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IMSG09: A ^{57}Fe - ^{119}Sn Mössbauer spectra computer fitting program with novel interactive user interface

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Abstract. A recently developed computer based ^{57}Fe - ^{119}Sn Mössbauer spectra fitting program is described. The program uses full Hamiltonian matrices to generate theoretical Mössbauer spectral contributions with which fits the experimental data based on a least-squares minimization procedure. The user of the program can exploit its interactive user interface to build and modify on-the-fly a starting theoretical model of proposed contributions without the need to write or alter the initial Mössbauer parameter values to or from any file. Changes in the Mössbauer parameters values for the proposed model can be made on the screen and the theoretical contributions can be displayed during those changes in real time together with the experimental spectrum in order to give the user the ability to approximate with the best and fast way the desired solution before launching the minimization procedure. Single as well as multiple sub-component contributions with Gaussian-type spreading of quadrupole splitting/shift or hyperfine magnetic field values can be realized to fit transmission, conversion electron or X-ray Mössbauer spectra of randomly or non-randomly oriented powder or single crystal samples. The program is currently written for $3/2 \rightarrow 1/2$ nuclear spin transitions but can be modified to include higher spins, as well as distributions of other types and of other Mössbauer parameters values.

1. Introduction

Mössbauer spectroscopy throughout its 50 years history has been established as a unique method for the investigation of the physical and chemical properties of materials. From its birth, this technique had gone through important developments both theoretically and experimentally [1]. One of the most important tools which follow these developments is the computer based programs utilized to fit Mössbauer spectra (MS) and determine quantitatively the Mössbauer parameters (MPs) in order to lead to the best interpretation of the experimental results.

In the past many useful programs based on several models of reproducing theoretical MS contributions have been released. Regardless of the specific program, its user has to propose a set of contributions with initial MPs, which will be used as the starting theoretical model to fit a given experimental spectrum, following usually a least-squares minimization procedure. It is well known that the success of this venture and the extraction of the best set of MPs with physical significance carrying important information, depend on the complexity of the given MS and on the proximity of the initial proposed model to the pursued solution [2]. However, in order to approximate this solution, the procedure of building the initial theoretical model in most of the programs requires to write, usually to a file, a group of starting MPs values for the set of proposed contributions, and then make several test runs by changing these values before the least-square minimization procedure is launched. Especially

in complex spectra with many different contributions, this procedure is quite difficult, time-consuming and it doesn't always leads to the desired approximation to the experimental data.

In this work we present, for the first time, a recently developed computer program, IMMSG09 (Ioannina Mössbauer Spectroscopy Group 2009), which fits MS with a least-squares minimization procedure. Among other characteristics, its novelty is based on its interactive-user-interface, which gives the ability to build and modify on-the-fly a starting theoretical model with a very quick and easy way, in order to produce the best first approximation to the experimental spectrum, without writing initial values to any file.

2. Structure and main procedures of the program

IMMSG09 is written in Delphi and an outline of the structure of its main components is given schematically in figure 1. It combines a number of visual (displayed on screen) and non-visual classes, which are properly connected to provide the final optical and numerical result of the fitting. An example of a snapshot of such a result after the successful termination of the minimization procedure for the ^{57}Fe Mössbauer spectrum of bulk Fe_3BO_5 at 4.2 K [3] is shown in figure 2.

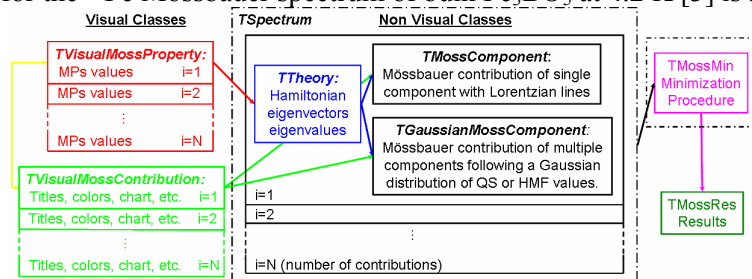


Figure 1. Structure of the main classes of the IMMSG09 program.

The user can import an experimental spectrum as a sequence of numbers in a column representing the counts in each channel (the maximum channel number is user-defined), collected from a Mössbauer spectrometer operated in multi-channel scaling mode, accompanied by the calibration constants for the particular spectrum. The TVisualMossProperty class is used to insert the proposed MPs from which the theoretical contributions are produced in order to build a model to fit the given spectrum. The theoretical points of each contribution, which are displayed on the screen together with the points of the experimental spectrum, are always calculated using full Hamiltonian matrices. At present, these matrices correspond to the ground and excited nuclear states with nuclear spins of $I_g=1/2$ and $I_e=3/2$ respectively and are expressed following the formalism of Kunding [4] and Hoy & Chandra [5]. This means that they can generate theoretical MS for the cases of ^{57}Fe and ^{119}Sn . However the structure of the program allows higher spins to be added in following versions.

The TTheory class uses the provided MPs to calculate the elements of the ground and excited Hamiltonian matrices, solves the Hermitian eigenvector-eigenvalue problem with the QR decomposition method, using the LAPACK 3.0 library [6] as realised in ALGLIB [7] and extracts the line positions of the theoretical contribution. The lines are generated as Lorentzians, but the program can be easily modified to include other types of functions in future versions. In this formalism [4, 5] the MPs entering the Hamiltonian matrices include: i) $QS=eV_{zz}Q/2$ in mms^{-1} , where e is the electron's charge, V_{zz} is the main component of the electric field gradient (EFG) tensor defining the z direction of the Kartesian system and Q is the nuclear electric quadrupole moment of the excited state, ii) $\eta=(V_{xx}-V_{yy})/V_{zz}$, the asymmetry parameter, iii) HMF in kG, the magnitude of the hyperfine magnetic field, iv) theta (θ) and phi (ϕ) in degrees, the polar and azimuthal angles defining the orientation of the HMF vector with respect to V_{zz} and v) alpha (α) and beta (β) in degrees, the polar and azimuthal angles defining the orientation of the γ -ray direction with respect to the V_{zz} direction. Apart from these, the global MPs of: vi) IS in mms^{-1} , the isomer shift, vii) HWHM in mms^{-1} , the half line-width ($\Gamma/2$) of the generated Lorentzian lines, viii) Int. in counts, the intensity of the far most left line of the generated multiplet, are also used to produce the sub-spectrum of the inserted contribution. The relative intensities of the resulting resonant lines are also determined by the TTheory. The user can choose between contributions corresponding to polycrystalline powder (arbitrary orientation), which is

the default case, and single crystal or oriented powder samples by ticking on the corresponding box. In each case the relative intensities of the absorption lines are calculated through the appropriate eigenvectors, the Glebsch-Gordan coefficients and the vector spherical harmonic matrices [4, 5].

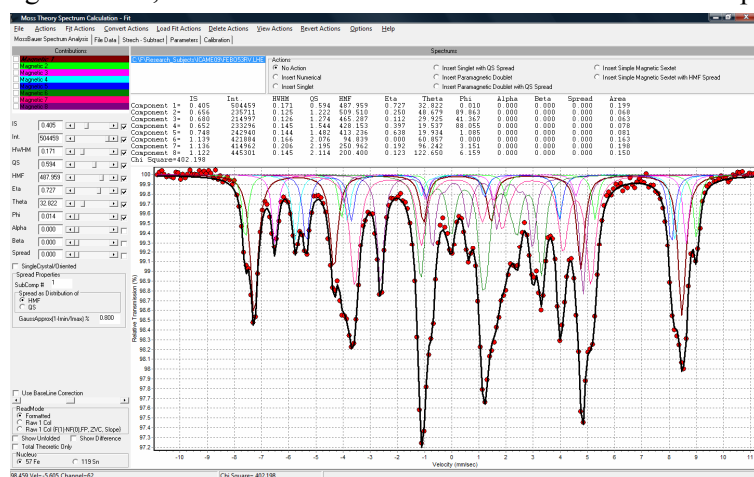


Figure 2. A snapshot of the user interface of the MSG09 program.

The user can also choose if the contribution will be inserted as a single component (in this case the TMossComponent class is used), or if it will allow a spreading of HMF (for the magnetic contributions) or QS (for the paramagnetic or magnetic contributions) values around a central HMF_C or QS_C value. In the second case the TGaussianMossComponent class is used in order to produce the contribution which is composed of the superimposition of a set of N_C+1 interlinked sub-components (the number N_C in the set is user-defined with a current upper limit of 900 components). All sub-components in the set are generated using the Hamiltonian matrices through TTheory and possess the same $\Gamma/2$. The intensity I_i and the HMF_i/QS_i values for the i sub-component of the set are calculated as a function of the maximum intensity I_C of the set (parameter Int. of the contribution), which corresponds to the central HMF_C/QS_C value (parameter HMF/QS), and the spreading σ (parameter Spread), following a Gaussian distribution function, which in the case of HMF values spreading can be written as:

$$I_i = I_C \exp \left\{ -\frac{(HMF_i - HMF_C)^2}{2\sigma^2} \right\}, \text{ where } HMF_i = HMF_C + S(2i - N_C)/2N_C, i = 0, 1, \dots, N_C, S = 2\sigma[2\ln(1/r)]^{1/2}$$

The user must choose the quantity $(1-r)$, where r is the minimum to maximum intensity ratio $r = I_0/I_C$, for which the minimum (HMF_0) and maximum (HMF_{N_C}) values of the set will be calculated. In addition case-dependent boundary conditions eliminating the intensities of those generated sub-components of the set having $HMF_i < 0$ also apply. The same distribution is also applied for QS values spreading, however with no boundary conditions in this case. Although currently only the Gaussian distribution is used for the calculation of the spreading of HMF/QS MPs values, the structure of the program allows any other distribution function to be added formally, which could also involve other MPs (like IS, η , θ etc.) as well.

While the experimental spectrum is displayed on the screen, the user can choose between two ways to insert a theoretical contribution: (i) insert a contribution by giving all the proper starting MPs numerically from the keyboard, or (ii) clicking with the mouse on the screen at the positions of those main resonant lines which he/she thinks that correspond to a certain contribution of the spectrum. In case (ii), the starting MPs of IS, QS, Int. and HMF are calculated and inserted automatically in the appropriate insertion MPs boxes using the velocities v_i (in mms^{-1}) detected from the 'clicked' positions on the screen (at the x-velocity axis) and the relations: a) $IS = (v_1 + v_2)/2$, $QS = (v_2 - v_1)$, with two (v_1, v_2) clicks in the case of paramagnetic doublet contributions (for a paramagnetic singlet only one click for v_1 is necessary, and then $IS = v_1$ and $QS = 0$) and b) $IS = (v_1 + v_2 + v_3 + v_4)/4$, $QS = (v_1 - v_2 - v_3 + v_4)/4$ and $HMF = \{(v_4 - v_1) \cdot (330/10.6248 \text{ kG/mms}^{-1})\}$ (for ^{57}Fe spectra) [8], with four (v_1, v_2, v_3, v_4) clicks at the outer lines of the sextet in the case of magnetic contributions; the Int. parameter in each case is calculated as the length in the y axis (in counts) between the first clicked position (for v_1) and the baseline of the spectrum. It is obvious that these values, calculated from the clicked positions, are

good approximations to the expected corresponding real MPs of the contribution in the simple cases of having either diagonalized Hamiltonian matrices, or small perturbations in main diagonalized Hamiltonian matrices, i.e. when the electric quadrupole interaction can be taken as a small perturbation upon the main magnetic interaction [8]. In these cases, when the EFG is not considered to be axially symmetric ($\eta \neq 0$) and η , θ and ϕ cannot be uniquely determined, QS includes also η , $QS = \Delta E_Q = eV_{zz}Q \cdot (1 + \eta^2/3)^{1/2}/2$ in the case of paramagnetic contributions and θ and ϕ as well in the case of magnetic contributions, $QS = 2\varepsilon = eV_{zz}Q \cdot (3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi)/4$ [9]. QS then represents the combined parameters ΔE_Q or 2ε and the individual η , θ , ϕ values are inserted as equal to 0. Depending on the nature of the contribution to be inserted, the user can choose between a number of six different kinds displayed in the appropriate box, including paramagnetic singlets and doublets as also magnetic sextets, with or without QS or HMF spreading. For all other cases the user must choose the first numerical insertion method (i). Regardless of the insertion method, the displayed characteristics (title, color, chart etc.) of each contribution are controlled by the TVisualMossContribution class.

After insertion, all the MPs of the contribution (IS, Int., $\Gamma/2$, QS, HMF, η , θ , ϕ , α , β , σ) can be modified just by using the appropriate sliders provided for each parameter, or the arrows from the keyboard. For every change in its value through the movement of the slider or arrow, the contribution is recalculated by TTheory and redisplayed on the screen instantly. The limiting values of the slider, as well as other display and chart parameters are user-defined from a special window. The user can insert limitless number of contributions (practically restricted by the amount of the available memory of the system) in order to build the initial theoretical model to fit the spectrum. After insertion of all desired contributions and appropriate manipulation of their MPs targeting the best -user determined- initial approximation to the experimental data, the minimization procedure can be launched. The user must define those MPs for each contribution which will be free to vary in the minimization procedure by checking their appropriate boxes. Currently all MPs are varied independent of each other, but correlations between MPs variation (within the same contribution or between different ones) are scheduled to be included in following versions of the program.

IMSG09 fits MS based on least squares (minimum χ^2) minimization procedure. The program currently follows the well known Levenberg-Marquardt algorithm [10] for the minimum χ^2 convergence, through the use of the LAPACK 3.0 library [6] as realized in ALGLIB [7], but it is designed to adapt other minimization methods too. It can be compiled to run in all major computer operating systems including Microsoft WindowsTM (98, ME, 2000, XP, Vista), Unix-Linux, MacintoshTM and others.

3. Conclusions

IMSG09 introduces a new way to fit MS, using an interactive user interface to approximate on-the-fly the best proposed theoretical model to the experimental data before the final minimization procedure. We hope that the current inclusion of different cases of theoretical contributions, as well as the ability to expand in additional cases will give the 'Mössbauer community' a useful tool for MS analyses.

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