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The maximum entropy method in the analysis of the Mössbauer spectra

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Abstract The paper shows the possibility of reconstruction of the distribution of hyperfine field parameters without prior assumptions concerning correlations between parameters. The method used is the maximum entropy method and the distributions considered concern the magnetic field and isomer shift. The results obtained are very encouraging and show the feasibility of the proposed method.

Key words Bayesian logic • maximum entropy method • Mössbauer spectra

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Introduction

The maximum entropy method (MEM) stems from the so-called Bayesian logic [11]. It was used to analyze many spectroscopic data [2, 3, 7, 9]. However, this method was not as yet extensively applied to the analysis of Mössbauer spectra where presence of the distribution of hyperfine field parameters makes the spectra complicated and their interpretation becomes ambiguous because of the assumptions one makes in order to get the hyperfine field distributions.

In short, when the Zeeman interaction is dominating, the Mössbauer spectrum consists of lines measured as a function of the source velocity $V(i)$, where $i = 1,2,\ldots,N$ with N being usually 256. In a typical experiment with ^{57}Fe-based absorption, for a given hyperfine magnetic field B (in Tesla), isomer shift IS (in mm/s) and quadrupole splitting QS (in mm/s) the recoilless absorption should occur at the following six velocities (Zeeman sextet):

$$v_1 = B^*(3g_{3/2} - g_{1/2})/2 + \mathrm{QS} + \mathrm{IS}$$
$$v_2 = B^*(g_{3/2} - g_{1/2})/2 - \mathrm{QS} + \mathrm{IS}$$
$$v_3 = B^*(-g_{3/2} - g_{1/2})/2 - \mathrm{QS} + \mathrm{IS}$$
$$v_4 = B^*(g_{3/2} + g_{1/2})/2 - \mathrm{QS} + \mathrm{IS}$$
$$v_5 = B^*(-g_{3/2} + g_{1/2})/2 - \mathrm{QS} + \mathrm{IS}$$
$$v_6 = B^*(-3g_{3/2} + g_{1/2})/2 + \mathrm{QS} + \mathrm{IS},$$

where the gyromagnetic factors for ^{57}Fe nucleus are:

$$g_{3/2} = -0.067897 \text{ mm/s/T}, g_{1/2} = 0.118821 \text{ mm/s/T}.$$

In the case of infinitely thin absorber, the line intensities are:

Line number	Unpolarized radiation	Circularly polarized radiation
1	$I_1 = 3(1 + c_2)/16$	$I_1 = 3(1 + c_2 + 2c_1)/16$
2	$I_2 = (1 - c_2)/4$	$I_2 = (1 - c_2)/4$
3	$I_3 = (1 + c_2)/16 = I_1/3$	$I_3 = (1 + c_2 - 2c_1)/16$
4	$I_4 = I_3$	$I_4 = I_1/3$
5	$I_5 = I_2$	$I_5 = I_2$
6	$I_6 = I_1$	$I_6 = 3I_3$

where

(1) $$c_1 = <\cos\Theta>, \quad c_2=<\cos^2\Theta>$$

with Θ being an angle between the direction of a photon and the direction of magnetization of a sample. The averaging runs over all possible grains and domains in the sample [14].

A given ith line contributes to the jth channel in the velocity spectrum, the intensity being proportional to

(2) $$J_j = \frac{I_i}{\left(V(j)-v_i\right)^2+\left(\Gamma/2\right)^2}$$

where the natural width, Γ, of the line from the Mössbauer source is 0.22–0.25 mm/s.

In the general case of dominating magnetic interaction, one deals with the distribution of all five parameters appearing in the above formulas i.e. B, IS, QS, c_1 and c_2. There exist methods of reconstructing the hyperfine magnetic field distribution [4–6, 10, 12, 13, 15, 16] from measured spectra. However, in order to make such reconstruction one has usually to assume a certain correlation between, e.g., the hyperfine field B and the isomer shift IS. To the best knowledge of the authors, there is no code enabling one to get the distributions of B and IS independently of each other. Obviously, the situation becomes much more complex if the distributions of other parameters have to be taken into account. This paper shows that such task can be feasible when the analysis is carried out by means of the maximum entropy method. The first successful attempt to use this method for a single parameter distribution was published by Brand and Le Caer [1]. Dou *et al.* [8] were using the Bayesian inference theory to obtain the distribution of one parameter (B) assuming linear coupling of two other parameters (IS and QS) to B. Their approach, however, was not the MEM approach in strict sense.

Maximum Entropy Method

Assume that the whole space of parameters (five-dimensional in the most general case) was divided into pixels and the value ρ_j denotes the probability of having the values of these parameters corresponding to this particular pixel. Because the line intensities are linear in the densities, the intensities W_i measured at ith velocity channel will be given by:

(3) $$W_i = \sum_{j=1}^{N_{pix}} r_{ij}\rho_j$$

where $i = 1,\ldots,N$ and the transformation matrix $\{r_{ij}\}$ can easily be evaluated from the expressions given in the Introduction.

In accordance with the principles of the MEM, one has to maximize the information entropy:

(4) $$\mathrm{S} = -\sum_{j=1}^{N_{pix}}\left[\rho_j \ln\left(\rho_j/\rho_j^0\right)-\rho_j+\rho_j^0\right]$$

under the constraint of minimum of the χ^2 misfit function and proper normalization of the spectra calculated from the reconstructed distribution ρ. The simplest normalization condition is obtained from requiring that the sum of measured intensities W_i and the sum of intensities T_i corresponding to the distribution ρ be equal. The respective Lagrangian of the problem is

(5) $$\mathrm{L} = \alpha\mathrm{S}-\frac{1}{2}\chi^2-\alpha\gamma\sum_{j=1}^{N_{pix}} b_j\rho_j$$

where:

$$b_j = \sum_{i=1}^{N} r_{ij}, \qquad \chi^2 = \sum_{l=1}^{N}\frac{1}{\sigma_l^2}\left(W_l-T_l\right)^2$$

where σ_l denotes the uncertainty of the W_l, while α and γ are the Lagrange multipliers. One can check that in the ideal case the values b_j should be independent of the index j, so one can set $b_j = b$, and the final equations to solve have the shape of

(6) $$\rho_j = \mathrm{Z}\cdot\frac{\rho_j^0 e^{-\frac{1}{2\alpha}\frac{\partial\chi^2}{\partial\rho_j}}}{\sum_{j=1}^{N_{pix}}\rho_j^0 e^{-\frac{1}{2\alpha}\frac{\partial\chi^2}{\partial\rho_j}}}$$

where $$\mathrm{Z} = \frac{\sum_{i=1}^{N} W_i}{b}.$$

There are N_{pix} strongly non-linear eq. (6). To solve such a number of equations is a real problem. However, because the Mössbauer spectra are measured usually in 256 channels only, instead of solving N_{pix} equations one can solve $N = 256$ equations with respect to the "theoretical" intensities T_j:

(7) $$T_j = \sum_{l=1}^{N_{pix}} r_{jl}\rho_l.$$

Substituting eqs. (6) and (7) one can see that one gets the required equations with respect to the set of $\{T_j\}$. This set can be solved by the Newton-Raphson method.

In the practical case, we encounter the problem of finding an optimum parameter α. The parameter γ is obtained, if necessary, by a strict requirement of the spectrum normalization. The search for optimum α parameter is a tedious task, but our experience shows that once good χ^2 is obtained, the change in the optimum α value results in rather insignificant changes in the reconstructed distributions.

Results

Three cases were considered.
(1) the distribution of hyperfine magnetic fields consisting of three Gaussian distributions,
(2) the simultaneous Gaussian distributions of the field B and the isomer shift IS,
(3) the case (1) with added Gaussian distributions of IS, non-correlated with the values of the magnetic field B.

For each simulated distributions, the Mössbauer spectrum was calculated and the noise corresponding to the assumed Poisson statistics was added to the simulated spectrum. Next, by means of the MEM with ignorant prior (ρ_j^0 = const) the distribution $\{\rho_j\}$ was reconstructed. The parameter α was chosen so as to obtain χ^2 close to 1. The results are presented in Figs. 1–3.

In the first case, the reconstruction is almost perfect. There are some artifacts on the low-field side which show the tendency of splitting of the peak at the lowest field. This shows that one has to be careful with jumping to conclusions about such splitting. Happily, it is easy to make a check and see whether this kind of effect does not arise from the statistics or from the calculation method itself.

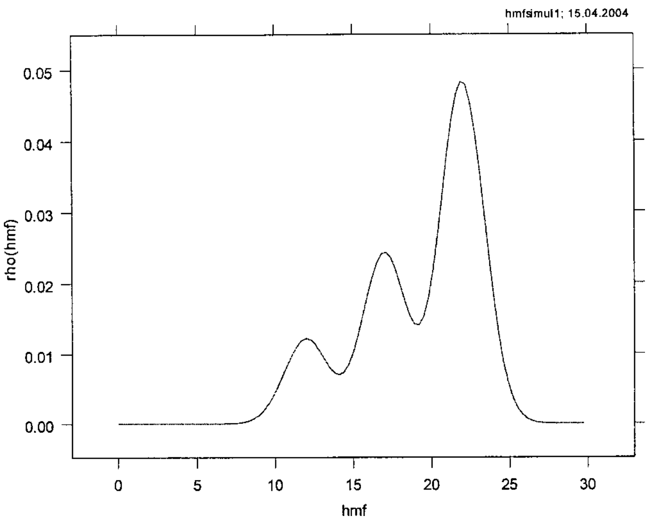

Fig. 1a. Simulated distribution of hyperfine magnetic fields.

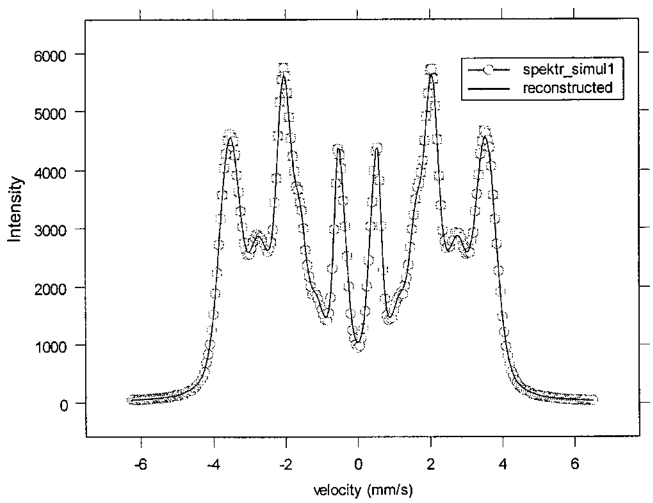

Fig. 1b. Spectrum obtained for the distribution shown in Fig. 1a. The solid line shows reconstructed spectrum.

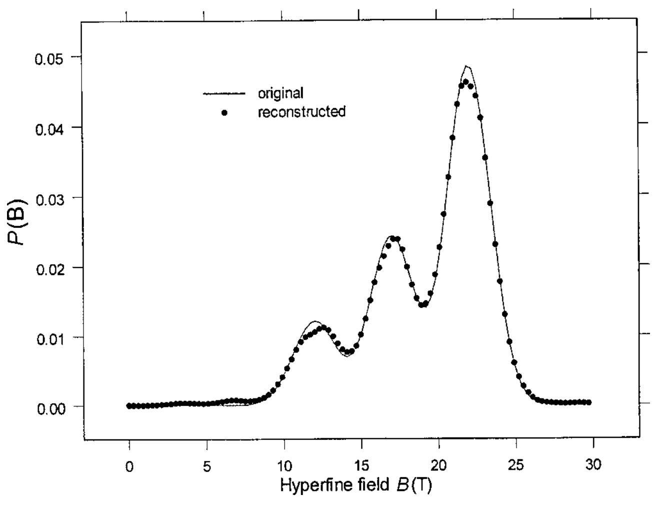

Fig. 1c. Reconstructed distribution of the hyperfine magnetic fields (dots) compared with the simulated original distribution (thick line).

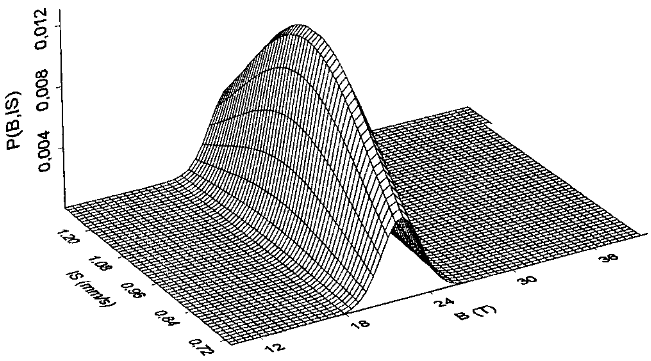

Fig. 2a. Simulated distribution of hyperfine parameters B and IS.

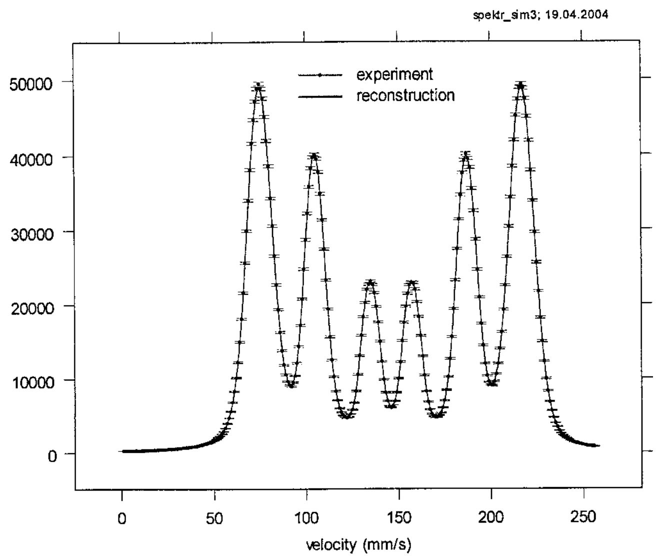

Fig. 2b. Simulated and reconstructed spectra for the distribution shown in Fig. 2a.

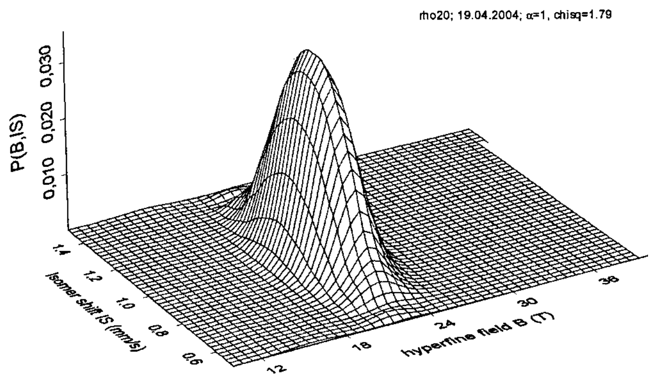

Fig. 2c. Reconstructed distribution in (B,IS)-plane. Note that the range of IS is broader than in Fig. 2a.

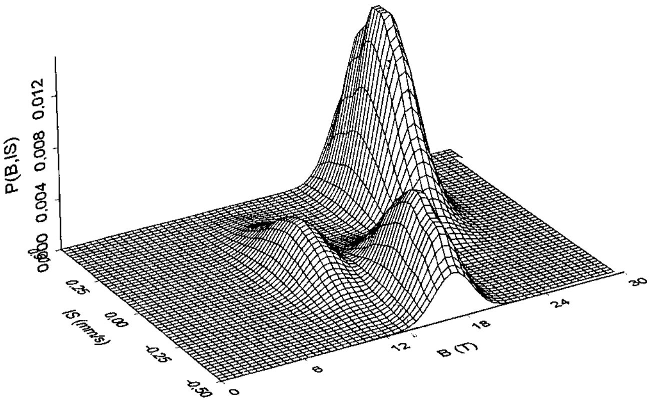

Fig. 3a. Simulated distribution of B and IS parameters.

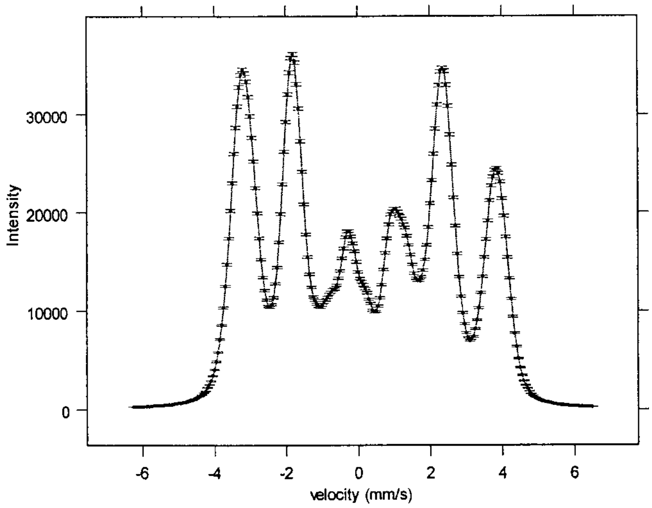

Fig. 3b. Simulated and reconstructed spectra for the distribution shown in Fig. 3a.

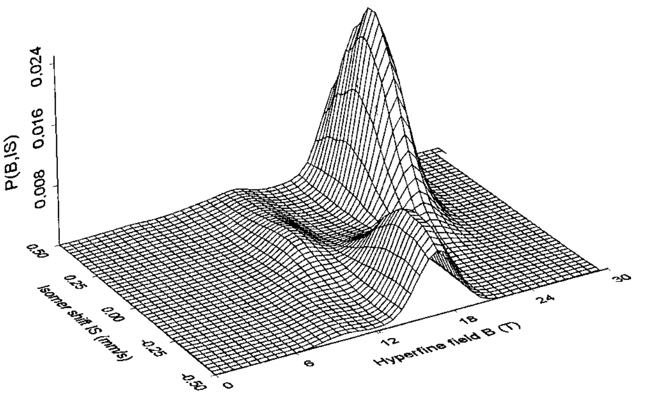

Fig. 3c. Reconstructed distribution from the spectrum shown in Fig. 3b.

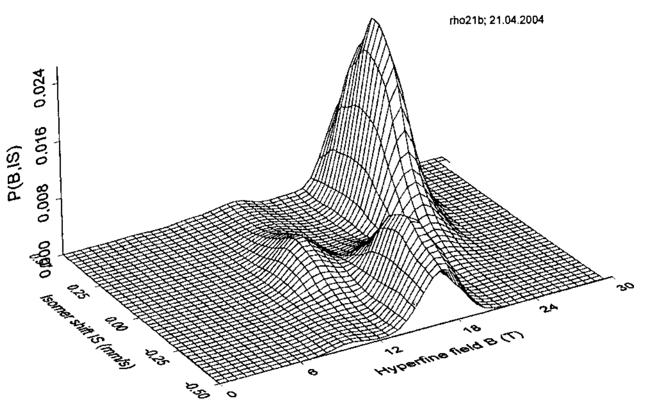

Fig. 3d. Reconstructed distribution from the spectrum with statistics 10 times better than in Fig. 3b.

There is no doubt that the field distribution with a single peak in two-dimensional space B–IS is very well reconstructed (Fig. 2) without any necessity of assuming, e.g., a linear relationship between the two parameters of interest. In the most difficult case studied in this paper, Fig. 3, it is seen that the positions of the peaks are well reproduced. However, the peaks with lower intensities are reproduced with decreasing accuracy: the lower the field, the broader the distribution, so the peak intensity becomes much lower than the originally simulated one. This is not strange in light that MEM is showing the distributions as close to the prior as possible, and the prior was taken homogeneous in all the space. When the statistics in the measured spectrum increases, the reconstruction becomes also better. This is shown in Fig. 3d, which displays the reconstruction from the spectrum with statistics 10 times better than shown in Fig. 3b.

Conclusions

We have checked the feasibility of the maximum entropy method in reconstruction of the hyperfine distribution of field parameters in the Mössbauer spectra. The results turn out to be very promising. The reconstructions made were of high quality, even if the reconstructed and simulated distributions were not identical. We believe that this kind of reconstruction can become an excellent starting point to the interpretation of the measured spectra in physical terms.

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