiplet Analysis

The Lorentzian multiplet analysis is a standard analysis that permits the user to fit several Lorentzian *singlets*, *doublets* or *sextets*, corresponding to paramagnetic sites with or without a quadrupole splitting and sites with a magnetic hyperfine field and a quadrupole shift (within the first-order perturbation limit).

### 2.2.1 Domains of Applicability

- this model assumes the hyperfine interactions are *effectively static*.
- this model assumes that the observed line shapes can be modelled as Lorentzian lines. This may not be the case for thick absorbers or in the presence of non-Lorentzian hyperfine parameter distributions. If such inhomogeneous broadening occurs, the VBF (section 2.3) or xVBF (section 2.4) methods should be used to include arbitrarily-shaped hyperfine parameter distributions.
- for magnetic sites, the *first-order perturbation result* is used, so the quadrupole shift should be much smaller than the magnetic Zeeman splitting ( $\frac{e^2qQ}{4} \ll g^* \mu_N H_{hf}$ ), or you may assume that  $\mathbf{H}_{hf}$  is aligned along the EFG  $\mathbf{z}$  axis and that the EFG has an axial symmetry,  $\eta=0$ .
- no thickness effects are taken into account, so the peak widths obtained by this method will depend on the absorber thickness. If absolute (intrinsic) widths are desired, thickness correction should be performed, or a thin absorber ( $t_a \ll 1$ ) should be used.

### 2.2.2 Model Parameters

#### Global Parameters

`Background` (in counts)                      the off-resonance background of the spectrum

#### Singlet Sites (parameters for each site)

`CS` (in mm/s)                      the center shift  
`Area` (in counts mm/s)              total spectral area of the site (proportional to the site population)  
`w` (in mm/s)                      the HWHM of the peak

#### Doublet Sites (parameters for each site)

`CS` (in mm/s)                      the center shift  
`QS` (in mm/s)                      the quadrupole splitting ( $\Delta$ )  
`Area` (in counts mm/s)              total spectral area of the site (proportional to the site population)  
`A-/A+` (no units)                      the ratio of the spectral areas of the low velocity peak to the high velocity peak  
`w+` (in mm/s)                      the HWHM of the high velocity peak

$w-/w+$  (no units) the ratio of the HWHMs of the low velocity peak to the high velocity peak.

#### Sextet Sites (parameters for each site)

$CS$ (in mm/s)	the center shift
$epsilon$ (in mm/s)	the quadrupole shift ( $\epsilon$ )
$z$ (in mm/s) or $H$ (in T or kOe)	the hyperfine Zeeman splitting ( $g^* \mu_N H$ ) or the hyperfine magnetic field
$Area$ (in counts mm/s)	total spectral area of the site (proportional to the site population)
$A1/A3$ (no units)	ratio of the spectral areas of peak 1 to peak 3
$A2/A3$ (no units)	ratio of the spectral areas of peak 2 to peak 3
$w3$ (mm/s)	the HWHM of peaks 3 and 4
$w1/w3$ (no units)	the ratio of the HWHMs of peak 1 (and 6) to peak 3 (and 4)
$w2/w3$ (no units)	the ratio of the HWHMs of peak 2 (and 5) to peak 3 (and 4)

### 2.2.3 References

- Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).

This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15).  
Read this reference for a discussion on error analysis.

### 2.2.4 File Format

Recoil uses the .lor extension to denote files of this type of analysis. Though it can read MOSMOD .pal files, the new format is quite different due to the implementation differences.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil Lorentzian Site Analysis v1.0
Docname
Dataname
bkg sig_bkg fit_bkg
chisq
uncertainties_method

[Singlet Sites]
num_sites
site_1
...

[Doublet Sites]
num_sites
site_1
...

[Sextet Sites]
num_sites
site_1
...
```

## 10 Chapter 2. Analysis Models

```
[Comment]
comment
...
--end comment--
```

Each singlet site is formatted as follows:

```
CS sig_CS fit_CS
Area sig_Area fit_Area
w sig_w fit_w
```

Each doublet site is formatted as follows:

```
CS sig_CS fit_CS
QS sig_QS fit_QS
Area sig_Area fit_Area
A-/A+ sig_A-/A+ fit_A-/A+
w+ sig_w+ fit_w+
w-/w+ sig_w-/w+ fit_w-/w+
```

Each sextet is formatted as follows:

```
CS sig_CS fit_CS
epsilon sig_epsilon fit_epsilon
z sig_z fit_z
Area sig_Area fit_Area
A1/A3 sig_A1/A3 fit_A1/A3
A2/A3 sig_A2/A3 fit_A2/A3
w3 sig_w3 fit_w3
w1/w3 sig_w1/w3 fit_w1/w3
w2/w3 sig_w2/w3 fit_w2/w3
```

In all cases, `sig_p` represents the 95% confidence interval on parameter `p` and `fit_p` its fitting status (0 if frozen, 1 if adjusted).

## 2.3 Voigt-based Fitting (VBF) Analysis

The Voigt-based fitting method (VBF) provides the means to obtain reliable distributions of hyperfine parameters for multiple generalized sites in a spectrum. Two types of generalized sites are considered: paramagnetic generalized sites which can have a distribution of quadrupole splittings and magnetic generalized sites which can have a distribution of magnetic hyperfine fields.

The primary hyperfine parameter's distribution is represented by a sum of Gaussian components, enabling it to have nearly any shape.

Secondary (or slave) hyperfine parameters, such as the center shift for paramagnetic generalized sites or the center shift and quadrupole shift for magnetic generalized sites can be linearly coupled to the primary hyperfine parameter.

### 2.3.1 Domains of Applicability

- this model assumes the hyperfine interactions are *effectively static*.

- for magnetic sites, the *first-order perturbation result* is used, so the quadrupole shift must always be much smaller than the magnetic Zeeman splitting ( $\frac{e^2qQ}{4} \ll g^* \mu_N H_{hf}$ ), or you may assume that  $\mathbf{H}_{hf}$  is aligned along the EFG  $z$  axis and that the EFG has axial symmetry,  $\eta=0$ .
- the *thin-absorber limit* is assumed, but *slight* thickness broadening can be modelled by increasing the experimental Lorentzian HWHM. Since thickness effects can substantially alter extracted distributions, it is recommended to perform a thickness correction and only analyse thin-limit spectra to obtain reliable distributions.

### 2.3.2 Model Parameters

#### Global Parameters

<i>Lorentzian HWHM</i> (in mm/s)	the elemental multiplet Lorentzian HWHM, also called $W_0$
<i>Background</i> (in counts)	the off-resonance background of the spectrum

#### QSD Sites (parameters for each site)

<i>delta0</i> (in mm/s)	
<i>delta1</i> (no units)	coupling parameters between the center shift $\delta$ and the quadrupole splitting $\Delta$ : $\delta = \delta_0 + \delta_1 \Delta$
<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>A-/A+</i> (no units)	ratio of the spectral areas of the low energy peak to the high energy peak
Each component of the quadrupole splitting distribution has three parameters:	
<i>p</i> (no units)	the weight of the component (sum of $p$ 's is 1)
<i>&lt;QS&gt;</i> (in mm/s)	the average quadrupole splitting of the component (or the position of the Gaussian component)
<i>sigma</i> (in mms)	the Gaussian width (std. dev.) of the component

#### HFD Sites (parameters for each site)

<i>delta0</i> (in mm/s)	
<i>delta1</i> (no units)	coupling parameters between the center shift $\delta$ and the Zeeman magnetic splitting $z$ : $\delta = \delta_0 + \delta_1 z$
<i>epsilon0</i> (in mm/s)	
<i>epsilon1</i> (no units)	coupling parameters between the quadrupole shift $\epsilon$ and the Zeeman magnetic splitting $z$ : $\epsilon = \epsilon_0 + \epsilon_1 z$
<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>A1/A3</i> (no units)	ratio of the spectral areas of peak 1 to the peak 3
<i>A2/A3</i> (no units)	ratio of the spectral areas of peak 2 to the peak 3
Each component of the Zeeman splitting $z$ (or hyperfine magnetic field $H$ ) distribution has three parameters:	
<i>p</i> (no units)	the weight of the component (sum of $p$ 's is 1)
<i>&lt;z&gt;</i> (in mm/s) or <i>&lt;H&gt;</i> (in T or kOe)	the average Zeeman splitting ( $z = g^* \mu_N H$ ) or magnetic field of the component (or the position of the Gaussian component)
<i>sigma</i> (in mms, T or kOe)	the Gaussian width (std. dev.) of the component

## 12 Chapter 2. Analysis Models

### 2.3.3 References

- Rancourt, D.G. and Ping, J.Y. Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy, *Nucl. Instrum. Meth. Phys. Res.* **B58** (1991) 85.

This is the original article describing the method and its application. A must-read to use this method.

- Puerta, J. and Martin, P. Three and four generalized Lorentzian approximations for the Voigt lineshape. *Appl. Opt.* **20** (1981) 3923.

This article describes the numerical approximation used in Recoil to generate a Voigt lineshape. Several typographical errors were reported in Rancourt, D.G., *Nucl. Instrum. Meth. Phys. Res.* **B44** (1989) 199.

- Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).

This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15). Read it for a discussion on error analysis.

### 2.3.4 File Format

Recoil uses the .vbf extension to denote files of this type of analysis. Though it can read MOSMOD .pac, .paq and .pah files, the new format is quite different due to the implementation differences.

The first line states the type of file, with a version identifier. The following is a description of version 1.01 of the file format:

```
Recoil VBF Analysis v1.01
Docname
Dataname
bkg sig_bkg fit_bkg
hwhm sig_hwhm fit_hwhm
chisq
uncertainties_method

[QSD Sites]
num_sites
QSDsite1
...

[HFD Sites]
num_sites
HFDsite1
...

[Comment]
comment
...
--end comment--
```

Each QSD (paramagnetic) site is saved in the following format:

```
site_name
area sig_area fit_area
A-/A+ sig_A-/A+ fit_A-/A+
delta0 sig_delta0 fit_delta0
```

```

delta1 sig_delta1 fit_delta1
num_components
comp_1
...

```

Where each component is saved as:

```

p sig_p fit_p
<QS> sig_<QS> fit_<QS>
sigma sig_sigma fit_sigma

```

Each HFD (magnetic) site is saved in the following format:

```

site_name
area sig_area fit_area
A1/A3 sig_A1/A3 fit_A1/A3
A2/A3 sig_A2/A3 fit_A2/A3
delta0 sig_delta0 fit_delta0
delta1 sig_delta1 fit_delta1
num_components
comp_1
...

```

Where each component is saved as:

```

p sig_p fit_p
<z> sig_<z> fit_<z>
sigma sig_sigma fit_sigma

```

In all cases, *sig\_p* represents the 95% confidence interval on parameter *p* and *fit\_p* its fitting status (0 if frozen, 1 if adjusted).

## 2.4 Extended Voigt-based Fitting (xVBF) Analysis

The extended Voigt-based fitting method (xVBF) provides the means to obtain reliable multidimensional distributions of hyperfine parameters for multiple generalized sites in a spectrum. Two types of generalized sites are considered:

- paramagnetic generalized sites which can have simultaneous distributions of center shifts and quadrupole splittings, and
- magnetic generalized sites which can have simultaneous distributions of center shifts, quadrupole shifts and magnetic hyperfine fields.

Each hyperfine parameter distribution is represented by a sum of Gaussian components, enabling it to have nearly any shape.

Within a generalized site, pairs of distributions of hyperfine parameters are correlated by a correlation parameter  $\rho$ .

### 2.4.1 Domains of Applicability

- this model assumes the hyperfine interactions are *effectively static*.



## 14 Chapter 2. Analysis Models

- for magnetic sites, the *first-order perturbation result* is used, so the quadrupole shift must always be much smaller than the magnetic Zeeman splitting ( $\frac{e^2qQ}{4} \ll g^* \mu_N H_{hf}$ ), or you may assume the  $\mathbf{H}_{hf}$  is aligned along the EFG  $\mathbf{z}$  axis and that  $\eta = 0$ . Pay close attention to this limit when the distributions span a large range.
- the *thin-absorber limit* is assumed, but *slight* thickness broadening can be modelled by increasing the elemental multiplet Lorentzian HWHM. Since thickness effects can substantially alter extracted distributions, it is recommended to perform a thickness correction and only analyse thin-limit spectra to obtain reliable distributions.

### 2.4.2 Model Parameters

#### Global Parameters

<i>Lorentzian HWHM</i> (in mm/s)	the elemental multiplet Lorentzian HWHM, also called $W_0$
<i>Background</i> (in counts)	the off-resonance background of the spectrum

#### Paramagnetic Sites (parameters for each site)

<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>A-/A+</i> (no units)	ratio of the spectral areas of the low energy peak to the high energy peak
<i>r &lt;CSQS&gt;</i> (no units)	the correlation parameter $\rho_{\delta\Delta}$ between the CS ( $\delta$ ) distribution and the QS ( $\Delta$ ) distribution

Each component of the center shift distribution has three parameters:

<i>p</i> (no units)	the weight of the component (sum of $p$ 's is 1)
<i>&lt;CS&gt;</i> (in mm/s)	the average center shift of the component
<i>sigma</i> (in mms)	the Gaussian width (std. dev.) of the component

Each component of the quadrupole splitting distribution has three parameters:

<i>p</i> (no units)	the weight of the component (sum of $p$ 's is 1)
<i>&lt;QS&gt;</i> (in mm/s)	the average quadrupole splitting of the component
<i>sigma</i> (in mms)	the Gaussian width (std. dev.) of the component

#### Magnetic Sites (parameters for each site)

<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>A1/A3</i> (no units)	ratio of the spectral areas of peak 1 to the peak 3
<i>A2/A3</i> (no units)	ratio of the spectral areas of peak 2 to the peak 3
<i>r &lt;CSQS&gt;</i>	correlation parameter $\rho_{\delta\epsilon}$ between the center shift distribution and the quadrupole shift distribution
<i>r &lt;CSHF&gt;</i>	correlation parameter $\rho_{\delta z}$ between the center shift distribution and the Zeeman splitting distribution
<i>r &lt;QSHF&gt;</i>	correlation parameter $\rho_{\epsilon z}$ between the quadrupole shift distribution and the Zeeman splitting distribution

Each component of the Zeeman splitting  $z$  (or hyperfine magnetic field  $H$ ) distribution has three parameters:

<i>p</i> (no units)	the weight of the component (sum of $p$ 's is 1)
<i>&lt;CS&gt;</i> (in mm/s)	the average center shift of the component
<i>sigma</i> (in mms)	the Gaussian width (std. dev.) of the component

Each component of the quadrupole shift distribution has three parameters:

$p$ (no units)	the weight of the component (sum of $p$ 's is 1)
$\langle QS \rangle$ (in mm/s)	the average quadrupole shift of the component
$\sigma$ (in mms)	the Gaussian width (std. dev.) of the component

Each component of the Zeeman splitting  $z$  (or hyperfine magnetic field  $H$ ) distribution has three parameters:

$p$ (no units)	the weight of the component (sum of $p$ 's is 1)
$\langle z \rangle$ (in mm/s) or $\langle H \rangle$ (in T or kOe)	the average Zeeman splitting or magnetic field of the component
$\sigma$ (in mms, T or kOe)	the Gaussian width (std. dev.) of the component

### 2.4.3 References

- Lagarec, K. and Rancourt, D.G. Extended Voigt-based analytic lineshape method for determining N-dimensional correlated hyperfine parameter distributions in Mössbauer spectroscopy, *Nucl. Instrum. Meth. Phys. Res.* **B129** (1997) 266.

This is the original article describing the method and its application. A must-read to use this method.

- Puerta, J. and Martin, P. Three and four generalized Lorentzian approximations for the Voigt line shape. *Appl. Opt.* **20** (1981) 3923.

This article describes the numerical approximation used in Recoil to generate a Voigt line shape. Several typographical errors were reported in Rancourt, D.G., *Nucl. Instrum. Meth. Phys. Res.* **B44** (1989) 199.

- Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).

This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15). Read this reference for a discussion on error analysis.

### 2.4.4 File Format

Recoil uses the .xvf extension to denote files of this type of analysis.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil xVBF Analysis v1.0
Docname
Dataname
bkg sig_bkg fit_bkg
hwhm sig_hwhm fit_hwhm
chisq
uncertainties_method

[QSD Sites]
num_sites
QSDsite1
...
```

## 16 Chapter 2. Analysis Models

```
[HFD Sites]
num_sites
HFDsite1
...

[Comment]
comment
...
--end comment--
```

Each QSD (paramagnetic) site is saved in the following format:

```
site_name
num_CS_comp num_QS_comp
area sig_area fit_area
A-/A+ sig_A-/A+ fit_A-/A+
r<CSQS> sig_r<CSQS> fit_r<CSQS>
CS_comp_1
...
QS_comp_1
...
```

Where each component is saved as (x can be CS or QS):

```
p sig_p fit_p
<x> sig_<x> fit_<x>
sigma sig_sigma fit_sigma
```

Each HFD (magnetic) site is saved in the following format:

```
site_name
num_CS_comp num_QS_comp num_HF_comp
area sig_area fit_area
A1/A3 sig_A1/A3 fit_A1/A3
A2/A3 sig_A2/A3 fit_A2/A3
r<CSQS> sig_r<CSQS> fit_r<CSQS>
r<CSHF> sig_r<CSHF> fit_r<CSHF>
r<QSHF> sig_r<QSHF> fit_r<QSHF>
CS_comp_1
...
QS_comp_1
...
HF_comp_1
...
```

Where each component is saved as (x can be CS, QS or z):

```
p sig_p fit_p
<x> sig_<x> fit_<x>
sigma sig_sigma fit_sigma
```

In all cases, `sig_p` represents the 95% confidence interval on parameter `p` and `fit_p` its fitting status (0 if frozen, 1 if adjusted).

## 2.5 Full Static Hamiltonian Site Analysis

The full static hamiltonian site analysis is a powerful way to fit a spectrum using the exact line shape obtained from the mixed static interaction Hamiltonian. In all, five types of sites can be modelled simultaneously,

representing:

- the *single crystal case*, where all angles and hyperfine parameter magnitudes have discrete values;
- the *crystalline powder average*, where the  $\gamma$ -ray angles are averaged out, but the  $\mathbf{H}_{\text{hf}}$  orientation relative to the EFG is preserved. This corresponds to a powder of small, randomly oriented crystallites in which the orientation of the  $\mathbf{H}_{\text{hf}}$  is fixed with respect to the EFG system within each crystallite;
- the *randomly oriented EFG average*, where the EFG orientation is averaged out, but the orientation of the  $\gamma$ -ray with respect to the magnetic hyperfine field is constant. This is useful to model the behaviour of a crystalline powder in an applied magnetic field when all the moments are aligned in the same direction;
- the *mosaic sample average*, where the azimuthal angle of the  $\gamma$ -ray in the EFG system is averaged out. This corresponds to a mosaic sample in which the  $\mathbf{H}_{\text{hf}}$  orientation in the EFG system is fixed, but there is a random orientation of the EFG x-y plane with respect to the incident  $\gamma$ -ray. For example, this may be found in a layered material which has a perfect stacking of the layer planes perpendicular to the z axis of the EFG system, but with a random orientation (on average) of each layer with respect to the others;
- the *complete orientation average*, where all angles are averaged:  $\gamma$ -ray and  $\mathbf{H}_{\text{hf}}$  orientation. This is applicable in the case of a powder ( $\gamma$ -ray is randomly oriented with respect to each crystallite) when the angles between the EFG and  $\mathbf{H}_{\text{hf}}$  are randomly oriented due to spin and/or structural disorder. As a result, the  $\gamma$ -ray also has a random orientation with respect to the local EFG.

### 2.5.1 Domains of Applicability

- applicable for all magnitudes of hyperfine interactions (including electric monopole, quadrupole and magnetic dipole interactions)
- assumes that the hyperfine interactions are *effectively static*
- does not admit distributions of hyperfine parameters (*note*: angle averages are equivalent to a uniform distribution of angles), so only sites with discrete hyperfine parameter values can be modelled.
- does not include thickness effects, though *slight* thickness effects can be modelled by an increase in the Lorentzian HWHM of each site.

### 2.5.2 Model Parameters

Fig. 1 (below) shows the assignment of the angles for the general configuration.

#### Global Parameters

*Background* (in counts)                      the flat, off-resonance background of the spectrum

#### Single Crystal Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the hyperfine magnetic field
$e^2qQ/2$ (in mm/s)	the electric quadrupole interaction parameter
<i>eta</i> (no units)	the EFG asymmetry parameter $\eta$
<i>w</i> (in mm/s)	the Lorentzian HWHM of the peaks

## 18 Chapter 2. Analysis Models

<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>phi_Hq, theta_Hq</i> (in °)	the azimuthal and polar angles of $\mathbf{H}_{\text{hf}}$ in the EFG principal axes coordinate system
<i>phi_gq, theta_gq</i> (in °)	the azimuthal and polar angles of the incident $\gamma$ -ray direction in the EFG tensor principle axes coordinate system

### Powdered Crystal Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the hyperfine magnetic field
$e^2qQ/2$ (in mm/s)	the electric quadrupole interaction parameter
<i>eta</i> (no units)	the EFG asymmetry parameter $\eta$
<i>w</i> (in mm/s)	the HWHM of the peaks
<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>phi_Hq, theta_Hq</i> (in °)	the azimuthal and polar angles of $\mathbf{H}_{\text{hf}}$ in the EFG tensor principal axes coordinate system

### Randomly Oriented EFG Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the hyperfine magnetic field
$e^2qQ/2$ (in mm/s)	the electric quadrupole interaction parameter
<i>eta</i> (no units)	the EFG asymmetry parameter $\eta$
<i>w</i> (in mm/s)	the HWHM of the peaks
<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>theta_gH</i> (in °)	the angle between the incident $\gamma$ -ray direction and the magnetic field $\mathbf{H}_{\text{hf}}$

### Mosaic Crystal Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the hyperfine magnetic field
$e^2qQ/2$ (in mm/s)	the electric quadrupole interaction parameter
<i>eta</i> (no units)	the EFG asymmetry parameter $\eta$
<i>w</i> (in mm/s)	the HWHM of the peaks
<i>Area</i> (in counts mm/s)	total spectral area of the site (proportional to the site population)
<i>phi_Hq, theta_Hq</i> (in °)	the azimuthal and polar angles of $\mathbf{H}_{\text{hf}}$ in the EFG tensor principal axes coordinate system
<i>theta_gq</i> (in °)	the angle between the incident $\gamma$ -ray direction and the <i>z</i> principal axis of the EFG tensor.

### Randomly Oriented EFG and $\mathbf{H}_{\text{hf}}$ Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the hyperfine magnetic field
$e^2qQ/2$ (in mm/s)	the electric quadrupole interaction parameter
<i>eta</i> (no units)	the EFG asymmetry parameter $\eta$
<i>w</i> (in mm/s)	the HWHM of the peaks

Area (in counts mm/s)    total spectral area of the site (proportional to the site population)

**NB:** In MOSMOD 6, the angles  $\phi_{Hq}$  and  $\theta_{Hq}$  were referred to as  $\phi$  and  $\theta$ , while  $\phi_{gq}$  and  $\theta_{gq}$  were referred to as  $\alpha$  and  $\beta$ . To avoid confusion between the angles used in this document, indices are added to designate the direction and the reference system ( $g$ ,  $H$  and  $q$  for the  $\gamma$ -ray direction, the  $\mathbf{H}_{\text{hf}}$  direction and the EFG tensor principal axes system respectively), and  $\phi$  and  $\theta$  are consistently used to designate azimuthal and polar angles.

### 2.5.3 References

- Blaes, N., Fischer, H. and Gonser, U. Analytical expression for the Mössbauer line shape of  $^{57}\text{Fe}$  in the presence of mixed hyperfine interactions. *Nucl. Instrum. Meth. Phys. Res.* **B9** (1985) 201.

This article presents a derivation of an analytical expression for the line shape for the static mixed-interaction Hamiltonian. Its expressions are directly used in this analysis document (note: the angles referred to in the article are not necessarily the same as the ones in this document, but they can easily be transformed from one reference system to the other).

- Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).

This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15). Read this reference for a discussion on error analysis.

### 2.5.4 File Format

Recoil uses the .fsh extension to denote files of this type of analysis. Though it can read MOSMOD .pan files, the new format is quite different due to the implementation differences.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil Full Static Hamiltonian Site Analysis v1.0
Docname
Dataname
bkg sig_bkg fit_bkg
chisq
uncertainties_method

[Single Crystal Sites]
num_sites
site_1
...

[Powdered Crystal Sites]
num_sites
site_1
...

[Random EFG Sites]
num_sites
site_1
...
```

## 20 Chapter 2. Analysis Models

```
[Mosaic Crystal Sites]
num_sites
site_1
...

[Random EFG and H Sites]
num_sites
site_1
...

[Comment]
comment
...
--end comment--
```

Each single crystal site is formatted as follows:

```
site_name
CS sig_CS fit_CS
e2qQ/2 sig_e2qQ/2 fit_e2qQ/2
eta sig_eta fit_eta
z sig_z fit_z
w sig_w fit_w
Area sig_Area fit_Area
phi_Hq sig_phi_Hq fit_phi_Hq
theta_Hq sig_theta_Hq fit_theta_Hq
phi_gq sig_phi_gq fit_phi_gq
theta_gq sig_theta_gq fit_theta_gq
```

Each powdered crystal site is formatted as follows:

```
site_name
CS sig_CS fit_CS
e2qQ/2 sig_e2qQ/2 fit_e2qQ/2
eta sig_eta fit_eta
z sig_z fit_z
w sig_w fit_w
Area sig_Area fit_Area
phi_Hq sig_phi_Hq fit_phi_Hq
theta_Hq sig_theta_Hq fit_theta_Hq
```

Each randomly oriented EFG site is formatted as follows:

```
site_name
CS sig_CS fit_CS
e2qQ/2 sig_e2qQ/2 fit_e2qQ/2
eta sig_eta fit_eta
z sig_z fit_z
w sig_w fit_w
Area sig_Area fit_Area
theta_gH sig_theta_gH fit_theta_gH
```

Each mosaic crystal site is formatted as follows:

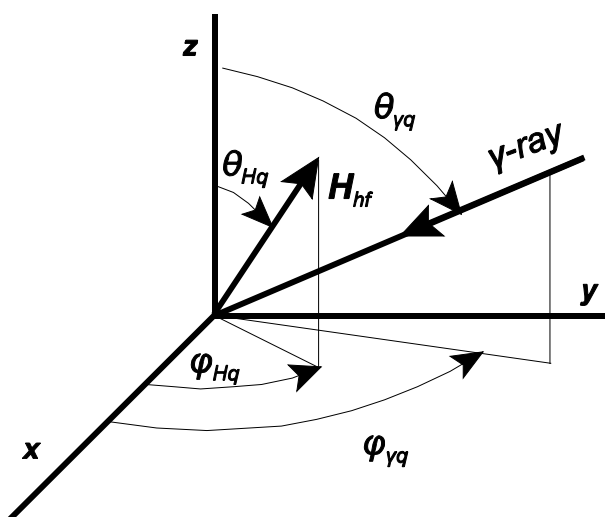
```
site_name
CS sig_CS fit_CS
e2qQ/2 sig_e2qQ/2 fit_e2qQ/2
eta sig_eta fit_eta
z sig_z fit_z
w sig_w fit_w
Area sig_Area fit_Area
phi_Hq sig_phi_Hq fit_phi_Hq
```

```
theta_Hq sig_theta_Hq fit_theta_Hq
theta_gq sig_theta_gq fit_theta_gq
```

Each randomly oriented EFG and H site is formatted as follows:

```
site_name
CS sig_CS fit_CS
e2qQ/2 sig_e2qQ/2 fit_e2qQ/2
eta sig_eta fit_eta
z sig_z fit_z
w sig_w fit_w
Area sig_Area fit_Area
```

In all cases,  $\text{sig}_p$  represents the 95% confidence interval on parameter  $p$  and  $\text{fit}_p$  its fitting status (0 if frozen, 1 if adjusted).



**Figure 1.** The  $H_{hf}$  and incident  $\gamma$ -ray orientation angles in the EFG tensor principal axes system

## 2.6 Dynamic Line Shape Site Analysis

The dynamic line shape site analysis is a powerful analysis method to treat dynamic effects in a spectrum. The line shape used is the one derived by Blume and Tjon (see references) which uses a stochastic model for the fluctuation of the magnetic hyperfine field.

The model assumes that the hyperfine field fluctuates randomly between two directions along the same axis. Its fluctuation can be characterized by any of the following pairs of parameters:

- $\tau_+$  and  $\tau_-$  the average dwell times along the + and - directions between flips;
- $f_+$  and  $f_-$  the average jump frequencies ( $f_+ = 1/\tau_+$ ,  $f_- = 1/\tau_-$ ), or
- $\bar{f} = (f_+ + f_-)/2$  and  $\rho = (f_+ - f_-)/2$ , the average and half difference of the frequencies

Currently, only one type of site is available, in which the magnetic hyperfine field is assumed to flip parallel to the  $z$  direction of an axially symmetric EFG ( $\eta = 0$ ). The result is applicable for all magnitudes of the electric quadrupole and magnetic dipole interactions, since the magnetic hyperfine field is aligned in the EFG  $z$  axis direction and  $\eta = 0$ .



## 22 Chapter 2. Analysis Models

### 2.6.1 Domains of Applicability

- this model assumes the hyperfine field fluctuates stochastically between  $+H$  and  $-H$  along the EFG  $z$  axis with  $\eta = 0$ . All other parameters are treated as static.
- no parameter distributions are included, so only homogeneous broadening is taken into account. Slight distributions may be modelled (at your own risk) by varying the intrinsic Lorentzian HWHM of the site.
- no thickness effects are taken into account, so peak broadening due to dynamic effects cannot be resolved from thickness effects, and the model might produce erroneous results. If correct modelling is desired, thickness correction should be performed beforehand, or a thin absorber ( $t_a \ll 1$ ) should be used.

### 2.6.2 Model Parameters

#### Global Parameters

*Background* (in counts)                      the flat off-resonance background of the spectrum

#### H || (EFG)<sub>z</sub> Sites (parameters for each site)

<i>CS</i> (in mm/s)	the center shift
<i>QS</i> (in mm/s)	the quadrupole shift
<i>z</i> (in mm/s) or <i>H</i> (in T or kOe)	the magnetic Zeeman splitting ( $z = g^* \mu_N H$ ) or the magnetic hyperfine field <i>H</i>
<i>Area</i> (in counts mm/s)	the total spectral area of the site (proportional to the site population)
<i>w</i> (in mm/s)	the intrinsic Lorentzian HWHM
<i>A1/A3</i> (no units)	the ratio of the spectral areas of peak 1 (or 6) to peak 3 (or 4)
<i>A2/A3</i> (no units)	the ratio of the spectral areas of peak 2 (or 5) to peak 3 (or 4)
<i>f</i> (in mm/s)	the average flip frequency ( $f = (f_+ + f_-)/2$ )
<i>rho</i> (in mm/s)	the half difference of the flip frequencies ( $\rho = (f_+ - f_-)/2$ )

### 2.6.3 Parameter Constraints and Implementation Details

The following constraints are imposed in this model:

- the Zeeman splitting (*z*) or the magnetic hyperfine field (*H*) must be positive or nil;
- the intrinsic Lorentzian HWHM (*w*) must be greater than twice the intrinsic (Heisenberg) Lorentzian HWHM for an ideal source (see the isotope.ini file description for details);
- the area ratios (*A1/A3* and *A2/A3*) must be positive or nil;
- the average flip frequency (*f*) must be positive. Because of the details of the implementation, a value of 0 is not accepted and will be replaced by the effectively nil value of  $10^{-10}$ ;
- since the frequencies must be positive, the absolute value of *f* should be greater than the absolute value of  $\rho$ . This is not imposed during the fit, so you must check it yourself;

The following mathematical expression is used to evaluate the spectral contribution of each peak for each site:

### 2.6.4 References

- Blume, M. and Tjon, J.A. Mössbauer spectra in a fluctuating environment, *Phys. Rev.* **165** (1968) 446.  
This is the reference where the analytical expression for the line shape is derived, and where all the theory and assumptions about the model are explained. It also contains many useful references regarding this topic.
- Rancourt, D.G. and Ping, J.Y. Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy, *Nucl. Instrum. Meth. Phys. Res.* **B58** (1991) 85.  
Section 3 of the article discusses the range of applicability of effectively static behaviour.
- Rancourt, D. G., *Analytical Methods for Mössbauer Spectral Analysis of Complex Materials*, in *Mössbauer Spectroscopy Applied to Magnetism and Material Science*, Volume 2, edited by G. J. Long and F. Grandjean. Plenum Press, New York, 1996.  
This chapter includes many simulations of dynamic spectra to show the effect of the various parameters.
- Press, W.H, Teukolsky, S.A., Vetterling, W.T. and Flannery Brian P. Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> edition, Cambridge University Press (1992).  
This reference is the starting point for the fitting algorithms and error analysis methods (chapter 15). Read this reference for a discussion on error analysis.

### 2.6.5 File Format

Recoil uses the .dls extension to denote files of this type of analysis. Though it can read MOSMOD .pab files, the new format is quite different due to the implementation differences.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil Dynamic Line Shape Site Analysis v1.0
Docname
Dataname
bkg sig_bkg fit_bkg
chisq
uncertainties_method

[Parallel Sites]
num_sites
site_1
...

[Comment]
comment
...
--end comment--
```

Each parallel (H || EFG<sub>z</sub>) site is formatted as follows:

```
CS sig_CS fit_CS
QS sig_QS fit_QS
z sig_z fit_z
```

## 24 Chapter 2. Analysis Models

```
Area sig_Area fit_Area
w sig_w fit_w
A1/A3 sig_A1/A3 fitA1/A3
A2/A3 sig_A2/A3 fitA2/A3
f sig_f fit_f
rho sig_rho fit_rho
```

In all cases, `sig_p` represents the 95% confidence interval on parameter `p` and `fit_p` its fitting status (0 if frozen, 1 if adjusted).

## 2.7 Source HWHM Extraction

### 2.7.1 Domains of Applicability

The source line width can be somewhat larger than the natural Heisenberg width of the nuclear transition (in fact, the source emission line shape can be non-Lorentzian) due to inhomogeneous broadening from crystal defects, even in well suited materials such as Rh and Cu (for  $^{57}\text{Co}$ ) that are designed to give single-lined sources. Also, radiation damage can increase the density of crystal defects as a source ages.

When you wish to determine the experimental Half-Width at Half-Maximum (HWHM) of your source, you can use this module to analyse the spectrum of a sample whose thickness and intrinsic cross-section are known. Using these parameters, the HWHM of the source is obtained by fitting the spectrum to the thin-source transmission integral excluding polarization effects (see reference).

### 2.7.2 Model Parameters

To extract the source line width, it is recommended that you enter and freeze the value for  $t_a$ , while refining the other parameters.

#### Global Parameters

<i>Background</i> (in counts)	the flat off-resonance background of the spectrum
<i>Gamma</i> (in mm/s)	the HWHM of the source
<i>Etam_fs</i> (in counts mm/s)	the total area of recoilless $\gamma$ -rays (including corrections due to mass absorption). Usually left as a fitting parameter.
<i>Ta</i> (no units)	the Mössbauer thickness of the absorber. This can be calculated based on the mass and area of the absorber, as well as its composition and recoilless fraction factor ( $t_a = f_a n_a \sigma_0$ )

### 2.7.3 Cross-section file

You must supply Recoil with a cross-section file which contains the intrinsic cross-section of the absorber, normalized to  $\sigma_0$ , the cross-section at resonance for the isotope. You can find the value of  $\sigma_0$  in the `isotopes.ini` configuration file. Sample cross-section files are provided for common reference absorbers.

The first line contains the number of points contained in the spectrum, and the following lines contain the velocity and normalized cross-section (space or tab separated). When creating a cross-section file, please insure that the sampling points are sufficiently closely spaced to enable Recoil to perform a proper integration of the cross-section.

In generating your own cross-section files, you may use the Voigt peak fit or the Lorentzian Site Analysis modules to generate the cross-section data, but you will have to modify these files to suit the required format.

### 2.7.4 References

- Rancourt, D.G., McDonald, A.M., Lalonde, A.E. and Ping, J.Y., Mössbauer absorber thicknesses for accurate site populations in Fe-bearing minerals. *American Mineralogist* **78** (1993) 1.

Eq. (5) in this reference is the transmission integral expression that we have used. This article presents all the relevant assumptions and is highly recommended reading regarding thickness effects.

### 2.7.5 File Format

Recoil uses the .gam extension to denote files of this type of analysis.

The first line states the type of file, with a version identifier. The following is a description of version 1.0 of the file format:

```
Recoil Source HWHM Extraction v1.0
Docname
Dataname
Cross-section_name
chisq
uncertainties_method
bkg sig_bkg fit_bkg
gamma sig_gamma fit_gamma
etamfs sig_etamfs fit_etamfs
ta sig_ta fit_ta

[Comment]
comment
...
--end comment-
```

# Chapter 3

## Utilities

### 3.1 Debye Model Calculations

Several relevant parameters in Mössbauer spectroscopy can be calculated by using the Debye model of lattice vibrations. The Debye Model Calculator lets you perform such calculations.

At a given temperature, the fraction of recoilless absorption (or emission) events is given as

$$f = e^{-k_{\gamma}^2 \langle x^2 \rangle} \quad (1)$$

where  $k_{\gamma}$  is the wave number of the incident (or emitted) gamma-ray and  $\langle x^2 \rangle$  is the average squared displacement of the probe nucleus. Within the Debye model framework, this can be calculated (in any unit system) and yields

$$\ln f = -\frac{E_{\gamma}^2}{Mc^2 k\Theta_D} \left[ \frac{1}{4} + \left( \frac{T}{\Theta_D} \right) \int_0^{\Theta_D/T} \frac{x dx}{e^x - 1} \right] \quad (2)$$

where  $E_{\gamma}$  is the gamma-ray energy and  $M$  is the mass of a probe atom.  $\Theta_D$  is the Debye temperature of the sample, and  $T$  is the sample temperature.

Similarly, the second-order Doppler shift, which results from the average squared velocity of the probe nucleus

$$\begin{aligned} SOD &= \frac{\langle v^2 \rangle}{2c^2} E_{\gamma} \text{ (energy units)} \\ &= \frac{\langle v^2 \rangle}{2c} \text{ (velocity units)} \end{aligned} \quad (3)$$

can be calculated (in SI units) within the Debye model framework as

$$SOD \text{ (m/s)} = -\frac{3 k\Theta_D}{2 Mc} \left[ \frac{3}{8} + 3 \left( \frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \right] \quad (4)$$

The *1 Measurement* page of the Debye model calculator deals with four parameters: the temperature  $T$  (in K), the Debye temperature  $\Theta_D$  (in K), the recoilless fraction  $f$  (no units) and the second-order Doppler shift  $SOD$  (in mm/s). By entering any pair of parameters (except  $f$  and the  $SOD$ ), the other two can be calculated. This may be useful, for example, to estimate  $f$  at a given temperature knowing the Debye temperature to determine the duration of an experiment (remember to calculate them for the source *and* the absorber).

The 2 *Measurements* page works similarly but is used to obtain the Debye temperature based on measurements at two different (and known) temperatures. Two options can be used:

- a) The first option is to enter the time-normalized spectral areas of an absorber at the two temperatures. The ratio of  $f$  factors is assumed to be equal to the ratio of areas (if the absorber is sufficiently thin,  $t_a \ll 1$ , or its spectrum was corrected for thickness effects), so the Debye temperature can be calculated:

$$\frac{A_1}{A_2} = \frac{f(\Theta_D, T_1)}{f(\Theta_D, T_2)} \Rightarrow \Theta_D . \quad (5)$$

If the source was at different temperatures during the two measurements, spectral areas must be corrected for the ratio of the  $f$  factors of the source.

- b) The other option is to use the center shift (CS) at two different temperatures. Assuming that the isomer shift (IS) is temperature independent, since  $CS = IS + SOD$ , the difference in center shifts is equal to the difference of SODs, enabling a calculation of the Debye temperature. In addition, it is possible to calculate the isomer shift (sometimes referred to as the chemical isomer shift) of the absorber:

$$CS_1 - CS_2 = SOD(\Theta_D, T_1) - SOD(\Theta_D, T_2) \Rightarrow \Theta_D . \quad (6)$$

For both spectra, the center shifts must be calculated with reference to the same calibration material (at one given temperature) and must be corrected for the source SOD if the source was at different temperatures for the two measurements.

## 3.2 Ideal Thickness Calculations

Using the derivation by Long *et al.*, it is possible to calculate the thickness of a sample for which the signal-to-noise ratio is largest for a given acquisition time. It is referred to here as the *ideal thickness* of the absorber.

By assuming the thin-absorber limit is respected, Long calculated the ideal thickness for two distinct experimental situations:

- a) when the non-Mössbauer contribution to the background is small compared to the Mössbauer contribution ( $\eta_M f_s$ ), the ideal thickness is

$$t_{id} = \frac{1}{\mu_e} \quad (7)$$

- b) when the non-Mössbauer contribution to the background is large compared to the Mössbauer contribution ( $\eta_M f_s$ ), the ideal thickness is

$$t_{id} = \frac{2}{\mu_e} \quad (8)$$

where  $\mu_e$  is the electronic mass absorption coefficient of the sample for the  $\gamma$ -ray energy used. In most cases, these produce thicknesses which fall outside the thin-limit condition used to derive them. However, even for thick absorbers, the ideal thickness is found to be between these two values. Rancourt *et al* () measured the ideal thickness for a wide range of Fe content in layer silicates and found that, experimentally, the value is approximately

$$t_{id} \approx \frac{1}{\mu_e} . \quad (9)$$

This is the *ideal thickness* reported by Recoil. For some extreme conditions (e.g. isotopically enriched samples), the ideal thickness may be different, but we are confident that this value will always yield a

## 28 Chapter 3. Utilities

thickness that gives a near maximum signal-to-noise ratio.

The mass absorption coefficient is calculated by using the weight fractions  $p_z$  of all the elements in the sample's chemical formula:

$$\mu_e(E_V) = \sum_Z p_Z \mu_{e_z}(E_V) \quad (10)$$

This produces an ideal thickness expressed as a mass of sample per unit area. By supplying the holder diameter Recoil calculates the sample mass or, using the density, it can give the sample thickness. The effective Mössbauer thickness can also be calculated by supplying an estimated value for the recoilless fraction  $f_a$ .

We recommend the article of Rancourt *et al* (1993) for a detailed discussion of both ideal and thin-limit absorber thicknesses.

### 3.3 The Mössbauer Thickness

The effective Mössbauer thickness can also be calculated by providing the chemical composition of the sample as well as its mass and area. It can be applied to many Mössbauer isotopes, but we will describe it here using  $^{57}\text{Fe}$ . Using these parameters, the number of  $^{57}\text{Fe}$  per unit area  $n_a$  can be calculated, which in turn results in a dimensionless Mössbauer thickness when multiplied by the intrinsic resonant cross-section  $\sigma_0$  of the transition and a user supplied absorber recoilless fraction  $f_a$ . Here are the formulas which are used:

$$n_a = \frac{m N_A}{A M} n a \quad (11)$$

where  $m$  is the sample mass,  $A$  its area,  $N_A$  is Avogadro's number,  $M$  is the molar (or molecular) mass of the sample,  $n$  the number of Fe atoms per formula unit and  $a$  is the abundance of the Mössbauer isotope. The dimensionless absorber thickness is then given by:

$$t_a = f_a n_a \sigma_0 \quad (12)$$

where  $f_a$  is the absorber recoilless fraction and  $\sigma_0$  is the resonant absorption cross-section for the transition. The parameters for a given Mössbauer isotope are given in the isotopes.ini initialization file.

A detailed discussion of the effective relevance of  $t_a$  in causing spectral thickness effects for specific spectral types is given in Rancourt *et al* (1993) and Ping and Rancourt (1992).

### 3.4 References

- Long, G.J. *et al.*, Mössbauer Effect Reference and Data Journal **6**(2) (1983) 42.
- Rancourt *et al.*, *American Mineralogist* **78** (1993) 1.
- Ping, J.Y. and Rancourt, D.G., *Hyperfine Interactions* **71** (1992) 1433.

# Chapter 4

## How Do I...



### 4.1 Analyse a spectrum ?

1. In the project view, press the **Start New Analysis** button
2. Select the type of analysis from the popup menu
3. Fill in the initial parameters and set their fitting status
4. Select the **Analyse | Fit Spectrum** menu command
5. View the final results in the different views available
6. Select the **View | New View...** menu command to create a new view, including a report view, which can be printed for your records



Use the following keyboard shortcuts to do things faster:

- use **Ctrl+F** as an accelerator key for the **Analyse | Fit Spectrum** menu command
- use **Tab** to switch between panes and dialog box controls in the parameters view
- use **Shift+F10** to activate the context-sensitive popup menu (equivalent to a right mouse click)

### 4.2 Create a calibration file ?

1. Select the **Utilities | Calibrate...** menu command
2. Select the raw data file which will be used to obtain the folding parameters (the calibration data file)
3. In the fit settings window,
  - Add peaks by double-clicking the left mouse button at the new peak position
  - Change a peak position or range by dragging it to the new position
  - Remove an unwanted peak by dragging it outside of the spectrum range
4. Select the automatic or manual peak fitting option
5. In the manual mode, select **Accept** (default) or **Reject** for each peak
6. In the peak list window, select the calibration material used
7. Tell the wizard if its guess of the phase (i.e. energy ordering of peaks) is correct
8. Assign a code to the peaks (if you are not satisfied with the automatic assignment)
9. View the velocity waveform and the residuals to determine if you want to save the calibration
10. Select **Finish** to save the calibration file



- a) If you use a calibration material that is not in the default list, simply add it to the `calibrat.ini` file using an ascii text editor.
- b) If the peaks' signal-to-noise ratios are medium to good (anything above 15:1), use the automatic fitting mode and check the final residuals. If you are not satisfied, return to the start using the **Back** button and start over using the manual mode to see which peaks were not fit properly.
- c) If you are using a laser calibration system, you can manually create a calibration file that is readable by Recoil by entering, the slope (velocity/channel) and intercept (space or TAB)



separated) of the low and high channels on two separate lines in an ascii file.

### 4.3 Fold a spectrum ?

1. Make sure you have already created a calibration file
2. Select the Utilities | Fold Spectrum... menu command
3. Select the raw data file from the file open dialog box
4. Select the calibration file from the file open dialog box
5. Save the resulting folded data file by selecting the File | Save menu command



Recoil can also used MOSMOD calibration files (.anl).

### 4.4 Calculate the ideal thickness for a sample ?

1. Select the Utilities | Ideal thickness... menu command
2. Select the Mössbauer isotope to be used in the experiment
3. Select the type of the chemical formula (stoichiometric or mass fractions)
4. Enter the stoichiometric (indices represent atomic fractions) or mass fraction (indices represent mass fractions) chemical formula of the sample
5. The ideal sample mass per unit area is automatically calculated
6. For more details, select the Next button and fill in the required property to get the one you want (holder diameter → sample mass, sample density → sample thickness,  $f_a \rightarrow t_a$ )



This *ideal thickness* is the uniform thickness which results in the optimal signal-to-noise ratio for a given acquisition time. (See Rancourt *et al.*, *American Mineralogist* **78** (1993) 1.)

### 4.5 Calculate the Mössbauer thickness of a sample ?

1. Select the Utilities | Mössbauer thickness... menu command
2. Select the Mössbauer isotope used in the experiment
3. Select the type of the chemical formula (stoichiometric or mass fractions)
4. Enter the stoichiometric (indices represent atomic fractions) or mass fraction (indices represent mass fractions) chemical formula of the sample
5. Enter an approximate value for the absorber recoilless fraction parameter ( $f_a$ )



This information can be used to determine if and to what extent thickness effects are present. In addition, the degree of thickness effects depends in a sensitive way on the actual spectral shape. (See Rancourt *et al.*, *American Mineralogist* **78** (1993) 1; Ping, J.Y. and Rancourt, D.G., *Hyperfine Interactions* **71** (1992) 1433.)

# Chapter 5

## Configuring Recoil



### 5.1 The isotopes.ini File

Information about the isotopes that is used by Recoil is stored in a file named `isotopes.ini` in the directory where Recoil was installed. Although it is not meant to be edited, you may wish to change the default isotope (which is  $^{57}\text{Fe}$ ) used by Recoil or update the values that are stored there.

Specific information about the parameters is given in the file itself, which can be opened in Notepad or any ASCII text editor. We recommend you make a backup of the distribution version in case something goes wrong.

Only isotopes with  $l = 1/2 \rightarrow 3/2$  transitions are allowed, and the values for  $^{57}\text{Fe}$ ,  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  are already entered, as found in the *Mössbauer Effect Data Center 1989 tables* and *Chemical Rubber Co. Handbook* (70<sup>th</sup> edition).

### 5.2 The calibrat.ini File

To obtain folding (calibration) parameters, the spectrum of a known absorber must be taken. This file contains the line positions for the calibration materials that can be used in Recoil. By default, it contains the values for  $\alpha\text{-Fe}$  (metallic iron),  $\alpha\text{-Fe}_2\text{O}_3$  (hematite) and  $\text{Na}_2(\text{FeC}(\text{NO})_3 \cdot \text{H}_2\text{O})$  (sodium nitroprusside or SNP) at the standard temperature and pressure conditions.

You may want to add you own materials to this file, so they can be selected when performing a calibration in Recoil.

### 5.3 General Program Options

Several global settings can be modified to customize Recoil to your preferences. These settings are accessible with the `Edit | Preferences` menu command which displays the Preferences dialog box. The changes are preserved in the Windows registry so they do not have to be reset every time you start Recoil.

#### 5.3.1 Units of the Magnetic Hyperfine Field

Recoil can be customized to suit your needs or habits when dealing with magnetic hyperfine fields. The Units tab in the Preferences dialog box lets the user choose between 3 display options:

$z$ (in mm/s)	displays the Zeeman splitting of the excited in mm/s (this is used internally)
$H$ (in kOe)	displays the magnetic hyperfine field in kOe (converted from $z$ )

## 32 Chapter 5. Configuring Recoil

$B$  (in T) displays the magnetic hyperfine field in T (converted from  $z$ )

The conversion factor between  $z$  and  $B$  is the gyromagnetic ratio that is given for the isotope in the isotopes.ini file, which is expressed in mm/s/T. The conversion between  $B$  and  $H$  is simply  $1 \text{ T} = 10 \text{ kOe}$ .

**NOTE:** in the VBF analysis, the coupling parameters are always expressed as coupling parameters with  $z$  (no conversion of the coupling parameters is performed when the T or kOe options are selected)

### 5.3.2 Fitting Options

You can also set several options related to the fitting procedure and display during the fitting process. You can specify parameters such as:

- the standard number of iterations to be performed before pausing (default is continue until convergence is achieved)
- the number of iterations to perform before updating the document views (default is update views after each iteration)
- the convergence criterion to end a fit (default is  $\Delta\chi^2/\chi^2 < 10^{-4}$ )

You can also specify whether a dialog box indicating the progress of the fit is displayed or not and whether detailed uncertainty calculations should be written to a file (named covar.dat, bootstrap.dat or mcerror.dat) or not. This last option is useful when detailed uncertainties must be calculated on values which are functions of several fitting parameters since they necessitate all the covariances or all the Monte Carlo realisations used to calculate normal parameter uncertainties. (See Chapter 6)

### 5.3.3 Mössbauer Source

Finally, for people using an isotope other than  $^{57}\text{Fe}$ , you can specify which isotope you are using and whether the selected isotope should be used as the default when starting Recoil. Source information is not written to the parameter files of the analysis so it must be selected every time the isotope used is not the default isotope (this will probably not be the case in future versions of Recoil). See the section on the isotopes.ini configuration file and the file itself for more information (it is readable and writeable in ASCII form).

# Chapter 6

## Error Calculations

---

We now describe the four methods that are used to obtain reliable error estimates. Any one of the methods can be selected after a fit is performed, and it will be the default selection for the next fit.

The first two methods rely on the shape of the  $\chi^2$  function at the minimum that was found, whereas the other two are based on Monte-Carlo techniques. More details and references are given in chapter 15 of Numerical Recipes (William *et al.*, Numerical recipes in C: the art of scientific computing, 2<sup>nd</sup> ed., Cambridge University Press (1992)).

### 6.1 $\chi^2$ Topology Methods

Under certain circumstances, it is possible to obtain parameter uncertainties based on the shape of the  $\chi^2$  function around its minimum:

- a) the measurement errors must be normally distributed;
- b) the parameter errors must not be too large as to extend outside a region where a linearization of the model is numerically valid.

In such a case, the error on a single parameter can be obtained by determining at what value of that parameter the  $\chi^2$  function reaches a certain boundary ( $\Delta\chi^2 = 1$  for 67% confidence) when all other parameters are optimized. Two methods are available to determine this value:

- i. by using the matrix of second derivatives of  $\chi^2$  at the minimum and calculating the error by assuming the function is parabolic around the minimum (which should be guaranteed by condition (b) above);
- ii. by the “brute force” method which solves the boundary equation for each parameter

Both methods are available in Recoil for your convenience, but should only be used when the fit is correct, that is when the residuals are uncorrelated and normally distributed around 0 and the  $\chi^2$  value is within one sigma or so of its ideal value.

#### 6.1.1 Using the Covariance Matrix

When an analytical model is available, the Levenberg-Marquardt algorithm is used to locate the minimum of the  $\chi^2$  function, and it internally uses the covariance matrix at each iteration. It is then natural to use that information to obtain error estimates.

The  $\chi^2$  function is defined as

$$\chi^2 = \sum_{i=0}^N \frac{(y_i - f(x_i))^2}{\sigma_i^2} \quad (13)$$

which gives the following Hessian components (matrix of the second-derivatives with respect to the model parameters):

$$(H)_{jk} = \frac{\partial^2 \chi^2}{\partial p_j \partial p_k} = 2 \sum_{i=1}^N \frac{1}{\sigma_i^2} \left[ \frac{\partial f}{\partial p_j} \frac{\partial f}{\partial p_k} - (y_i - f(x_i)) \frac{\partial^2 f}{\partial p_j \partial p_k} \right] \quad (14)$$

In practice, only the first derivatives of the model function are calculated, and the second term is considered to be nil. If the model truly describes the observed data, the deviations  $y_i - f(x_i)$  should be random and independent of the model function, so the second term should average to 0.

The covariance matrix is then calculated as the inverse of the Hessian of the  $\chi^2$  function at its minimum.

$$[C] = [H]^{-1} \quad (15)$$

Its diagonal elements represent the variance ( $\sigma_j^2 = C_{jj}$ ) (67% confidence) of each of the fitting parameters, while each off-diagonal element represents the covariance of the corresponding pair of parameters. These off-diagonal terms are representative of the correlations between the parameters. When calculating the error on a function of multiple parameters, the covariance must be taken into account.

In Recoil, 95% confidence errors are stated, so the 67% value is multiplied by 1.96.

### 6.1.2 Using the Constant $\chi^2$ Boundary

As described above, the confidence interval on a parameter is given by the values at which the  $\chi^2$  increase around the minimum is by a given value  $\Delta\chi^2$ . For 95% confidence, when a single parameter interval is desired (the desired parameter is frozen, while all others are optimized to solve for the new  $\chi^2$  minimum),  $\Delta\chi^2 = 3.84$ . The routine simply solves for  $\chi^2(p_i) = \chi^2_{\min} + 3.84$  for each parameter, on the low and high side, then reports the average value.

When the option to save the error calculation details to file is enabled, the low and high side errors can be found in the file.

## 6.2 Monte Carlo Methods

Monte Carlo methods use a completely different approach to the ones presented above since they do not depend on the  $\chi^2$  function or the fitting algorithm. In both of the methods presented here, the basic idea is to produce  $N$  synthetic data sets which are statistically equivalent to the observed data set. Each synthetic data set is fitted, producing  $N$  sets of the model parameters. Its is then possible to extract whatever information is required from the distributions of each parameter. In particular, the standard deviation of each parameter is calculated from the distribution and multiplied by 1.96 to produce a 95% confidence interval.

The two methods simply differ in the way they produce the synthetic data sets.

### 6.2.1 Using the Bootstrap Method

The Bootstrap method is a sampling method that is used to produce a statistically equivalent synthetic data set from the observed data set, irrespective of any model. To use this method, there is a requirement regarding the nature of the data, but it is respected in the case of a common Mössbauer spectrum: the data points must be independent and identically distributed (this is true since a spectrum can be constructed as a set of measurements at random velocities — it is not necessary mathematically nor physically to measure the

velocities sequentially, it is simply easier) and it is not unphysical to make two measurements at the same velocity: they can be included in the  $\chi^2$  function as two distinct points. A simple example where this requirement is not respected is a measurement where a Fourier transform of the data is obtained (e.g. Fourier transform infrared spectroscopy). In such a case, the order of the points matters since there is a temporal correlation between the data points.

In short, the Bootstrap method produces a synthetic data set by replacing data points in the observed data set by other points from the observed data set. As such, the new set of points will contain points that are redundant, and some which are missing. This is OK since nothing prevents us from removing data points as if they were never measured, and adding a point twice is like measuring the intensity twice at the same velocity, and since the observed intensity was measured, without an underlying model, we can only assume that it is the most probable value for a second measurement.

The replacement data set is generated by randomly keeping or choosing a replacement data point such that  $\sim 37\%$  ( $1/e$ ) of the points are duplicated. Each synthetic data set is then fit to obtain statistics about the parameter distributions.

The advantage of this method is that it does not rely on an underlying model, so it will give a good estimate for the robustness of the parameters for a given model to a data set, *even if the fit is not statistically correct*.

### 6.2.2 Using Counting Statistics

A more natural and direct approach can also be used if you are confident that the model is correct. Since the only unavoidable measurement errors that occur in Mössbauer spectroscopy measurements are due to counting statistics, it is possible to generate synthetic data sets from the ideal, fitted model by simply adding noise which is distributed according to the correct distribution. For intensity measurements, the counting process produces a Poisson distribution of intensities, which is well approximated by a normal (Gaussian) distribution for  $I > 30$ , with  $\sigma = \sqrt{I}$ .

Recoil simply uses the refined model to generate synthetic spectra which are refined to obtain statistics on the parameter distributions. This is also a very good method to determine the precision (due to statistical noise) you can obtain for a given measurement duration (a given signal-to-noise ratio).

## Chapter 7

# Differences Between Recoil and MOSMOD



For analysis purposes, anything that was done with the DOS-based MOSMOD program can also be done in Recoil. In addition, new features have been added to Recoil to make it more powerful and easier to use. We will now discuss the differences between the two programs that relate to their common features.

### 7.1 Using Isotopes Other Than $^{57}\text{Fe}$

Recoil can now deal with any isotope which has a  $l = 1/2$  to  $l = 3/2$  transition. The parameters for each isotope are kept in a file called isotopes.ini. There are two parameters for the  $^{57}\text{Fe}$  isotope which are different between Recoil and MOSMOD:

	<i>Recoil</i>	<i>MOSMOD</i>	<i>description and comment</i>
M of $^{57}\text{Fe}$ (g/cm <sup>3</sup> )	56.935396	57	atomic mass of $^{57}\text{Fe}$ , used in thickness calculations. The Recoil value is from the CRC Handbook (70 <sup>th</sup> edition).
Z =  g/g*	1.7500	1.7509	ratio of nuclear g-factors of ground and excited states (the uncertainty on the Recoil parameter, obtained from the MEDC 1989 nuclear gyromagnetic factors is 0.0004, whereas the uncertainty on the MOSMOD value, obtained from the standard splitting (MEDC 1989 value) of $\alpha\text{-Fe}$ is 0.0012, so the new value was preferred). This represents a difference of only 0.15 kOe for a splitting of 300 kOe and is usually smaller than the statistical error.

### 7.2 Differences in the Implementations of the Analyses

#### 7.2.1 N-line fitting with Voigts or Lorentzians (MOSMOD 3)

Instead of distinguishing between the two line shapes, the general Voigt line shape is always used. However, by default, the Gaussian width is set as nil, which makes it a pure Lorentzian line shape. Here are additional differences:

- there are no limits on the number of peaks or refined parameters
- the area of each peak is fit, not its Lorentzian height. This makes it easier to compare between peaks that have different widths.

- the Lorentzian HWHM is not constrained to be the same for all peaks, as was the case when fitting to Voigt lines. In this new implementation, all peak parameters are completely independent.
- several parameters are ensured to be physically acceptable:
  - the width of a peak must be at least as large as the intrinsic (Heisenberg) Lorentzian HWHM, since this is the mathematical limit for thickness corrections. In practice, peak widths should be larger than the experimental Lorentzian HWHM, which is double the intrinsic Lorentzian HWHM.

### **7.2.2 Thickness Correction (MOSMOD 4)**

The calculations performed in this module are now menu options for the Voigt peak Fitting analysis document. The only difference with MOSMOD is the ability to use any lineshape produced by Voigt fitting (even if the peaks are all Lorentzian, or a mixture of pure Lorentzian peaks and Voigt peaks).

### **7.2.3 Lorentzian Site Analysis (MOSMOD 5)**

- there are no limits on the number of sites or refined parameters
- the *total area* of the site is refined, instead of the Lorentzian height of a peak. This provides simpler site population comparisons between sites, and more reliable error calculations, avoiding error propagation from multiple parameters.
- the ratio of peak widths can now be refined, to possibly model hyperfine parameter distributions (in the case of sextets) or correlations (in the case of doublets). By default, the ratio of widths is always 1 (as in MOSMOD).
- several parameters are ensured to be physically acceptable:
  - the quadrupole splitting of a doublet must be positive
  - the Zeeman splitting (or magnetic hyperfine field) of a sextet must be positive
  - the width of a peak must be at least as large as twice the Heisenberg HWHM of the source
  - area ratios of peaks are forced to be positive

### **7.2.4 Full Static Hamiltonian Site Analysis (MOSMOD 6)**

This type of analysis has been completely redesigned to make use of the analytical expression for the exact line shape, making it much faster and more versatile. Here are a few differences. See the analysis description for information on the added analysis options.

- there are no limits on the number of sites or refined parameters
- the *total area* of the site is refined, instead of the Lorentzian height of a peak. This provides simpler site population comparisons between sites, and more reliable error calculations, avoiding error propagation from multiple parameters.
- several parameters are ensured to be physically acceptable:
  - the site's HWHM is forced to be larger than twice the Heisenberg HWHM of the source
  - the Zeeman splitting (or magnetic hyperfine field) is forced to be positive



### 7.2.5 Blume and Tjon Dynamic Line Shape Site Analysis (MOSMOD 7)

- there are no limits on the number of sites or refined parameters
- the *total area* of the site is refined, instead of the Lorentzian height of a peak. This provides simpler site population comparisons between sites, and more reliable error calculations, avoiding error propagation from multiple parameters.
- the average spin flip frequency  $f$  and half difference frequency  $\rho$  are used as parameters instead of the direct flip frequencies. This makes it easier to perform a fit while guaranteeing that certain constraints are respected, such as  $\rho = 0$  ( $f_+ = f$ ).
- several parameters are ensured to be physically acceptable:
  - the site's HWHM is forced to be larger than twice the Heisenberg HWHM of the source
  - the Zeeman splitting (or magnetic hyperfine field) is forced to be positive

### 7.2.6 Voigt-based Fitting (MOSMOD 8, 9 and 10)

All three modules are combined into one analysis document, equivalent to MOSMOD 10.

- there are no limits on the number of sites, components or refined parameters.
- the component's *height* is no longer used. Instead, the *relative contribution* of the component to the hyperfine parameter distribution (QSD or HFD) of its generalized site is used, while ensuring that the sum of the component contributions is 1. This ensures that a complete generalized site can be transferred from one spectrum to another, with, as only refined parameter, the area of the site. In MOSMOD, all component heights had to be left optimized when a generalized site was transferred between spectra, possibly changing the total hyperfine parameter distribution of the generalized site.
- the site's total area is now refined, instead of the Lorentzian height of a single peak. This way, a direct comparison of the areas of sites provides site population ratios, regardless of the peak area ratios or the shapes of the peaks. Also, this provides accurate error calculations on the area to avoid error propagation from multiple parameters.
- several parameters are now ensured to be physically acceptable:
  - the *Lorentzian HWHM* is forced to be at least as large as twice the Heisenberg HWHM of the source
  - the *area ratios* of peaks are forced to be positive
  - the *Gaussian widths* of distribution components are forced to be positive

### 7.2.7 Differences in the Utilities (MOSMOD 0, 1 and 2)

The always available Utilities menu provides the user with the ability to get calibration parameters from a calibration file, fold a spectrum using calibration parameters (from a Recoil or a MOSMOD calibration, or a similar calibration file containing parameters from a laser calibration). Various calculations based on the Debye Model can also be performed as in MOSMOD, but in a more interactive way. Calculations of a known absorber's Mössbauer thickness or its ideal Mössbauer thickness can also be done more easily than before.

## Chapter 8

# File Formats

### 8.1 Folded Mössbauer Data Files

Recoil can read several types of file formats to retrieve folded Mössbauer data. When using the internal folding procedure, Recoil produces a tab-delimited ASCII file containing the velocities and intensities for each channel. The format is the following:

```
number_of_channels
v1\tI1
...
```

```
Recoil folded data document v1.0
[Comment]
..
--end comment--
```

where `number_of_channels` is the number of data points in the file and `\t` denotes a TAB character (will be interpreted as spaces by most word processors) which makes the format easily readable by spreadsheet or graphing programs. The comment section is optional, but it will be used as the default comment for any analysis document using this data document. This format is also readable by MOSMOD analysis modules. In any case, the velocities need not be regularly spaced, as you would get in sine mode.

In addition to this format, Recoil can read simple space or tab delimited files where the number of channels is omitted. In this case, Recoil reads all the lines in the file and interprets lines with two numbers as the velocity and intensity. A comment section (ending with an “--end comment--” line) can also be used in these files.

In all cases, the number of data points is arbitrary and virtually unlimited ( $2^{32}-1$ ).

The file extension associated with folded Mössbauer data is “.fld”.

### 8.2 Raw Mössbauer Data Files

When the folding procedure or a velocity calibration is performed, a file containing raw, unfolded data, is retrieved. Recoil can also read several formats which only contain a stream of TAB or SPACE or LINE delimited integer intensities. In addition to this format, Recoil can read binary files produced by the EG&G program for their multichannel scaler. If you desire other binary file formats to be read, please contact the authors with the complete file format and it may be included in future revisions of Recoil.

### 8.3 Analysis Documents

Refer to chapter 2 for the file formats of the analysis documents. These formats are supplied so you may extract the information for your own needs but it is not recommended that you change the files because Recoil is sensitive to the exact lines present in the files.

## 8.4 Fit Spectrum Files

When saving data from a *Plot View*, the format depends on the type of analysis performed. A header naming the type of file is always on the first line, followed by lines for each velocity point. Each line contains TAB-delimited values of: the velocity, the measured intensity, the calculated intensity and calculated intensities for each site (or generalized site) in the analysis. Note that the same calculated background is used for the site spectral components, so their sum will not be the same as the calculated spectrum.

The file extension associated with this type of file is “.fit”.

## 8.5 Probability Density Distribution Files

When saving data from a *Distribution View*, the file is formatted as a TAB-delimited ASCII file with the following format:

```
Recoil Probability Density Distribution Data v1.0
Analysis Name: name
X_axis_title\tY_axis_title
x1\t y1
...
```

Where \t denotes a TAB character. There are always 100 points saved to the file, and the current X axis limits are used to generate the X sampling values.

The file extension associated with this type of file is “.pdd”.