

Insight into

MossWinn 3.0

By

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In the two years passed since the ICAME 99 conference the work on MossWinn 3.0 has been completed. In this new version of the MossWinn program a wide range of new procedures has been invented and implemented. Here we present some of the scientifically interesting aspects of the work culminated in MossWinn 3.0 , the main topics being:



We introduce the new distribution engine of MossWinn 3.0 that provides the user with **unprecedented flexibility** when fitting distributions.



We reveal **why some existing Hamiltonian routines fail to calculate correctly the Mössbauer spectrum** for a certain set of physical parameters in the presence of mixed magnetic and electric quadrupole interactions, and show how the corresponding problem can be fixed.



We display a range of the **most interesting new features** introduced in MossWinn 3.0 .

The new distribution engine of MossWinn 3.0

When the new FIT menu system of MossWinn 3.0 was envisaged around 3 years ago, it was decided that the fitting of distributions should become a seamlessly integrated part of it. Furthermore, **the new distribution engine was to meet the requirement to be free from all the serious and annoying restrictions often encountered in other routines.** Now, the work has been done, and the result we consider to be a breakthrough in the field of Mössbauer spectrum analysis because of the unprecedented ease and flexibility the new routine has to offer. Actually, the fitting of distributions became so straightforward in version 3.0 that in the manual of MossWinn, consisting of more than one hundred pages, only 1 single page was enough to explain it

Capabilities of the new integrated distribution routine

- 1, **Able to fit distributions using the exact solution of Nuclear Hamiltonians as the elementary pattern.**
- 2, Able to fit distributions for arbitrary M1, E1, E2, M1+E2 Mössbauer transition with $I_e, I_g \leq 9/2$. Particularly, distributions can be fitted easily for ^{57}Fe , ^{119}Sn , ^{125}Te , ^{151}Eu , ^{121}Sb , ^{141}Pr , ^{129}I , ^{237}Np , ^{197}Au , and ^{161}Dy (25.655 keV).
- 3, Distributions can be fitted in any of the position type parameters, e.g. Magnetic field, Quadrupole splitting, V_{zz} , η , hyperfine field angles, relaxation rate etc. Arbitrary correlation function can be defined between parameters.
- 4, **Able to fit multiple distributions of different kind to the same spectrum.** For each spectrum up to 5 different distribution blocks can be defined.
- 5, Crystalline subspectra and distribution blocks can be combined arbitrarily.
- 6, Distributions with shared parameters, even together with crystalline subspectra, can be fitted simultaneously to up to 32 spectra.
- 7, Constrains can be defined for the relative area fraction (expressed as % of the total spectrum area) of distributions.

How to fit distributions using the exact solution of Nuclear Hamiltonians as the elementary pattern ?

This feature of the new distribution engine of MossWinn 3.0 attracted considerable interest. Therefore, next we explain how it is done in MossWinn along with the fit of multiple distributions of different kind. We start with the formulas taken from the original paper of J. Hesse and A. Rübartsch [J. Hesse, A. Rübartsch: J. Phys. E **7** (1974) 526.]:

$$S(v_i) = \sum_{j=0}^m P(H_j) \cdot L_6(H_j, v_i)$$

where v_i is the velocity, $L_6(H_j, v_i)$ is the value of the sextet with magnetic field H_j at the velocity v_i , $P(H_j)$ is the relative weight of the sextet $L_6(H_j, v_i)$ contributing to $S(v_i)$, the measured spectrum to be fitted by the distribution. By selecting m different H_j values one can tabulate $L_6(H_j, v_i)$, and the right side of the above equation can be written as a matrix-vector multiplication:

$$S_i = L_{ij} \cdot P_j \quad (i = 1..N, j = 1..m)$$

$S_i = S(v_i)$, N being the number of channels in the measured Mössbauer spectrum, and L_{ij} being equal to $L_6(H_j, v_i)$. Although the unknown P_j could be observed as $L_{ij}^{-1} S_i$, the distribution observed in this way would display unrealistic fluctuations caused by statistical errors. To regulate the smoothness of the observed distribution curve, J. Hesse and A. Rübartsch apply a **$D(m \times m)$ smoothing matrix**, that acts as a penalty function for distributions for which the sum of discrete second differences would be too high. It turns out that the sum of squared deviation between the measured spectrum S_i , and the model spectrum based on the P_j distribution curve will be minimum if P_j is calculated in the following way:

$$P_j = [L_{ki}^T \cdot L_{ij} + \mathbf{g} \cdot D_{kj}]^{-1} \cdot L_{ki}^T \cdot S_i$$

Where γ is the smoothing parameter. By examining the equations above, one can easily realize that there has never been made use of the fact that in the $(N \times m)$ matrix L_{ij} the values of a simple multiplet [sextet] are tabulated. In other words, **in the method of Hesse and Rübartsch nothing is assumed about the elementary pattern of the distribution**. One can choose this elementary pattern arbitrarily. Thus, we can also choose it to be the exact solution of a Nuclear Hamiltonian in the presence of mixed magnetic and electric quadrupole interactions

As an example next we assume that the measured spectrum can be fitted with two distributions: a quadrupole splitting distribution of a doublet and a magnetic field distribution calculated by using the exact solution of the nuclear Hamiltonian as the elementary pattern. We will need to calculate the matrix L for both distributions separately:

$$L_{ij}(\text{Doublet}) = L_2(QS_j, v_i) \quad \text{and} \quad L_{ij}(\text{Hamiltonian}) = \text{Hamiltonian}(H_j, v_i)$$

Then the two matrices have to be combined into one in the following way:
The smoothing matrix is built from the individual smoothing matrices of the two distributions in the following way (each distribution block can have its own independent γ smoothing parameter):

$$L_{ij} = \begin{bmatrix} \xrightarrow{j = 1..m_1+m_2} \\ L_{ij}(\text{Doublet}) \quad L_{ij}(\text{Hamiltonian}) \end{bmatrix}$$

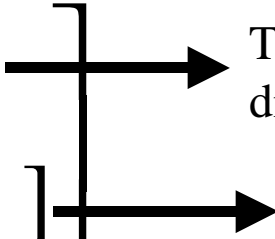
By using the very same equation as in the case of a single distribution, we derive the two distributions in a single step:

$$D = \begin{bmatrix} D(\text{Doublet}) & 0 \\ 0 & D(\text{Hamiltonian}) \end{bmatrix}$$

$$P_j = [L_{ki}^T \cdot L_{ij} + \begin{bmatrix} \mathbf{g}(\text{Doublet}) & 0 \\ 0 & \mathbf{g}(\text{Hamiltonian}) \end{bmatrix} \cdot D_{kj}]^{-1} \cdot L_{ki}^T \cdot S_i$$

The two separate distributions can be extracted from the resulted weight vector, P_j , as shown below:

$$P_j = \begin{bmatrix} [P_{j=1..m_1}] \\ [P_{j=m_1+1..m_1+m_2}] \end{bmatrix}$$



This vector describes the quadrupole splitting distribution of the doublet.

This vector describes the magnetic field distribution of the Hamiltonian pattern.

Why some existing Hamiltonian routines fail

to calculate correctly the Mössbauer spectrum for a certain set of physical parameters.

For today's powerful numerical algorithms the diagonalization of the Hamiltonian matrices encountered in the practice of Mössbauer spectroscopy is an easy job. Still, one has to be very careful when implementing these algorithms to serve the needs of Mössbauer spectroscopy: sometimes the textbooks do not take enough care to reveal all the features of the algorithms in a detailed manner. As a result, an unsatisfactorily safeguarded method can produce erroneous results in practice. In the followings we reveal why some existing Hamiltonian routines indeed fail to calculate correctly the Mössbauer spectrum for a certain set of physical parameters in the presence of mixed magnetic and electric quadrupole interactions, and show how the corresponding problem can be fixed.

The nuclear static Hamiltonian expressed in the eigensystem of the EFG is written as:
[W. Kündig: Nuclear Instruments and Methods **48** (1967) 219.]

$$H(I)_{m,m} = \mathbf{w}_Q \hbar \cdot [3m^2 - I \cdot (I + 1)] - \mathbf{w}_H \hbar \cdot m \cdot \cos \mathbf{b}$$

For the case of ^{57}Fe , for example, the $H(I)$ matrix of the excited ($I=3/2$) level is a 4x4 complex Hermitian matrix.

$$H(I)_{m,m+1} = \frac{-\mathbf{w}_H \hbar \cdot \sin \mathbf{b}}{2} \cdot \sqrt{I \cdot (I + 1) - m \cdot (m + 1)} \cdot e^{i\mathbf{a}}$$

$$H(I)_{m,m+2} = \frac{\mathbf{w}_Q \hbar}{2} \cdot \mathbf{h} \cdot \sqrt{[I \cdot (I + 1) - (m + 2) \cdot (m + 1)] \cdot [I \cdot (I + 1) - m \cdot (m + 1)]}$$

To calculate the energy shift of the degenerate energy levels of the $l_e=3/2$ excited nuclear level, induced by the hyperfine interactions, one has to solve the eigenproblem of $H(l=3/2)$ by deriving its eigenvalues and the corresponding eigenvectors. The problem of solving the eigenproblem of the H complex Hermitian matrix can be reduced to the solution of the eigenproblem of the following real symmetrical matrix [W.H.Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling: *Numerical Recipes, The Art of Scientific Computing*, Cambridge University Press, Cambridge, New York (1990) pp. 404]:

$$H_R = \begin{bmatrix} H_A & -H_B \\ H_B & H_A \end{bmatrix}$$

Where $H_A = \text{Re}(H)$ and $H_B = \text{Im}(H)$.

As H_R has twice the dimension of H , the number of eigenvalues and eigenvectors obtained for it is twice the number of eigenvalues and eigenvectors obtained for the matrix H .

One can show that if the complex vector $(u+i v)$ is the eigenvector of the H complex matrix, then the augmented matrix H_R has the following two vectors among its eigenvectors, both belonging to the same real eigenvalue:

$$q_1 = \begin{bmatrix} u \\ v \end{bmatrix} \quad \text{and} \quad q_1^+ = \begin{bmatrix} -v \\ u \end{bmatrix}$$

By solving the eigenproblem of the H complex matrix via the augmented problem of H_R , only one of these two eigenvectors (e.g. q_1) has to be taken into account.

Thus, by solving the augmented eigenproblem for the case of ^{57}Fe we obtain 8 eigenvectors from which only 4 are independent. Thus, one has the job to select the 4 independent eigenvectors from the 4 x 2 pairs of eigenvectors of H_R . And **this is the stage where some existing routines fail: from the 8 eigenvectors they fail to select 4 independent, but they select 4 among which one or two redundant pairs (e.g. q_1 and q_1^+) will be present.** As a result of such an error the routine will calculate the Mössbauer spectrum of ^{57}Fe as if the excited $I=3/2$ level had a sublevel (e.g. $m=-3/2$) twice and an another sublevel (e.g. $m=-1/2$) missing. Thus, in the resulting theoretical Mössbauer spectrum the Mössbauer absorption lines belonging to the missing sublevel will be absent, and the absorption lines belonging to the doubly represented sublevel will have their amplitude doubled.

We speculate that the reason why this selection procedure is not carried out correctly by some routines is that in many of the cases the q eigenvectors of H_R will follow each other in a specific order. Thus, authors could easily have the impression that they will *always* be in that specific order. However, as the statistics presented in the followings shows, they won't.

As an example, we investigated the behaviour of the QL diagonalization method described in W.H.Press et al.: *Numerical Recipes*, Cambridge University Press, Cambridge, New York (1990). We wanted to know in which order the method will produce the eigenvectors of H_R for the case of a mixed electric quadrupole + magnetic dipole hyperfine interaction. As the table shows, the order of eigenvectors depends strongly on the values of the polar and azimuthal angles.

Restrictions	Order TYPE A occurs ($q_1, q_2, q_3, q_4, q_1^+, q_2^+, q_3^+, q_4^+$)	Order TYPE B occurs ($q_1, q_1^+, q_2, q_2^+, q_3, q_3^+, q_4, q_4^+$)	Order TYPE C occurs (All other order types)
None [all random]	< 0.01 %	32.1 %	67.9 %
$\eta = 0$, others random	< 0.01 %	32.2 %	67.8 %
$H \parallel V_{zz}$, others random	100 %	0.0 %	0.0 %
$H \perp V_{zz}$, others random	< 0.01 %	44.9 %	55.1 %
Azimuthal angle = 0	100 %	0.0 %	0.0 %
Azimuthal angle = 90 [deg]	44.4 %	26.7 %	28.9 %

If not constrained, the values of H , V_{zz} , η , and the polar and azimuthal angles of H in the system of EFG were selected randomly from the intervals [0..60] Tesla, [0..20] 10^{21} V/m², [0..1], [0..90] and [0..90], respectively. Each row represents the results of 10^5 runs.

How to check your own routine

The obtained table of statistics suggests a way through which you can check whether the Hamiltonian routine you use is faulty or not. First select a fixed set of Mössbauer parameters expressed in the eigensystem of the EFG:

$$H = 29.37957 \text{ Tesla } (g_{3/2} * \mu_N * H = 2.0 \text{ mm/s})$$

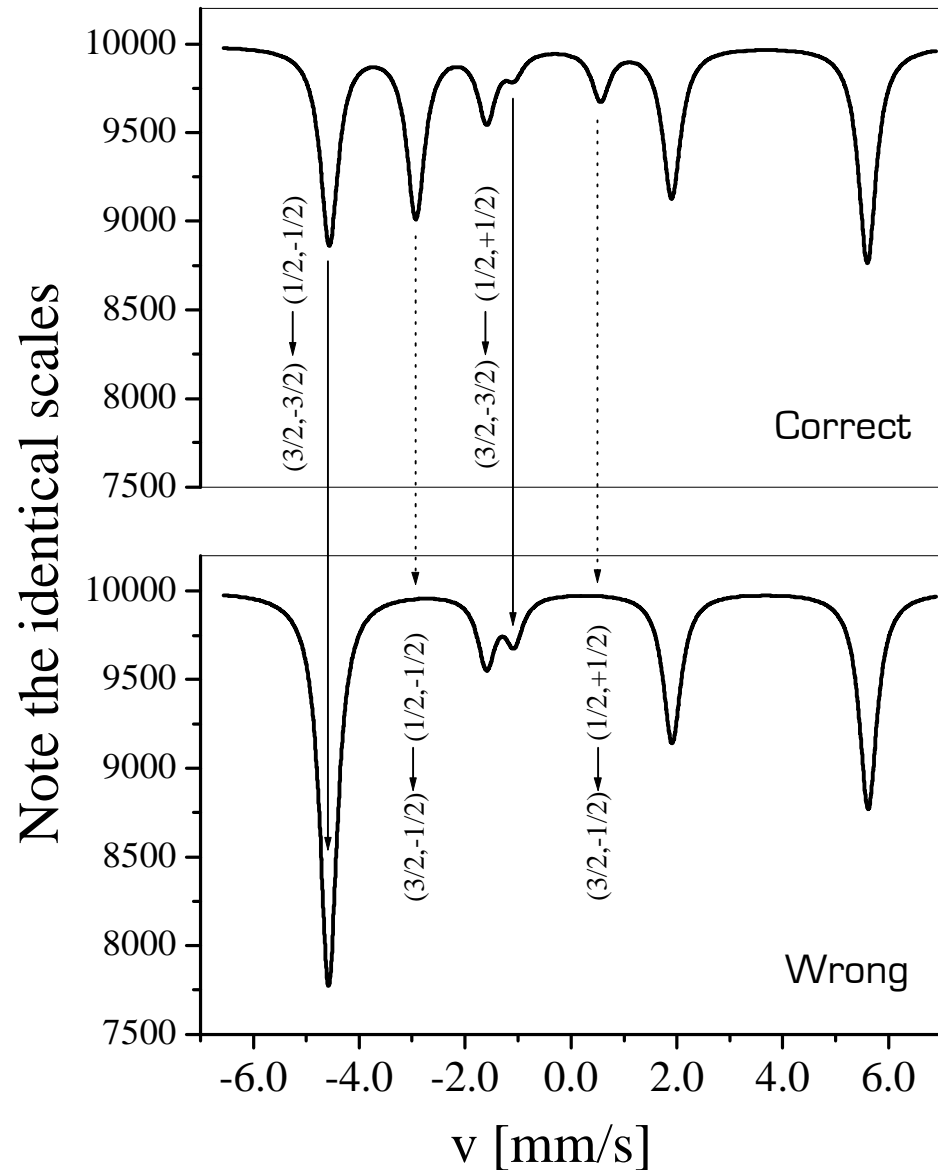
$$V_{zz} = 12.0 * 10^{21} \text{ V/m}^2 (e * Q_{3/2} * V_{zz} = 4.0 \text{ mm/s})$$

$$\eta = 0.5$$

Polar angle of H in the PAS system: 0 [deg]

Azimuthal angle of H in the PAS system: 75 [deg]

Then create model spectra with your routine by increasing the polar angle with a step of 5 [deg] from Polar angle = 0 [deg] to Polar angle = 90 [deg]. If the selection of eigenvectors is not done entirely correctly, then at some intermediate value of the polar angle the routine will produce theoretical Mössbauer spectra with missing absorption lines. An example is shown on the right for an existing routine that failed at Polar angle = 25 [deg].



Solution on the programmer s level

The main difficulty in the implementation of a routine that has the job to select the independent eigenvectors of H_R is that the diagonalization routine calculates eigenvectors with a finite level of precision. Therefore, the pairs of eigenvectors representing the same solution (e.g. q_1 and q_1^+) do not match *exactly*. However, we can define a quantity that gives a measure of relatedness when comparing two eigenvectors of H_R (q_1 and q_2): $q_1 = \begin{bmatrix} u_1 \\ v_1 \end{bmatrix}$ and $q_2 = \begin{bmatrix} u_2 \\ v_2 \end{bmatrix}$

$$\alpha(q_1, q_2) = \text{MINIMUM OF } \left\{ \frac{\text{abs}(v_1 + u_2)}{(\text{abs}(v_1) + \text{abs}(u_2))} + \frac{\text{abs}(u_1 - v_2)}{(\text{abs}(u_1) + \text{abs}(v_2))}, \right. \\ \left. \frac{\text{abs}(v_1 - u_2)}{(\text{abs}(v_1) + \text{abs}(u_2))} + \frac{\text{abs}(u_1 + v_2)}{(\text{abs}(u_1) + \text{abs}(v_2))} \right\}$$

If $q_2 = q_1^+$ then $\alpha(q_1, q_2) = 0$ (or in practice $\ll 1.0$). When selecting the 4 independent eigenvectors from $q_1..q_8$ we proceed as follows:

Put q_1 in the set of selected eigenvectors: E .

$\beta_{\max} := -1.0$;

For values of j going from 2 to 4 do the followings:

{

For values of i going from 2 to 8 do the followings:

{ if q_i is already in E then start next cycle of i ;

$\beta(q_i) := \text{MINIMUM OF } \alpha(q_i, E)$

if ($\beta_{\max} < \beta(q_i)$ or $\beta_{\max} < 0.0$) then $\beta_{\max} := \beta(q_i)$

}

The vector q_i , for which $\beta(q_i) = \beta_{\max}$, is the next independent eigenvector.

Put q_i into E .

}

Further features of MossWinn 3.0

⇒ **Supported Mössbauer transitions:**

Any M1, E1, E2, M1+E2 with $I_{\text{ground}}, I_{\text{excited}} \leq 9/2$

⇒ **Particularly supported Mössbauer**

isotopes: ^{57}Fe , ^{119}Sn , ^{125}Te , ^{151}Eu , ^{121}Sb , ^{141}Pr ,
 ^{129}I , ^{237}Np , ^{197}Au , ^{161}Dy (25.655 keV)

Built in Mössbauer models

1, Mixed Magnetic dipole + Electric quadrupole interaction **for all handled Mössbauer transitions**, for the following geometries (Each model can be fitted either in the **EFG** based or in the **H** based Principal Axis System):

- a, Single Crystal
- b, Mosaic
- c, Powder
- d, Powder with **Goldanskii-Karyagin Effect**

2, Blume-Tjon two state magnetic relaxation for ^{57}Fe , for powder geometry.

3, Usual linear models for $3/2 \rightarrow 1/2$ transitions (doublet, sextet, first order approximation etc.).

4, Built in support for arbitrary user programmed models, with example files provided.

5, For arbitrary M1, E1, E2, M1+E2 transitions the nuclear parameters (g factor, quadrupole moment, amplitude and phase of the E2/M1 ratio) can be fitted as well.

⇒ Supported absorption line shapes

- 1, Lorentzian
- 2, Lorentzian with dispersion (accounting for the interference between nuclear and atomic absorption)
- 3, Lorentzian with cosine smearing (accounting for geometrical effects)
- 4, Pseudo-Voigt

⇒ Transmission Integral

For all models, with the exception of distributions, for arbitrary (not only 2^n) channel number, for sinusoid as well as for linear velocity axis, for unfolded as well as for folded spectra, with the correct indication of subcomponents.

⇒ Simultaneous fitting of spectra

For all models including transmission integral, distributions, and user programmed models. Up to 32 Mössbauer spectra can be fitted simultaneously. Shared and unshared subspectra can be combined arbitrarily.

⇒ **ScanFit**

The new ScanFit feature of MossWinn enables the creation of ASCII data - ready for FIT - from bitmap images of scanned Mössbauer spectra.

⇒ **Data export**

Publication ready graphs - of spectra (including subspectra), of distributions, and of parameter correlations - can be printed or copied into the clipboard of MS Windows. Multiple spectra can be printed/copied on one page. Besides usual fit reports, Mössbauer parameters can as well be exported as tables being in order with respect to the value of one of the parameters.

Further Information

A limited number of copies of the full version of MossWinn 3.0 are available for a 30 days trial period. If you are interested, please, contact the author via:

author@mosswinn.com

For further information on the MossWinn program concerning availability and price, please, visit:

<http://www.mosswinn.com>