

Recent developments of the Reverse Monte Carlo
for POWder diffraction program

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0.1 Introduction

As generally known, single crystals consist of periodic, repeating units in the three dimensional space. This theory was proved almost one hundred years ago by observing distinct Bragg-reflected electromagnetic radiation, whose wavelength is in the order of 10^{-10} meters. The information, which we can obtain by studying the Bragg-peaks are the dimension of the unitcell, orientation of the single crystal by the position of the spots and the *average* unitcell's density map of that particles, which interact with the incoming radiation. This information is very powerful and used on various fields from basic science to engineering.

However, it does not provide any knowledge about short-range order correlations. This piece of information can be gained from relatively weak diffuse scattering, from x-ray absorption edge spectroscopy and in some cases from NMR.

In practice, the number of powder diffraction studies are greater than a magnitude in comparison with single-crystal studies. The reason is simple: it does not need to grow single crystal and the recording time of the diffraction pattern takes much less time. In the powder diffraction pattern, Bragg-reflections appearing as sharp peaks and diffuse scattering as broad waves.

The atomic range modeling of the Bragg and diffuse scattering pattern requires enormous computing power following the naive way. During the years, various atomic simulation procedures were developed to model them or some descended quantities. Within them, Reverse Monte Carlo [1] (in the following: RMC) is that simulation method, which produces consistent set of atomic configuration and experimental data. It reaches this goal by moving or swapping atoms randomly. The atomic models always consist of integer multiply of the unitcell in each crystallographic direction, usually between 6 and 20.

Among RMC simulation methods, RMCPOW [2] is the only one, where all of the fitting procedures performed in the Q-space. Its main idea is the next: reciprocal lattice points of the original unitcell are treated as Bragg-intensities and the remaining points as diffuse intensities. Bragg-contributions are convoluted with the resolution function and diffuse intensities produced by averaging over the space. The main advantage of this method, that it can deal with relatively low Q-range, makes it suitable for laboratory x-ray and traditional reactor based neutron diffractometers, which is available in our laboratory [3].

It has a disadvantage: to extend this method for high-Q range, enormous computational efforts are needed. The information, which we can get from high-Q data are mainly the nearest neighbours correlations. This would be important on the cases, where they are not known from other sources.

One possible way to solve this problem is using x-ray absorption information [4]. If an atom absorbs a photon, whose energy is slightly more than excitation energy of the absorber's shell, it can emit one electron. This photoelectron is able to be backscattered on the surrounding atoms and absorbing again in the absorber atom. This case, a photon emission is able to be taken place. This appears as a secondary effect and can be observed as small modulations on the absorption curve vs. energy. Thus, its name comes from the EXtended Absorption Fine Structure expression. This spectroscopy is element selective (we excite around the absorption edge by x-ray) and sensitive mainly the first neighbours (further order neighbours can be observed, but their contributions are relatively small). The another advantage of this technique, that it can be

done very short time at synchrotron radiation facilities.

0.2 Modeling the EXAFS signal

As it has been shown above, the main component of the EXAFS signal comes from the two-particle correlations. It is mainly sensitive to the small range correlations. Thus it does not have any difference of the data treatment even it would be amorphous or crystalline material. Our starting hypothesis was, that the same method, which is well established for RMC_POT [5] can be implemented in RMCPOW too.

If only the two particle correlations determine the EXAFS signal, the difference of the absorption rate from the background rate normalised by the background rate ($\chi_j(k)$) measured on slightly higher energy than the absorption edge of the "j" type of atom can be written [4]

$$\chi_j(k) = \sum_i \int_{r_{min_i}}^{r_{max_i}} F_i(k) S_j(k) \exp(-2r_i/\lambda_i(k)) \frac{\sin(2kr - \phi_{ij}(k)) g_{ij}(r)}{kr_i^2} 4\pi r^2 \rho_i dr_i, \quad (1)$$

where k is the wave number, i is the index of the backscatterer atom, whose backscattering amplitude is $F_i(k)$. The backscattering is phase dependent and varies with the wave number ($\phi_{ij}(k)$). The other terms are related to the inelastic losses (exponential term) and the change of the original physical state of the absorber atom due to effect of the environment ($S_j(k)$). The partial pair correlation function gives the rate of the local density of the i atoms in a r radius, dr thick shell from a kind of j atom and the average density. The remaining coefficients are needed to transform the pair correlation function into number density.

In practice, the terms of the above presented equation can be separated into two main ones. One is the number density, which can be interpreted by the modeling system. The another term is a transformation function, which shows the EXAFS signal by the function of wave number, when only 1 backscatterer atom is at the distance r . So, formally (1) can be simplified to

$$\chi_j(k) = \sum_i \sum_{r_{min_i}}^{r_{max_i}} A_{i,j}(k, r) 4\pi r^2 \rho_i g_{ij}(r) \Delta r_i. \quad (2)$$

Thus transformation function can be calculated via FEFF [6], which is a commonly used program for backscattering amplitude calculations for EXAFS. Gradually increasing the distance between the absorber and backscatterer atom, saving the result in a structured file, the $A_{i,j}(k, r)$ transformation function becomes ready for use. The pair correlation function is able to be calculated from the atomic configuration.

0.3 Howto fit EXAFS signal in RMCPOW?

Here, we are introducing the required files and control file for EXAFS fit.

0.3.1 Experimental datafile

Here, we do not mention about dataset evaluation procedure, but only the format of the datafile.

The experimental data should consist the next lines:

1st line Number of point

2nd line Comment line

3rd... lines Dataset

The dataset consist of two or three columns. The first variable can be the absolute energy, energy from the absorption edge in eV or the wave number in Å. The second column contains the measured intensities, normalised by the given factor of the wave number. The third column is the experimental error. The step size of the first column should be in correspondance with backscattering amplitude datafile.

0.3.2 Backscattering amplitude datafile

The backscattering amplitudes has several block of datasets. Its format is the following:

1st line Number of atomic types (corresponding to the configuration file: number of blocks), number of data points

For each block 1st line Comment line

Data lines Values of the transformation matrix. The row number corresponds the k, the column number corresponds to r.

To calculate the backscattering signal from FEFF, please find a manual [7].

0.3.3 Description of the changes of the datafile

Here, we describe all of the changes concerning the datafile. Only one line has been modified in the original version of the format: the experimental data fit line, where the number of exafs dataset is inserted between x-ray and single crystal constraints.

```
0 0 1 0 ! nexpn,nexpx,nexafs,nsingle
```

After the x-ray datasets, the EXAFS part is starting. Each experiment consist of two parts: The data part and the transformation related parts. The sample of the former is the next:

```
asse_15i_as_bft_k0.dat !Name of the file
2 2 0 3 !Data format: in / out, weight method: in/out
3.55 3.65 !Valid data range
0 !No. of excluded regions
.000008 3 3.0 !Sigma, error estimation, internal weighting
1 !Number of polinomial background
0.0 !Initial values
0 !To be fitted
```

```
1.0 0 !Normalisation coefficient and its flag
```

It starts with the name of the experimental datafile 0.3.1. The following line specifies the input and output data format. As we shown in 0.3.1, the incoming data can be scaled in absolute energy (0), relative energy from the absorption edge (1) or by the wave number (2). The first number is the input, the second one is the output format. The last two numbers are specifying the coefficient of the wave number, which is/should multiplied the input/output data. Here, the input data scaled in wave numbers and does not multiplied by any factors. The output also in wave number, but it should multiply by k^3 .

The next line is the requested range of the dataset, which should be fit. It is in the unit of the input. There is a possibility to set excluded region, which can be useful in the case of glitches. The following line contains the sigma parameter of the fit, the weighting scheme of the incoming datasets and the internal weighting. The weighting can be read from the third column (1), can be the square root of the experimental data (2) or constant overall the examined range (3). The RMCPOW keeps the original values of the experiment. For the fit, only the weights are modified such a way, that they behaves like the variable has been multiplied by k^x , where x is the internal weighting. In the example, the sigma is the same as all over the range and fitting will be done as both simulated and calculated $\chi(k)$ were multiplied by k^3 .

The following lines are the number of degree of the polinomial background, initial values and refinement flags (1 - fit, 0 -fix). Finally, there is a possibility to normalise the dataset.

The transformation related part looks like the follows:

```
1 !Absorber
0.0 3.4 0.1 !R min/max/step
as_edge.bs.dat !Name of the r->Q datafile
2.001 2.999 !Minimal and maximal limits belong to the 1st partials
2.001 2.999 !Minimal and maximal limits belong to the 2nd partials
2.001 2.999 !Minimal and maximal limits belong to the 3rd partials
```

The first line of this part specifies the absorber type according to the configuration. The next is the r space related parameters: starting, end, and step values. In contrast to RMC_POT, it does not need to fill zeroes and start r from zero, if we specify other values here. The next is the name of the backscattering amplitudes datafile. Finally, the following lines are the low and high limits of each partials which take into account in the calculation.

0.4 Validation and test

Here, I should notice, that compatibility with RMC_POT EXAFS experimental datasets and backscattering datafiles are exist (the reverse is not true). So, our test case was $As_{42.5}Se_{42.5}I_{15}$, which is available as an example of RMC_POT. Only the control file has been created for RMCPOW run, according to the modifications. The RMCP fully reproduced the EXAFS signal of the initial model configuration. Then, with RMCPOW the run continued and stopped at a given time. To validate the goodness of the update part of the program, initial

state calculation performed by RMC_POT. It is reproduced the stopped result satisfactory.

Bibliography

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