ISSN 1330–0016
CODEN FIZBE7

USE OF MONTE CARLO METHOD WITH SIMULATED ANNEALING ALGORITHM IN THE ANALYSIS OF MÖSSBAUER SPECTRA

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Received 29 March 2001;
Accepted 24 September 2001 Online 25 May 2002

A convenient and robust procedure for Mössbauer analysis based on Monte Carlo method is described. The method uses simulated annealing approach to find the optimum Mössbauer parameters in the Lorentzian profile as initial values for the Monte Carlo search program. A succession of solutions to the function describing the spectrum is then randomly generated until the solution with the minimum chi-square with respect to the experimental data is reached. The result having the reduced chi-square close to 1 shows the validity of the method.

PACS numbers: 05.10.Ln, 33.45.+x UDC 539.166

Keywords: Monte Carlo method, simulated annealing, global optimization, Mössbauer spectra

1. Introduction

The method presented in this paper concerns the Monte Carlo computation of a given Mössbauer spectrum and compares it with the experimental spectrum to find the best fit. For the theoretical computation, we express the spectrum in the Lorentzian line shape. For each line component, I, we assume [1]

$$I = \frac{A_j}{1 + [(x_i - P_j)/B_j]^2}\,, \tag{1}$$

where A_j, P_j and B_j are the height, the position and the half width at half maximum, respectively, for the j^{th} peak, and x_i is the i^{th} channel. Equation (1) leads to

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the expression for the total spectrum of n peaks and a count channel y_i such that

$$y_i = E + Fx_i + Gx_i^2 + \sum_{j=1}^{n} \frac{A_j}{1 + [(x_i - P_j)/B_j]^2}\,, \tag{2}$$

where E, F and G are the parameters for non-linear background. The quadratic background is of instrumental origin, mainly due to the periodical change of the detector solid angle during the movement of the transducer. The summation represents the sum of n Lorentzians.

The method proceeds iteratively starting from the solution to Eq. (2) in terms of optimum values of the peaks parameters, which are provided by simulated annealing algorithm (SAA), and generates a succession of solutions tending to the one that is consistent with the experimental data. The concepts of annealing in a combinatorial optimization were first introduced, in the early 1980's, by Kirkpatrick, Gelatt and Vecchi [2], and independently by Cerny [3]. These concepts are based on a strong analogy between the physical annealing process of solids and the problem of solving large combinatorial optimization problems. Pursuing this analogy, SAA is introduced as a stochastic method to avoid getting stuck in local, non-global minima, when searching for global minima [4]. A strong feature of this algorithm is that it finds high-quality solutions, which do not strongly depend on the choice of the initial solution, i. e., the algorithm finds the global minima by the currently tested point rather than the point which has initially been chosen. This feature enables the Monte Carlo search program to start with good initial values and thus the user can avoid conducting several trials, which have been necessary for setting suitable initial values.

In this paper, we use SAA with the modifications made by A. Corana et al. [5] and Goffe et al. [6] to obtain the parameters that will give a "best fit" to the experimental observations. We define the "best fit" in a least-squared sense, and look for those parameters which minimize the function χ^2, defined by

$$\chi^2 = \sum_{i=1}^{m} \frac{1}{y_i}[y(x) - y_i]^2\,, \tag{3}$$

where $y(x)$ is the experimental value, y_i is the calculated (theoretical) data, i is number of experimental measurements and m is the number of channels in the data collection system.

In each step of the algorithm search for the global minima, a trial point is randomly generated. The search process follows the path (the direction along which the trial points are generated) and moves both uphill and downhill to accept or reject the point. Any downhill step is accepted and the process is repeated from this new point. The uphill step is also accepted with a certain probability known as "Metropolis criterion" [7–8]. In this way, the search procedure 'escapes' from the local minima to the global (or near-global) minima.

2. *Description of the procedure*

2.1. *Simulated annealing algorithm*

SAA starts at some 'high' value of the control parameter, C, and a sequence of solutions S_i, with $i = 1, 2, 3, \ldots$, is generated until their average value of the cost function, χ^2, reaches a stable value. The step length is then adjusted and the best solution reached for this value of C is recorded as $S_{\rm opt}$. C is then carefully reduced until the termination criteria are met. The following steps explain how the algorithm proceeds:

(i) Set the initial value of the control parameter (C_0), the initial value of step length vector (L_s), the number of iterations before the control parameter reduction ($N_{\rm itr}$), the number of cycles before the step length adjustment (N_s), the value for termination criterion (ϵ_s), the control parameter reduction factor (α) and the starting values of the height (A_j), the peak position (P_j) and the half width at half maximum (B_j) of each peak in the spectrum.

(ii) Calculate the baseline.

(iii) Find the solution, S_j, to Eq. (1) in terms of A_j, P_j and B_j. Incorporating the baseline (as in Eq. (2)), find the corresponding χ^2 value according to Eq. (3).

(iv) Set $S_{\rm opt} = S_j$ and $\chi^2_{\rm opt} = \chi^2_j$.

(v) Generate a new solution, S'_j, with randomly selected values for the peak parameters by setting $A = A_j + RL_s$, $B = B_j + RL_s$ and $P = P_j + RL_s$, where R is a random number generated in the range [-1,1] by a pseudorandom number generator, and then calculate $\chi^{2\,\prime}_j$.

(vi) If $\chi^{2\,\prime} \leq \chi^2_j$, accept the solution S'_j. Set $S_j = S'_j$ and $\chi^2_j = \chi^{2\,\prime}_j$. If $\chi^{2\,\prime}_j > \chi^2_j$, use Metropolis criterion to decide on the acceptance or rejection of S'_j. That is, accept the solution with the probability p given by

$$p = \exp\left(\frac{\chi^2_j - \chi^{2\,\prime}_j}{C}\right) > R\,.$$

If the solution is accepted, set $S_j = S'_j$ and $\chi^2_j = \chi^{2\,\prime}_j$. Otherwise, this indicates that the solution lies outside the χ^2 domain, reject it and choose another one for the function evaluation.

(vii) If $\chi^{2\,\prime} < \chi^2_{\rm opt}$, set $S_{\rm opt} = S'_j$ and $\chi^2_{\rm opt} = \chi^{2\,\prime}_j$.

(viii) To widely sample the function, adjust L_s so that, approximately, half of the evaluation will be accepted.

(ix) Check whether the termination criteria are met. That is, if the final χ_j^2 values of the last iterations for each control parameter reduction differ from χ_j^2 at the current control parameter by less than ϵ_s, and the final χ_j^2 value at the current control parameter also differs from the current optimum χ_j^2 value by less than ϵ_s, report the optimized solution, S_{opt}, and its corresponding A_{opt}, P_{opt} and B_{opt}. If the termination criteria are not met, prepare for another loop by staring on the best current optima. Reduce C by an appropriate factor, α, and go to step (v) until convergence.

2.2. Monte Carlo method

If the values obtained from SAA are not optimal, as they usually are, good near-optimal values will then be obtained [5]. Whatever the case, generation of further solutions is required in order to get the best one. The following steps explain this point as follows:

(i) Use the optimal values A_{opt}, P_{opt} and B_{opt} resulting from SAA to calculate the theoretical spectra (recorded as y_k) according to Eq. (2) and calculate the corresponding χ_k^2.

(ii) Generate a sequence of random solutions, y_{k+l} (with $l = 1, 2, 3, \ldots$), around y_i. Calculate the χ_{k+l}^2 value corresponding to each solution.

(iii) Sort the theoretical data according to χ^2 values. Stop the program at a value ϵ_m, which is low enough that no further useful improvement can be expected, that is, when $\left| \dfrac{\chi_{k+l}^2 - \chi_{k+l-1}^2}{\chi_{k+l}^2} \right| \le \epsilon_m$.

(iv) Print the theoretical data, which belongs to the best χ^2 value (the smallest one).

3. Results and discussion

The method was applied to a simple Mössbauer spectrum of α-Fe, where the peaks are well resolved and their number is known: nine peaks appear in the spectrum presented in this paper. The plot of the computed spectrum and the experimental one is shown in Fig. 1. For the program execution, the following values of input parameters were used:

$$C = 100, \quad \alpha = 0.85, \quad \epsilon_s = 10^{-5}, \quad \epsilon_m = 10^{-6}, N_{\text{itr}} = 5, \quad N_s = 20.$$

The parameter ϵ_s was set to ensure that the solution had converged to the global minima, while ϵ_m was chosen to get the difference of successive χ^2 values that is sufficient to stop the calculation. As the search algorithm proceeds, the searched area is restricted to a suitable range by setting upper and lower bound values for

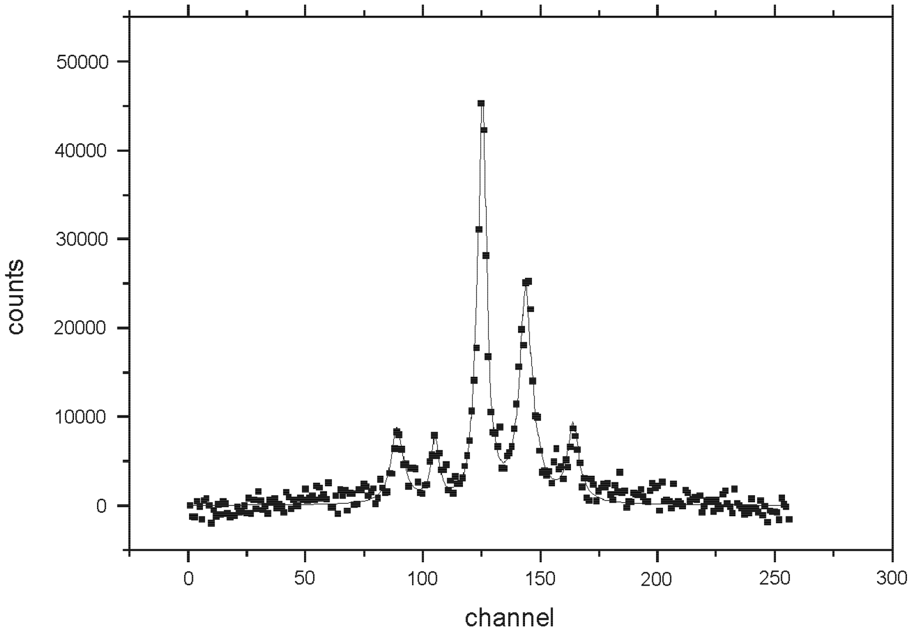

Fig. 1. Plotted output of Monte Carlo sum to nine Lorentzians (line) and experimental spectrum (squares).

TABLE 1. Result of simulated annealing.

Optimal chi-squired value (reduced)	1.43
Number of function evaluations	162001
Number of accepted evaluations	81020
Final value of C	0.304E-06
Step length	O(E-4)
Number of out of bound evaluations	0

the peak parameters. This restriction forces the algorithm to search only the region of interest so that very large values (which may cause floating-point errors) or very small values (which may not allow a complete search of the function) should not be run through the statistical function χ^2. Table 1 shows the result obtained by simulated annealing. Almost half of the function evaluations is accepted. This ensures that the step length vector is correctly adjusted and the function is widely investigated. Before the search procedure reaches the optimal values, a large number of intermediate results with different step length values are executed to give a valuable information about χ^2. Table 2 shows two steps from these intermediate results (from more than 150); the first step and the last step before using simulated annealing subroutine. The step length starts with a large value to give an approximate estimation of the function χ^2, and accordingly, most of the moves are accepted. As the control parameter C declines, the step length decreases and the calculation is focused on the most promising area.

TABLE 2. The intermediate result from SAA.

	Intermediate results	
	First step	Last step
Current value of C	100.0	0.3419E-6
Min function value so far	3.54	1.463
Total moves	900	900
Downhill	453	363
Accepted uphill	396	66
Rejected uphill	51	471
Step length	4.0	O(E-4)-O(E-5)
Trails out of bounds	0	0

The optimal solution given by SAA is quite useful for this method since only few solutions (21 in our case) need to be performed by Monte Carlo search for the best computed spectrum. Perhaps this is also useful for some other fitting procedures where good initial values are recommended. The constraints among the parameters can be easily applied without affecting smooth running of the program. The ability of the SAA to identify corner solutions for functions that do not exist in some regions [6] gives the possibility for finding the peak(s), if any, that was (were) not included in the computations.

The major limitation of this method is that it is costly in terms of function evaluations, i.e., to reach the global optima, C should be decreased slowly. This is a lengthy, time consuming process. However, the execution time can be minimized by an appropriate choice of α and N_{itr} prior to the calculation. Coupled with the rapid increase of computer power, this limitation will no longer affect the method and its applicability with regards to the computation time.

4. Summary and conclusion

We have applied the Monte Carlo method to analyze Mössbauer spectra. The application shows that SAA can be effectively used to Mössbauer analysis and offers a viable way of optimizing functions fit to Mössbauer data. The method is convenient for its simplicity and general applicability because no specific information about the function to be optimized is needed prior to application. Coupled with the fact that SAA is capable to optimize difficult functions (with large number of parameters), this procedure may also be used to analyze other profiles that describing Mössbauer spectra. The source code is written in Fortran and is available from the authors.

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PRIMJENA MONTE CARLO METODE S ALGORITMOM SIMULIRANOG OPUŠTANJA U ANALIZI MÖSSBAUEROVIH SPEKTARA

Opisujemo pogodan i snažan postupak za analizu Mössbauerovih spektara zasnovan na Monte Carlo metodi. Primjenjuje se pristup simuliranog opuštanja za nalaženje najpovoljnijih parametara Lorentzovih profila Mössbauerovih spektara koji su početne vrijednosti za Monte Carlo program traženja. Zatim se nasumice stvara niz rješenja za funkciju koja opisuje spektar dok se ne postigne rješenje koje je u najboljem skladu s eksperimentalnim podacima. Postignuti ishod je u dobrom skladu s mjerenim spektrom, što pokazuje vrijednost metode.