

PARAMETERIZATION OF MAGNETIC NANOPARTICLES MATHEMATICAL MODEL USING EVOLUTIONARY ALGORITHMS

PARAMETERIZAÇÃO DO MODELO MATEMÁTICO DE NANOPARTÍCULAS MAGNÉTICAS USANDO ALGORITMOS EVOLUCIONÁRIOS

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Abstract: In this paper, the evolutionary algorithms approach is applied to the parameterization of a mathematical model describing the Mössbauer spectra of nanogranular (or nanoparticle) magnetic systems. These systems exhibit physical properties very different from bulk specimens being of great interest for material science and its use as biosensors, magneto sensors, data storage, and magnetic fluids. The purpose of this work is to compare the performance between the Differential Evolution and the Evolutionary Strategies algorithms to optimize the model parameters which best fit the experimental Mössbauer spectra of nanoscale magnetic particles. Spectra of two samples (α - iron foil and NiFe_2O_4 nanoparticles) were recorded, at room temperature, by a conventional Mössbauer spectrometer using a scintillation detector in transmission geometry with a $^{57}\text{Co}/\text{Rh}$ source. Fits to Mössbauer spectra were done using spin hamiltonians to describe both the electronic and nuclear interactions; a model of superparamagnetic relaxation of two levels (spin $\frac{1}{2}$) and stochastic theory; a lognormal particle size distribution function as well as a dependency of the magnetic transition temperature and the anisotropy constant on particle diameter. The evolutionary algorithms have been implemented using Python programming language. For comparison, the two algorithms obey the termination criterion of 6000 evaluations of the objective function. The results presented show the efficiency of these algorithms in the optimization of the parameters and on the fits of the spectra.

Keywords: Magnetic nanoparticles. Mössbauer spectra. Differential evolution. Evolutionary strategies.

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Resumo: Neste artigo, a abordagem de algoritmos evolutivos é aplicada à parametrização de um modelo matemático que descreve os espectros Mössbauer de sistemas magnéticos nanogranulares (ou de nanopartículas). Esses sistemas exibem propriedades físicas muito diferentes das amostras de dimensões muito maiores, sendo de grande interesse para a ciência dos materiais para uso em biossensores, sensores de magneto, armazenamento de dados e fluidos magnéticos. O objetivo deste trabalho é comparar o desempenho entre os algoritmos de Evolução Diferencial e de Estratégias Evolutivas para otimizar os parâmetros do modelo que melhor se ajustem aos espectros Mössbauer experimentais de partículas magnéticas em nanoescala. Espectros de duas amostras (folha de ferro- α e nanopartículas de NiFe_2O_4) foram gravados, à temperatura ambiente, com um espectrômetro Mössbauer convencional, na geometria de transmissão, utilizanso-se um detector por cintilação e uma fonte de $^{57}\text{Co/Rh}$. Ajustes dos espectros Mössbauer foram feitos utilizando-se hamiltonianos de spin para descrever ambas as interações, eletrônicas e nucleares; um modelo de relaxação superparamagnéticas de dois níveis (spin $\frac{1}{2}$) e teoria estocástica; uma função distribuição lognormal de tamanho de partículas bem como uma dependência da temperatura de transição de fase magnética e da constante de anisotropia com o diâmetro da partícula. Os algoritmos evolucionários foram implementados utilizando-se a linguagem de programação Python. Para comparação, os dois algoritmos obedecem ao critério de terminação de 6000 avaliações da função objetiva. Os resultados apresentados mostram a eficiência desses algoritmos na otimização dos parâmetros e ajuste dos espectros.

Palavras-chave: Nanopartículas magnéticas. Espectros Mössbauer. Evolução diferencial. Estratégias evolucionárias.

1 INTRODUCTION

Magnetic materials and their devices represent a market of over 150 billion dollars each year (GUIMARÃES, 2005). As a result, it is a very intense research field. The magnetism of materials is one of the most fertile and active basic research fields of physics, not only for its technological and economic importance but because of the immense diversity of phenomena (GUIMARÃES, 2005).

From several technological applications, we can highlight the use of nanoscale magnetic particles in high-powerful magnets, soft magnetic materials with low energy loss, and new systems for the production of magnetic microsensors. Besides, there are plenty of other applications, existing or under development, such as pigments in paintings and ceramics, medical diagnosis, catalysis, magnetic fluids for targeted delivery of drugs in living organisms, and the use as a non-toxic insecticide (DORMANN; FIORANI, 1992; AGUILAR *et al.*, 2014). These particles are the basis of granular magnetic systems, which may be present in the forms of solid grains (ferrites), ferrofluids, and magnetic thin films. Due to the inherent nanostructure complexity, its response to external excitation is extremely difficult to model and predict. Their study generally involves several experimental techniques as Mössbauer spectroscopy, transmission electron microscopy, X-ray diffraction, magnetization, and magnetic susceptibility measurements.

In this paper, we propose an automated search for optimal fitting parameter values of Mössbauer line shape for ferrites and ferrofluids based on the model proposed by Pfannes and Dias Filho (FILHO, 2001; PFANNES *et al.*, 2001b; PFANNES *et al.*, 2001a).

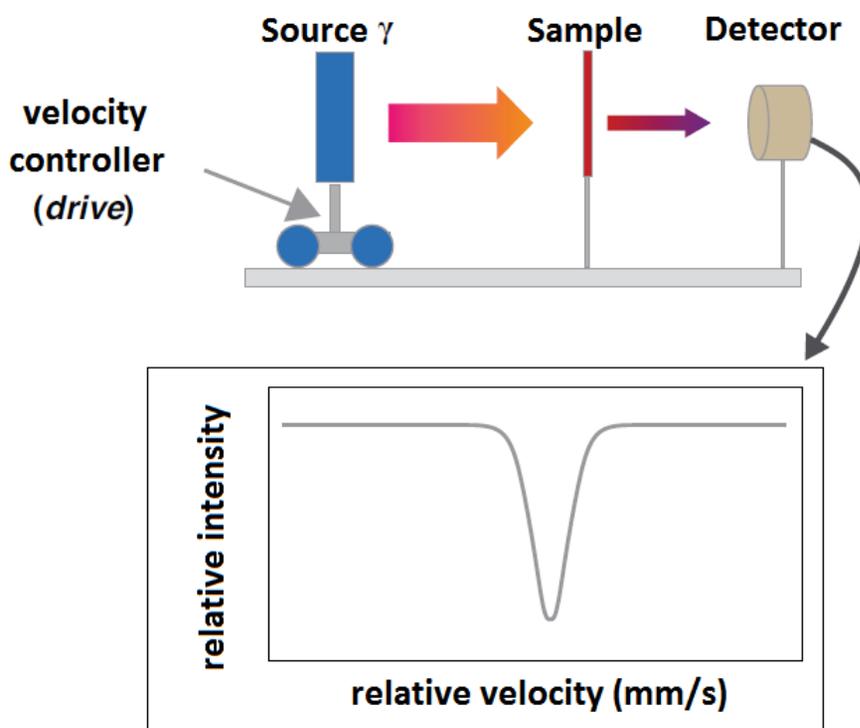
The paper is organized as follows. In section 2, the basic features of Mössbauer spectroscopy are introduced. Section 3 describes the mathematical model for the Mössbauer spectra simulations of ferrites and ferrofluids. In section 4, characteristics of evolutionary algorithms used in the model parameterization are identified. Section 5 presents the obtained results. Finally, we made conclusions and proposals for future works in section 6.

2 THE MÖSSBAUER EFFECT

The Mössbauer effect (nuclear resonance emission or absorption of gamma rays, recoilless) was discovered by Rudolf Mössbauer in 1958. Its main application is in Mössbauer spectroscopy, a very sensitive technique used to study hyperfine interactions (GOLDANSKII; HEBER, 1968; YOSHIDA; LANGOUCHE, 2013). This nuclear gamma resonant spectroscopy can be used to study a high number of phenomena based on the shift and splitting of nuclear energy levels and has been intensively used in several areas of scientific research. The wide

range of applications of this technique lies in their high accuracy (it gave an energy resolution better than 1 in 10^{13}) combined with their relative experimental simplicity and robustness. The main purpose of this article is to find good values for a set of parameters and fit the theoretical model to the experimental spectra.

Figure 1: Scheme of a typical experimental arrangement for Mössbauer spectroscopy and a sketch of a transmission spectrum.



Source: (PIRES, 2014).

The Mössbauer experiment, on the called transmission geometry, consists of drawing a curve of radiation transmitted through the sample to be studied as a function of the relative velocity between the source and the sample, as illustrated in Fig. 1.

3 MATHEMATICAL MODEL

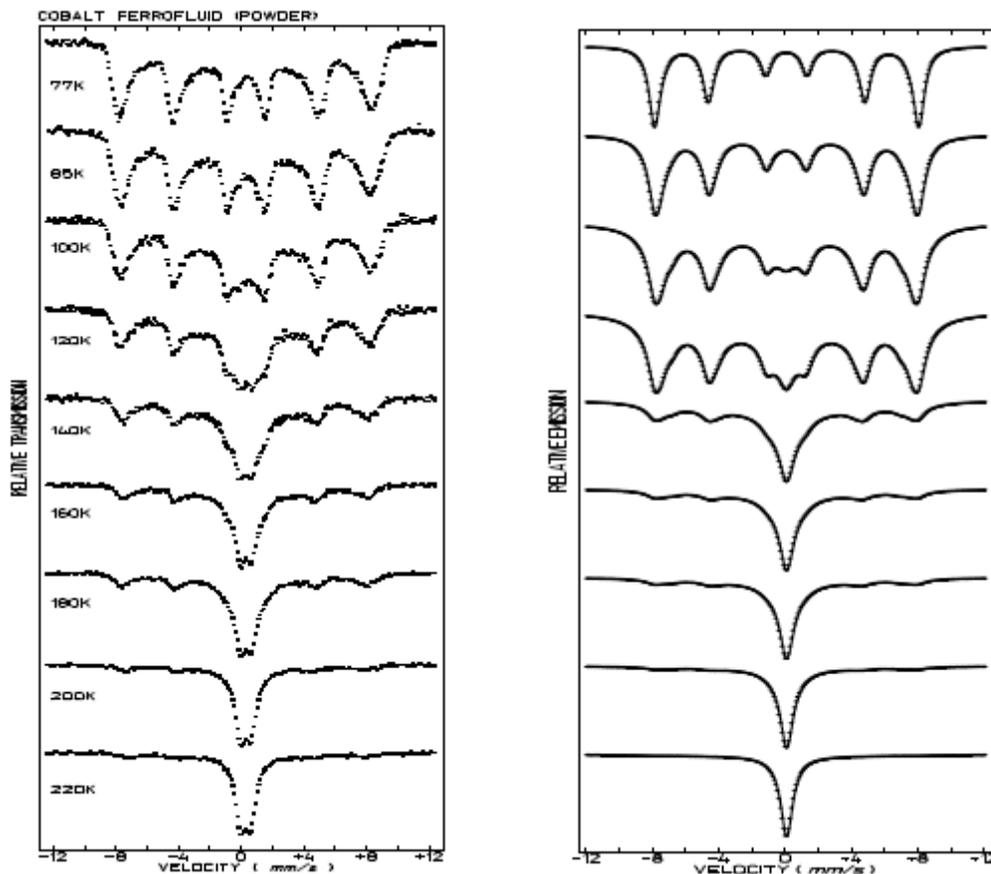
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In some cases, depending on the complexity of the spectrum to be fitted (e.g., relaxation effects, particle size distribution (MØRUP, 1981), available commercial programs for fitting Mössbauer spectra are not suitable, and in this case, a new model must be developed.

In our case here, we implemented a theoretical model with FORTRAN 90, using the IMSL subroutines package, available in some FORTRAN compilers. It includes a model of superparamagnetic relaxation (CLAUSER; BLUME, 1971), as well as a lognormal distribution of particle size (MØRUP, 1981). For more complex spectra line shapes, a dependence of the magnetic transition temperature and the magnetic anisotropy constant on the particle diameter must also be considered. It allows the variation of an extensive list of parameters and uses some static hyperfine parameters obtained from the literature.

In a simulation process, the parameters of the model are modified, generating a new spectrum each iteration. Without automatic control, like a fitting routine, it is almost impossible to find a good set of parameters due to the difficulty of performing an extensive search into space of possible values. Therefore, a proper evaluation of the model is not possible, as it often does not achieve a good match between experimental and theoretical spectra, as can be seen in Fig. 2.

Figure 2: Spectra cobalt ferrite (powder), CoFe_2O_4 , $d_0 = 4.3 \text{ nm}$ (left). Spectra obtained in the simulations (right)



Source: The authors.

4 EVOLUTIONARY ALGORITHMS

To automate the choice of the model parameters, we used two evolutionary algorithms with exciting features regarding the studied problem: The Differential Evolution (DE) and Evolution Strategies (ES) algorithms (BARBOSA, 2017).

4.1 Differential Evolution

The DE algorithm was developed by Price and Turn in 1995 (PRICE; STORN, 1995) for use in optimization problems. Among the main features we can mention (CHENG; HWAN, 2001):

- It is a stochastic search algorithm, originated from the mechanisms of natural selection;
- The algorithm is simple and easy to understand, with few control parameters to drive the optimization;
- It is effective to solve optimization problems with discontinuous objective function because it does not require information about the derivative;
- It is more robust to local optima; because it searches the global optimum solution manipulating a population of solutions, i.e., explores different regions in the search space.

The DE is based on population. Typically, the initial population is generated randomly and has a fixed size through the entire algorithm execution. This population is subjected to mutation, crossover, and selection operators.

The mutation process consists of generating new individuals, denoted modified vectors or donors, by adding the weighted difference between two random individuals in the population to a third individual.

In the crossover, the variables of an individual donor are mixed with the variables of a randomly chose individual (denoted target vector), resulting in the so-called experimental vector.

If the experimental vector represents a better solution than the target vector, it replaces the target vector in the next generation. So it is the selection process.

These operators are applied until a stopping criterion is reached, e.g., runtime or quantity of function evaluations.

4.2 Evolution Strategies

The ES was developed in the 60s, being focused on solving continuous parametric optimization problems. The first version, in which a parent generates a single downward (asexual), and they compete for survival, is known as (1+1)-ES (RECHENBERG, 1965; SCHWEFEL, 1975).

In this work, we used the version $(\mu + \lambda)$ - ES, where only μ selected individuals survive in the population composed of the current μ individuals and λ new generated individuals. In ES, the individual is represented by a vector $v = (x, \sigma)$ where x represents the search point and σ a vector of standard deviations used in the individual mutation process. This is a crucial feature of ES, which allows the self-fitting of its parameters.

Following the summarized algorithm of the version $(\mu + \lambda)$ - ES is presented:

- 1) initialize parent population: Is generated at random a population of μ individuals;
- 2) evaluate the fitness of each individual;
- 3) generate λ offspring forming the offspring population:
 - a) Select (randomly) two parents from the parent population;
 - b) Recombine the selected parents to create a recombinant individual;
 - c) Mutate the standard deviations set of the recombinant;
 - d) Mutate the search point set of the recombinant using the mutated standard deviations set;
- 4) evaluate the fitness of each individual in the offspring population;
- 5) select a new parent population: The μ best individuals of the offspring population, together with the parent population, are selected to form a new parent population;
- 6) goto 3 until termination criterion fulfilled.

5 RESULTS AND DISCUSSION

To evaluate the parameterization performance of the algorithm, we applied the DE and ES algorithms in the fitting procedure of the room temperature Mössbauer spectra for two samples: α - ^{57}Fe , the standard calibration Mössbauer spectrum, and a nickel ferrite powder. The spectrum of the second sample shows fast relaxation effects. All experiments involved in this work were carried out in the Physics Department, Federal University of Minas Gerais.

The experimental calibration spectrum, in which the sample is a foil of α - ^{57}Fe or α -iron foil, had the following fitted parameters: quadrupole splitting (Δ), A/g and A/e (related to the hyperfine field), the effect [EF(%)], the isomer shift (δ), the line width (Γ).

The experimental spectrum with fast relaxation, in which the sample is composed of NiFe_2O_4 nanoparticles, shows the collapse of the hyperfine magnetic field, typical of superparamagnetic relaxation in ferrite nanoparticles. X-ray diffraction suggests an average particle diameter of 5 nm for the nickel ferrite sample. The Mössbauer spectra for this sample was fitted considering the particle diameter and two sites, A and B, for the Fe^{3+} ions in the structure (hyperfine field 490 kOe and 515 kOe, respectively, at 4.2 K). The following parameters were fitted: the effect [EF(%)], the isomeric shift (δ), the line width (Γ), a constant related to the relaxation rate (FTR).

The evolutionary algorithms have been implemented using Python programming language. For comparison, the two algorithms obey the termination criterion of 6000 evaluations of the objective function. Each algorithm has been executed 30 times.

The parameterization problem is treated as a problem of minimizing the measure of the Root Mean Square Error, RMSE, of the points of the theoretical spectrum obtained by the model, compared to the experimental spectrum. Table 1 summarizes the results obtained by each algorithm for each studied spectrum. The values listed in Table 1 express the RMSE obtained by algorithms for the better and worse solutions, as well as for the median, mean, and standard deviation obtained over 30 runs. Based on these values, the performance of each algorithm was evaluated.

Table 1: Summary of results. Values express the RMSE in each case.

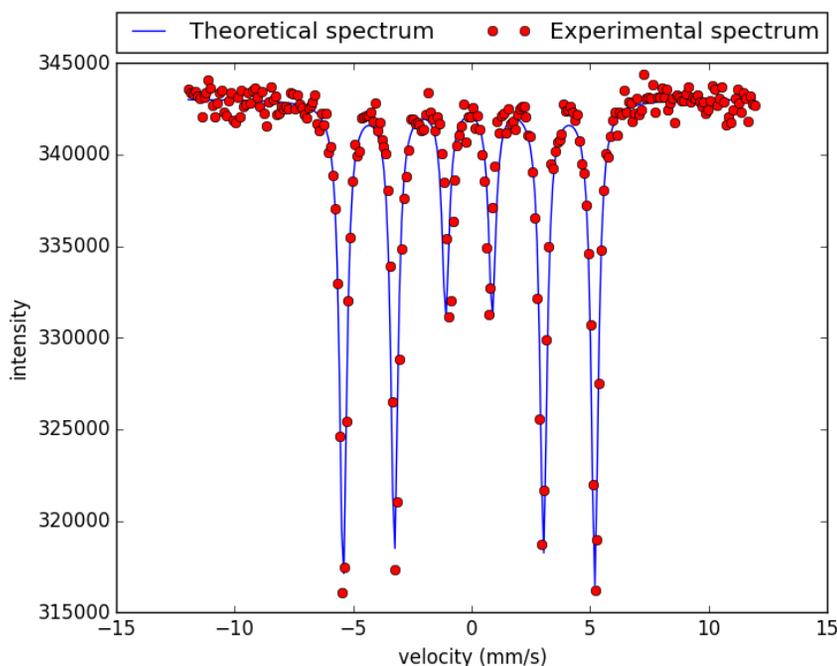
Solutions Resolution	Static Spectrum		Spectrum with fast relaxation	
	DE	ES	DE	ES
Best Solution	456.6717	456.7087	2218.4804	2219.3543
Worse Solution	3399.5198	3359.3983	5776.4215	4577.4786
Median	949.4141	474.0593	3145.5840	2254.9012
Mean \pm	1192.8597	862.1968	3559.7883	2368.3086
Standard deviation	± 743.1461	± 785.4515	± 1157.9140	± 416.4762

Source: The authors.

Normality tests indicate that for all samples, the results belong to a normal distribution. For this reason, we used the Student t-test, a parametric statistical test (CRAMÉR, 1946), with a 5% significance level to verify the statistical difference between the results obtained by the two tested algorithms. For the first experiment, fitting on the calibration spectrum parameters, the t-test showed no statistically significant difference between the results of the two algorithms,

although there is a difference in mean and median values, pointing to an outperformed ES algorithm. In the second experiment, the ES algorithm, averaging 2.368.3086, achieved a better performance than DE. It is worth mentioning that even the ES algorithm has presented similar performance to the DE algorithm, the best solutions were reached with the DE algorithm, and therefore both algorithms show good performances to get the parameters of the studied model.

Figure 3: Fit on the Mössbauer calibration spectrum for α - ^{57}Fe (alpha-iron), at 300 K.



Source: The authors.

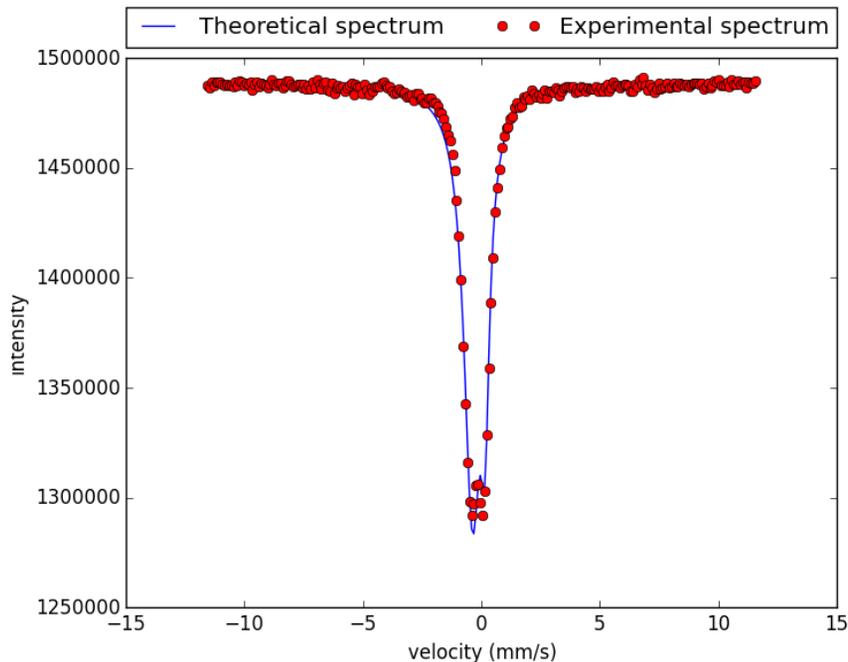
Figures 3 and 4 present the fitted spectra obtained by the model showing good agreement with the experimental spectra. Table 2 shows the parameter values used for the fitting. These values were obtained using the DE algorithm, which presented the best solution in the experiments.

Table 2: Summary of results. Values express the RMSE in each case.

Static Spectrum		Spectrum with fast relaxation			
Sub Spectrum 01		Sub Spectrum 01		Sub Spectrum 02	
Δ	0.004211	FTR	6.7044	FTR	6.7044
A/g	-657.9269	δ	-0.3785	δ	0.1574
A/e	-667.8075	Γ	0.8429	Γ	0.4223
δ	-0.1118 EF(%)	3.7650	EF(%)	0.1375	
Γ	0.3407				
EF(%)	0.0789				

Source: The authors.

Figure 4: Fit on the Mössbauer fast relaxation spectrum (NiFe_2O_4 nanoparticles at 300 K).



Source: The authors.

6 CONCLUSIONS

One of the great difficulties in the development of mathematical models, especially complex systems like the nanogranular magnetic, is to determine the best values to their parameters. In the method commonly used, the parameter values are manually changed by the researcher, who verifies the impact of this change on the model output. However, this method is inadequate since the search space is usually not well explored. To alleviate this difficulty this article proposed the parameterization model using evolutionary algorithms DE and ES.

The results showed that it is feasible to fit Mössbauer spectra using these algorithms, producing good output by the model. Future work includes the application of evolutionary algorithms in the simulation of more complexes Mössbauer spectra and, from our initial set of results, verify the possibility of improvements to the model.

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