Communication

Analysis of extended X-ray absorption fine structure spectra using annealing evolutionary algorithms

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An annealing evolutionary algorithm (AEA), which combines aspects of genetic algorithms and simulated annealing, is proposed to find the global minimum of a non-linear least square function for spectral fitting. By application of the algorithm to the fitting of structural parameters from experimental extended X-ray absorption fine structure (EXAFS) spectra of two Cu samples, it was found that reasonable results were obtained. Comparing with genetic algorithms and EXCURVE88, the AEA method is faster and more accurate in analysis of EXAFS spectra.

A simulated annealing algorithm (SAA) is a stochastic optimization method based on the Monte Carlo importance-sampling technique.[1] It starts from an initial point and takes a single point iterative strategy. The mechanism that it can accept not only the evolved but also the degenerated solutions with the Metropolis acceptance criterion during its annealing procedure, allows the SAA the potential to find the global minimum instead of falling into the local optima. As a global optimization algorithm, the SAA has been widely used to fit non-convex cost-functions arising in a variety of problems, such as the fitting of curves,[2] conformation analysis,[3] the analysis of atom–atom interactions[4] and the optimization of molecular clusters.[5] A genetic algorithm (GA) is another global optimization method which starts from an initial population and allows evolution by selection, recombination and mutation.[6–8] Compared with the SAA, the GA knows more about the explored areas of the whole space. In this paper a new algorithm combining aspects of population, selection and the simulated annealing procedure is proposed, named annealing evolutionary algorithm (AEA). Therefore the AEA has a larger possibility to escape from local optima than the SAA. Moreover, an improved SAA including a heating procedure for the determination of initial temperature and a local search procedure was implemented in the AEA.

Extended X-ray absorption fine structure (EXAFS) has been extensively used as a useful tool in structural studies in recent years.[9,10] Generally, standard sample comparison and least square curve fitting methods[11,12] are used to obtain structural information from EXAFS oscillation, such as EXCURVE88 by the RC Daresbury laboratory in the UK.[11] However, similar standard samples and reasonable initial parameters are needed in the analyzing procedures. Therefore, in our previous studies, the wavelet transform was introduced to process the EXAFS signal[13] and also the GA was used to analyze the EXAFS spectrum.[14] In this work, the AEA is applied to analyze the structural parameters from the EXAFS oscillation. It was completed by finding the global maximum fit of the experimental EXAFS spectra with their theoretical spectra starting from random initial parameters. EXAFS spectra of two Cu samples were investigated. The results showed that the fitting error is smaller than for the GA[14] and EXCURVE88[11] methods and the structural parameters obtained are reasonable.

Methods

Annealing evolutionary algorithms

In order to guide the searching procedure to effectively fine the global optimum and escape from the local optimum, simulated annealing algorithms should allow some knowledge about the whole search space to be obtained from the explored results. This has been implemented in the AEA by an evolutionary strategy based on the idea of population and selection. The AEA improves the population of candidate solutions by mutation and selection operation instead of the single point iterative strategy used by the SAA. The algorithm includes three parts: (1) the heating procedure to determine the initial temperature, (2) the annealing procedure to obtain the optimized solution, (3) the local searching procedure to obtain the best solution in which the annealing procedure is the key part, and the heating part is similar to the annealing part except for the acceptance criterion, *i.e.*, only the state with higher energy can be accepted. The whole procedure of the AEA used in this study can be described by the following steps in Fig. 1.

(1) Initialize the population and do the heating procedure; the results of temperature and population will be used as the starting point of the annealing procedure.

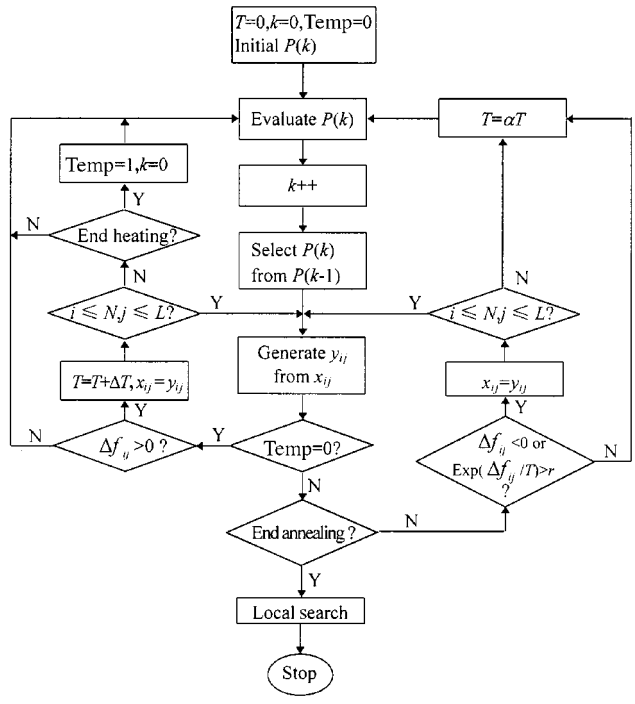

Fig. 1 Flow chart of the AEA.

(2) Start the annealing procedure with the initial temperature and population, and evaluate each individual of the population using an objective function.
(3) Select a new population from the previous one based on the fitness evaluated.
(4) Generate new solutions for each individual of the population which will be accepted or not according to the Metropolis criterion, and evaluate the new solutions.
(5) Decrease the temperature and return (3) until the termination criterion is satisfied.
(6) Do a local search to improve the final best solution.

In Fig. 1 $P(k)$ represents the population at the kth step, x_{ij} is the ith ($i \leqslant N$) individual in the population at the jth ($j \leqslant L$) step of each Mapkob chain, y_{ij} is a new solution generated from x_{ij}, $f(x_{ij})$ represents the evaluated value of x_{ij}, Δf_{ij} is $f(y_{ij}) - f(x_{ij})$, T_0 is the initial temperature evaluated by the heating procedure, α is the decreasing rate of temperature used in the annealing procedure, r is a real random number in [0,1], ΔT is the temperature increment in heating procedure and Temp is used to control the heating (Temp = 0) or annealing (Temp = 1) procedure.

For a given point x, the new solution y is generated by eqn. (1):

$$\begin{cases} x + r\psi(k, \mathrm{UB} - x) & \text{random} = 0 \\ x - r\psi(k, x - \mathrm{LB}) & \text{random} = 1 \end{cases} \tag{1}$$

in which r is a random real number $\in[0,1]$, LB and UB are the left and right boundary of the variable respectively. Function ψ is selected as follows:

$$\psi(k,x) = \left[1 - e^{-\left(\frac{k}{K+1}\right)^{\eta}}\right] x \tag{2}$$

where K is the total number of cooling steps and η is a descending parameter. It will return a value in the range (0, x), which will converge to zero along with an increase of k. Therefore the searching neighborhood can be automatically adjusted as the optimization process proceeds, and a local search is made at the end of the algorithms.

Analysis of EXAFS spectrum using the AEA

Based on its basic theory, the theoretical curve of EXAFS can be described by eqn. (3),[9]

$$\chi(k) = \sum_j \frac{N_i}{kr_j^2} |f_j(k)| \, e^{-k^2\sigma_j^2} e^{-2r_j/\lambda} \sin[2kr_j + \varphi(k) + 0.2625 r_j \Delta E_0 / k] \tag{3}$$

where r_j, N_j, σ^j and λ are the structural parameters of the jth coordination shell, representing coordination distance (r), coordination number (N), Debye-Waller factor (σ) and electron mean free path (λ), respectively, $\varphi(k)$ is the phase displacement of scattering, ΔE_0 is used to deduct the effect on the scattering phase displacement caused by the variation of chemical environment, $|f_j(k)|$ is the amplitude of scattering.

The aim for analyzing the EXAFS curve is to obtain the values of r_j, N_j, λ, σ_j and ΔE_0 in eqn. (3). Because the oscillation signal of a differing coordination shell is separated by FT filtering, generally only the five parameters for one coordination shell is considered. In order to use the AEA to optimize the five parameters, random initial values in given ranges were used. The span for parameters r, N, σ, λ and ΔE_0 are bounded respectively as the following: $2.0 \leqslant r \leqslant 3.0$, $8.0 \leqslant N \leqslant 12.0$, $0.0 \leqslant \sigma \leqslant 0.1$, $4.0 \leqslant \lambda \leqslant 10.0$, and $-30 \leqslant \Delta E_0 \leqslant 30$.

According to the least square principle, the objective function that is the fitted error for EXAFS spectrum fitting can be constructed as:

$$\mathrm{FI} = \frac{1}{\mathrm{NPT}} \sum_{i=1}^{\mathrm{NPT}} \left[C_{\mathrm{cal}}^i(k) - C_{\mathrm{exp}}^i(k)\right]^2 \tag{4}$$

in which,

$$C(k) = \chi(k) \times k^3 \tag{5}$$

where NPT is the number of points in the spectra and C_{cal} and C_{exp} correspond to the calculated and experimental spectrum respectively.

The AEA was used to optimize the five parameters by minimizing the objective function as in eqn. (4).

The experimental EXAFS spectra of Cu samples were investigated. The experimental EXAFS spectra were obtained at the EXAFS station of the Beijing Synchotron Radiation Factory (BSRF) on beam 4W1B using an Si^{III} double-crystal monochromator. The computer program was written in C++ language and implemented on a Pentium-266. In all calculations, the population size is 40, the maximum heating step is 60, the maximum cooling step is 200, the length of the Mapkob chain is 30, the temperature declining factor α is 0.93, and the descending parameter η in eqn. (2) is 4.

Results and discussion

Analysis of simulated EXAFS spectrum

In order to investigate the efficiency of the AEA in analyzing the spectrum of EXAFS, an oscillation was simulated by eqn. (3) from given structural parameters. Parameters used in the simulation and the results analyzed by the AEA are listed in Table 1. From Table 1, it is clear that parameters used to construct the simulated spectrum can be accurately obtained using the AEA to minimize the objective function FI as in eqn. (4). The comparison between the simulated spectrum and the fitted spectrum is shown in Fig. 2, and the FI obtained is also labeled in the figure. From both the figure and the value of FI, it can be seen that the fitting is satisfactory.

Analysis of experimental EXAFS spectra

In order to obtain the EXAFS oscillation signal, background removal, Fourier transform and Fourier filtering were con-

Table 1 Comparison between the structural parameters obtained by the AEA and in simulation

Parameter	N	r	σ	λ	ΔE_0
Simulated	8	2.52	0.0800	4.20	10.0
AEA	8	2.52	0.0799	4.16	9.30

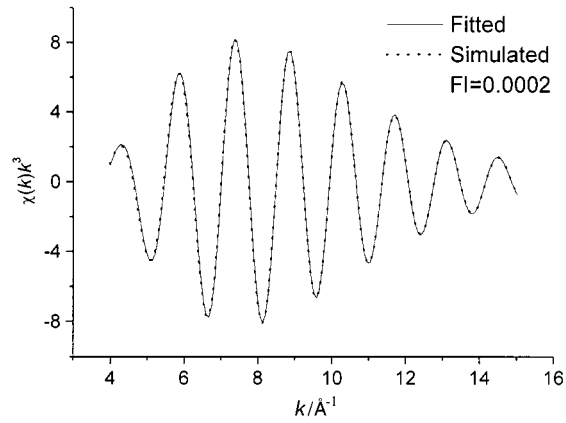

Fig. 2 Comparison between the simulated EXAFS oscillation and the fitted result by the AEA.

Table 2 Parameters of Cu^{I} obtained by the AEA, GAs and EXCURVE88

Parameter	*N*	*r*	σ	λ	FI
AEA	9	2.52	0.0829	4.17	0.0051
GAs	8	2.52	0.0753	4.38	0.0078
EXCURVE88	8	2.49	0.0165		3.2930

Table 3 Parameters of Cu^{II} obtained by the AEA, GAs and EXCURVE88

Parameter	*N*	*r*	σ	λ	FI
AEA	11	2.53	0.0869	4.59	0.0024
GAs	10	2.53	0.0784	4.56	0.0042
EXCURVE88	11	2.49	0.0180		0.0887

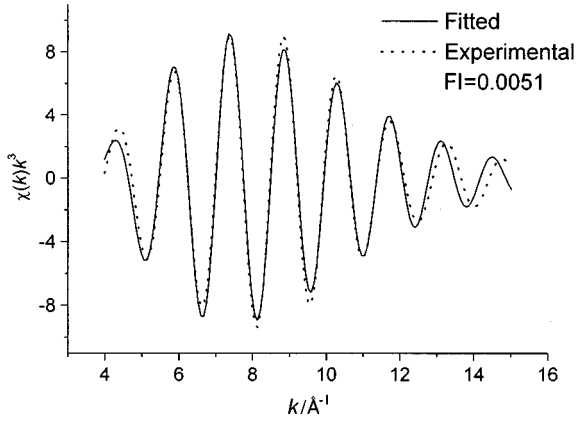

Fig. 3 Comparison between the experimental spectrum of Cu^{I} sample and the fitted result by the AEA.

ducted on the measured spectra. Two spectra of Cu samples were investigated. For comparison, three methods, AEA, GA, and EXCURVE88 were used to analyze the spectra. The results obtained by the three methods for sample I and sample II are listed in Tables 2 and 3, respectively. From both the tables, it can be seen that the value of FI optimized by the AEA was much less than the values obtained by the other two methods, and parameter *r* is well fitted by the three methods; nevertheless the values of parameter σ optimized by the first two methods are much different with EXCURVE88, but is closer to the value reported in ref. 12.

The comparisons between filtered experimental EXAFS oscillation and the fitted results for the two samples are shown in Fig. 3 and 4, respectively. From Figs. 3 and 4, superior fitting between experimental and analyzed spectra can be found.

Therefore the AEA can be used as a useful tool in the analysis of EXAFS spectra, and the advantage of it is that it does not need a standard sample and the results are independent of initial values of parameters.

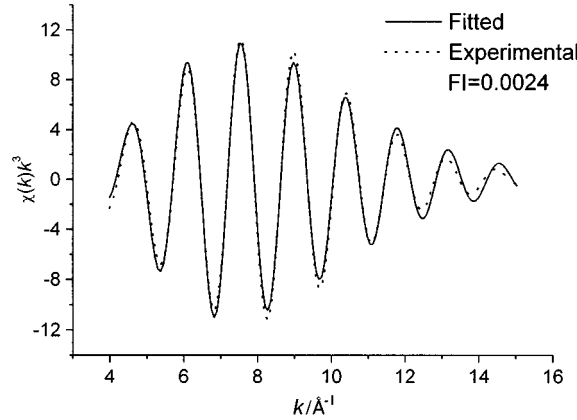

Fig. 4 Comparison between the experimental spectrum of Cu^{II} sample and the fitted result by the AEA.

Acknowledgements

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