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BUILDING PRIOR DENSITIES FOR MAXIMUM ENTROPY REFINEMENT OF X-RAY DATA FOR TOPOLOGICAL ANALYSIS

Ahmad Shuaib*[1], Abdul Waheed Anwar[1], Khurshid Aslam Bhatti [1], Ishrat Mubeen Dildar[1], Qasim Ali Chaudhary[2]

[1]Department of Physics, University of Engineering and Technology Lahore, Pakistan.

[2]Department of Mathematics, University of Engineering and Technology Lahore, Pakistan.

Abstract:

The aim of this research work is to develop a method to provide a reasonable "prior" electron density that can be used in the so-called "Maximum Entropy Method" (MEM) refinement of X-ray diffraction (XRD) data in order to reconstruct experimental electron density at a resolution allowing its accurate topological analysis. A program was developed which build electron density on a regular grid in the "Independent Atom Model" (IAM) approach, more precisely from the knowledge of individual "spherical" atomic scattering factors of the atoms constituting the unit cell of the studied compounds. IAM X-ray structure factors of bismuth and its prior density on a grid has been generated to be tested with the MEM "Enigma" software. Preliminary accuracy and performances have been compared when such reasonable "prior" density is used instead of starting with "flat" density.

Keywords: Electron Density, MEM, XRD, R-Factor

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* Corresponding Author email: ahmadshuaib@uet.edu.pk
Phone Off: 0092-42-99029204

1. Introduction

MEM is a powerful tool used for various crystallographic problems was introduced by Collins [1]. Electron density maximization by refinements and building of the real electron density plays an important role in the crystal structure analysis [2]. The bonding studies can give information of the atomic level properties that can be used for the preparation and growth of materials suitable for specific needs. Studies have been carried out for the electron distribution of important materials like aspherical electron density distribution, synchrotron radiation for the charge density using multipole analysis [3, 4]. In materials precise study of the bonding is always useful and interesting, yet no study can reveal exactly the real picture, because no two data sets of a crystalline system are identical. X-Ray diffraction elaborated the electron density distribution experimentally, however theoretical studies have also been used in crystallography for the application of MEM method to the problems which involve Fourier technique [5]. MEM has also been used to synchrotron powder X-ray diffraction data for the catalytic reduction of NO_x with NH_3 on fully dehydrated CHA-type zeolites [6].

In the present analysis, a program has been written in FORTRON 90 language in order to calculate a prior density to be used with MEM software.

2. Material and Methods

2.1 Atomic Centered density

In IAM, atomic densities are assumed to be spherically symmetric, with a radial dependence equal to that of the theoretical ground state of isolated atoms. IAM approach is a good approximation for the heavier atoms for which the valence shell is a minor part of the total density. Whereas this model is less successful for the lighter atoms [4].

κ-formalism is the simple modification of the IAM model, which makes it possible to allow for charge transfer between atoms. In the κ-formalism, the atomic density is formulated as:

$$\rho_{atom} = \rho_{core} + \rho'_{valence}(\kappa r) = \rho_{core} + P_v \kappa^3 \rho_{valence}(\kappa r)$$

where,

P_v = valence shell population parameter

κ = parameter which allows the expansion and contraction of the valence shell.

The scattering factor of the valence density component can be obtained by the Fourier transformation. Since we consider spherical atoms,

$$f'_{valance}\left|\vec{Q}\right| = \int \left[P_{valence}(\vec{r})\kappa^3 \rho_{valence}(\kappa r)\right] e^{i\vec{Q}.\vec{r}} dr$$

By replacing r and Q in the exponent by κ r and Q/κ, respectively and writing κ^3dr=4π κ^2d(κr),

$$f'_{valence}\left|\vec{Q}\right| = f_{valence}(Q/\kappa)$$

From above relation it is clear that k -modified scattering factor can be obtained directly from the unperturbed IAM scattering factors. The k - structure factor formalism is,

$$F(Q) = \sum_j \left[\left\{ P_{j,c} f_{j,core}(Q) + P_{j,v} f_{j,valence}(Q/\kappa) \right\} \exp(2\pi i Q.r_j) \right]$$

Where scattering factors $f_{j,core}$ and $f_{j,valence}$ are normalized to one electron and $P_{j,c}$ and $P_{j,v}$ are the core and valence electron populations respectively.

Multipole density formalism is a valence-density formalism in which the density of each atom is described as [7]:

$$\rho_{at(r)} = P_c \rho_{core}(r) + P_v k^3 \rho_{valence}(kr) + \sum_{l=0}^{l_{max}} k'^{3} R_l(k' r) \sum_{m=0}^{l} P_{lm} {}^{*}Y_{lm}(\theta, \phi)$$

Where first two parts in the above equation includes the spherical core density and the spherical extended/reduced part of the valence density and this part is κ -dependant. In addition the summation includes the aspherical feature of the valence density expressed as a combination of the spherical harmonics $Y_{lm}(\theta,\phi)$.

For atomic form factor according to the multipole formalism, applying the Fourier transformation, the aspherical atom scattering factor of atom 'j' can be written as,

$$f_j(Q) = P_{j,c} f_{j,core}(Q) + P_{j,v} f_{j,valence}\left(\frac{Q}{\kappa'}\right) + \sum_{l=0}^{l_{max}} \sum_{m=0}^{l} \sum_{p} P_{lmp} f_{lmp}\left(\frac{Q}{\kappa'}\right)$$

In which the multipole scattering factor $f_{lmp}(Q)$ are the orientation- dependant Fourier transformations of the spherical harmonic deformation functions developed on real spherical harmonics (p= ±).The structure factor expansion according to above relation is:

$$f(Q) = \left[\left\{ p_{j,c} f_{j,core}(Q) + p_{j,v} f_{j,valence}(Q/k) + 4\pi \sum_{l=0}^{l_{max}} \sum_{m=0}^{l} p_{lm\pm} i^{l} \langle j_l(Q/k) \rangle d_{lm\pm}(\beta, v) \right\} \exp(iQ.r_j) \right]$$

Where,

$f_{lmp}(Q) = 4\pi i^{l} \langle j_l \rangle d_{lmp}(\beta, v)$,

d_{lmp} = Real spherical harmonics (P=±)

$\langle j_l \rangle = \int j_l(Qr) R_l(r) r^2 dr$

2.2 Maximum entropy method (MEM)

MEM is a tool that can yield high resolution electronic charge density from a limited number of diffraction data (much less than in themultipolar approach). The first application of MEM to a charge density was performed for Si, and provided with detailed structural information including bonding characteristics among atoms [8]. Subsequently, it has been applied to a wide variety of materials and revealed several important aspects of the nature of electronic structures from the view-point of charge density.

MEM is an information based technique that was first developed in the field of radio astronomy to enhance the obtained images from noisy data [9]. The entropy expression for ‘N’ identical particles distributed over ‘m’ boxes, each populated by n_i particles, where ‘q_i’ is the prior probability for the i^{th} box to contain n_i particles is given, according to Jaynes [10], by:

$$S = -\sum_i n_i \ln n_i + \sum_i n_i \ln q_i = -\sum_{i=1}^{m} n_i \ln \frac{n_i}{q_i}$$

In Crystallography, MEM was introduced by Collins [1], who expressed the information entropy as a sum over M grid points in the unit cell as,

$$S[\rho(r)] = -\sum_{j=1}^{M} P(r) \ln\{P(r)/m(r)\}$$

Applying an iterative procedure, the entropy $S[\rho(r)]$ is maximized subject to the constraint.

The algorithm of entropy maximization is nonlinear and must be applied iteratively. Convergence is thus achieved in a two-step process for which first the χ^2 = N constraint is satisfied (last part of the right term of above equation) and subsequently the entropy ‘S’ is maximized.

2.3 Prior density

MEM often yields better results if one can provide with a reasonable prior density. One way to achieve this is to build a prior density from the IAM. If one can build atomic densities and convolute them with thermal atomic motion, by summing up over all atoms, one can expect to construct a reasonable prior density. In our case we construct atomic radial electron distribution from analytical expressions of atomic scattering factor approximations to which we apply isotropic thermal motion. The atomic structure factors $f_j|\vec{Q}|$ for isolated atoms or ions are given in these tables as the sum of Gaussian. We show below that then ρ_j is also a sum of Gaussian.

Analytical approximations can be found in handbooks of crystallography for spherical atomic structure factor, in the range (Q<8π), $f_j\,(s) = \sum_j A_j e^{-B_j s^2}$

Where, $\frac{\sin\theta}{\lambda} = \frac{Q}{4\pi}$, and $f_j(Q/4\pi) = \sum_j a_j \exp\left\{-\frac{B_j}{(4\pi)^2} Q^2\right\}$

Analytical expression for the corresponding radial density applying standard formula [11],

$$\rho(r) = \sum_j a_j \left(\frac{B}{\pi}\right)^{3/2} \exp(-Br^2)$$

It comes to be the sum of Gaussian. Therefore if structure factor is the sum of Gaussian, the density of the atoms is also the sum of Gaussian.

2.4 Program in FORTRAN

A program has been developed using FORTRAN90 language in order to calculate a prior density to be used with MEM software. The schematic diagram of the program is given in figure 1.

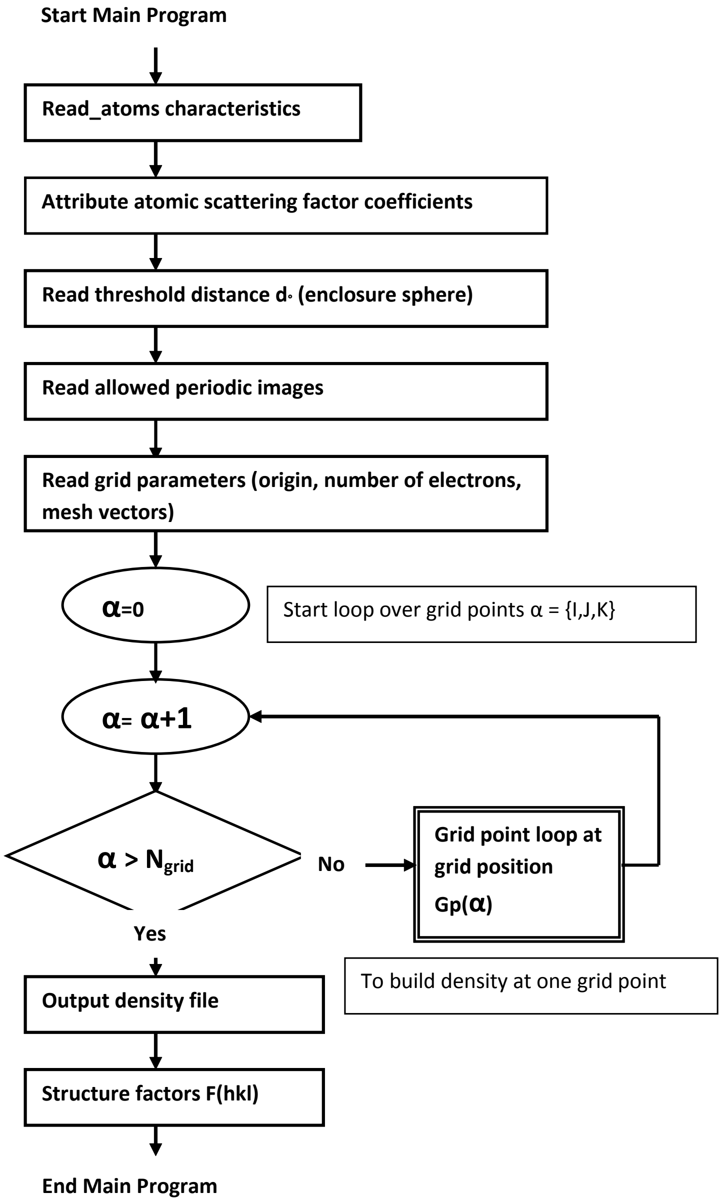

Figure 1: Schematic diagram of main program

After reading atom's characteristics: electron number, position and isotropic thermal motion parameter (Read_atom file procedure), corresponding atomic scattering factor coefficients are read. Then the program loops are taken over all grid points and for each grid point all contributing atoms, including periodic images within a given sphere of enclosure (e.g: d=15 Å) are taken into account. The program can also build a list of cell structure factors F(hkl) of the IAM model that can be used as test input for testing Maximum Entropy Method.

3. RESULTS AND DISCUSSION

ENIGMA software have been used to test the developed programe on bimuth [12]. Bismuth crystalises in the rhombohedral system R-3m with unit cell parameter a = 4.746 Å and angle α = 57.230°. There are two Bi atoms (83 electrons) related by inversion center with the special position (u,u,u) where u=0.234. From bismuth atomic scattering factors a set of unit cell crystallized bismuth structure factors F(hkl) for |h|, |k|, |l| ranging from 0 to 10 and a prior density on a grid of 64×64×64 points were built. In order to refine the uncomplete (|h|, |k|, |l| ranging from 0 to 10) set of F(hkl) starting with our defined “non-flat” prior density or a “flat” density, the two approaches are tabulated below. In both “non-flat” and “flat” prior cases the value of the Lagrange parameter needed to get convergence of the iterative process was of the order of 10^{-5}. Higher value could probably be used if we had given larger artificial uncertainties to the structure factors (5%).

In order to compare the agreement of the refinement process the final χ^2 and the reliable factor (*R*-factor) have been used, which is commonly used in crystallography, defined as:

$$R = \frac{\sum \left| F_{obs} - F_{calc} \right|^2}{\sigma_{obs}^2}$$

3.1 Evolution of MEM refinement from defined prior density

Prior electronic density for bismuth on a grid has been built from atomic scattering factors, is used as prior density for bismuth structure factors refinement with the maximum entropy software ENIGMA as shown in figure 2.

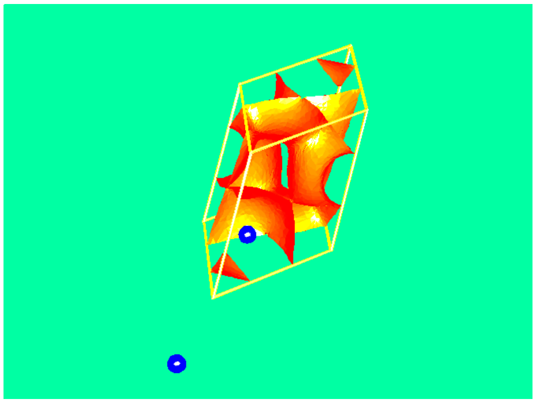

Figure 2: Defined prior electron density, contour 0.02e$^-$/Å^3

The defined prior density is used for bismuth structure factors refinement with the maximum entropy software ENIGMA to get electronic densities at different iterations. . Electronic densities obtained after 50, 500, 10000 iterations has been shown in figure 3.

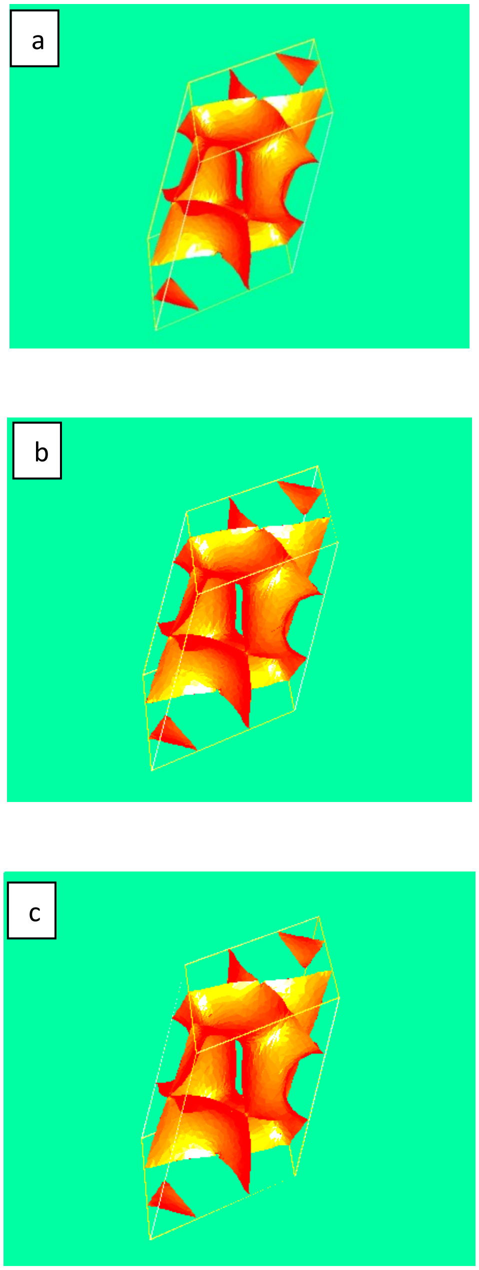

Figure 3: Electron densities obtained after a) 50 cycles, b) 500cycles, c) 10000 cycles, contour 0.02e$^-$/Å^3, using defined prior density.

Corresponding graphical representations of *R*-factor and χ^2 are shown in figure 4. It can be clearly seen that even at the beginning the value R- Factor of Prior density is less than 1%, then it decreases very rapidly. Similarly it can be seen that there is significant decrease in the constraints χ^2 after some iterations.

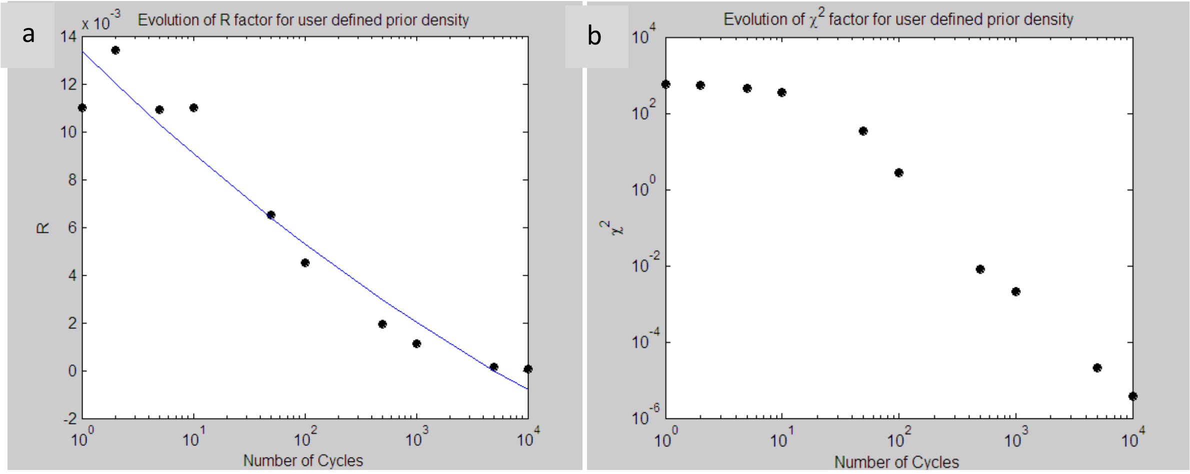

Figure 4: Graphical representation of a) *R*-factor, b) χ^2 , for defined prior density.

3.2 Evolution of MEM refinement from flat prior density

By using MEM software ENIGMA starting from flat density, one can obtain electron densities 100, 10000, 200000 iterations as shown in figur5. Corresponding graphical representations of *R*-factor and χ^2 are shown figure 6. It shows that even after several hundred of thousands iterations value of *R*-factor is much more few %. Similarly, it can be seen that there is no significant decrease in the constraints χ^2.One can see that redistribution from flat initial density occurs in the vicinity of the principal *R*–3m axis, but it takes hundreds of thousands cycles before real concentration at the real atomic positions occurs.

By comparison of evolution of electron density for bismuth both for flat prior density and defined prior density, it can be seen that electronic densities obtained by the use of defined prior density is quite good as compared with the electronic densities obtained by flat prior density. It can also be noticed that the use of defined prior density acquires less time in the process of building required density and acceptable values of the *R*-factor. To obtain convergence one can see that using flat prior density is a very slow process and the initial density could not be achieved with enough accuracy.

4 Conclusion

According to the results obtained, the method developed to provide reasonable “prior” electron density to be used in the MEM refinement of X-ray diffraction data in order to reconstruct experimental electron density, seems to be efficient. In the case of bismuth, from the comparison, it has been observed that redistribution (concentration) of electron density at the real atomic positions takes hundreds of thousands of cycles of MEM refinement in the case of “flat” initial density whereas with the use of “defined prior” density concentration of electron density at real atomic positions takes only few hundreds of cycles to reach acceptable reliability R-factor, which gives an agreement of the efficiency of our program.

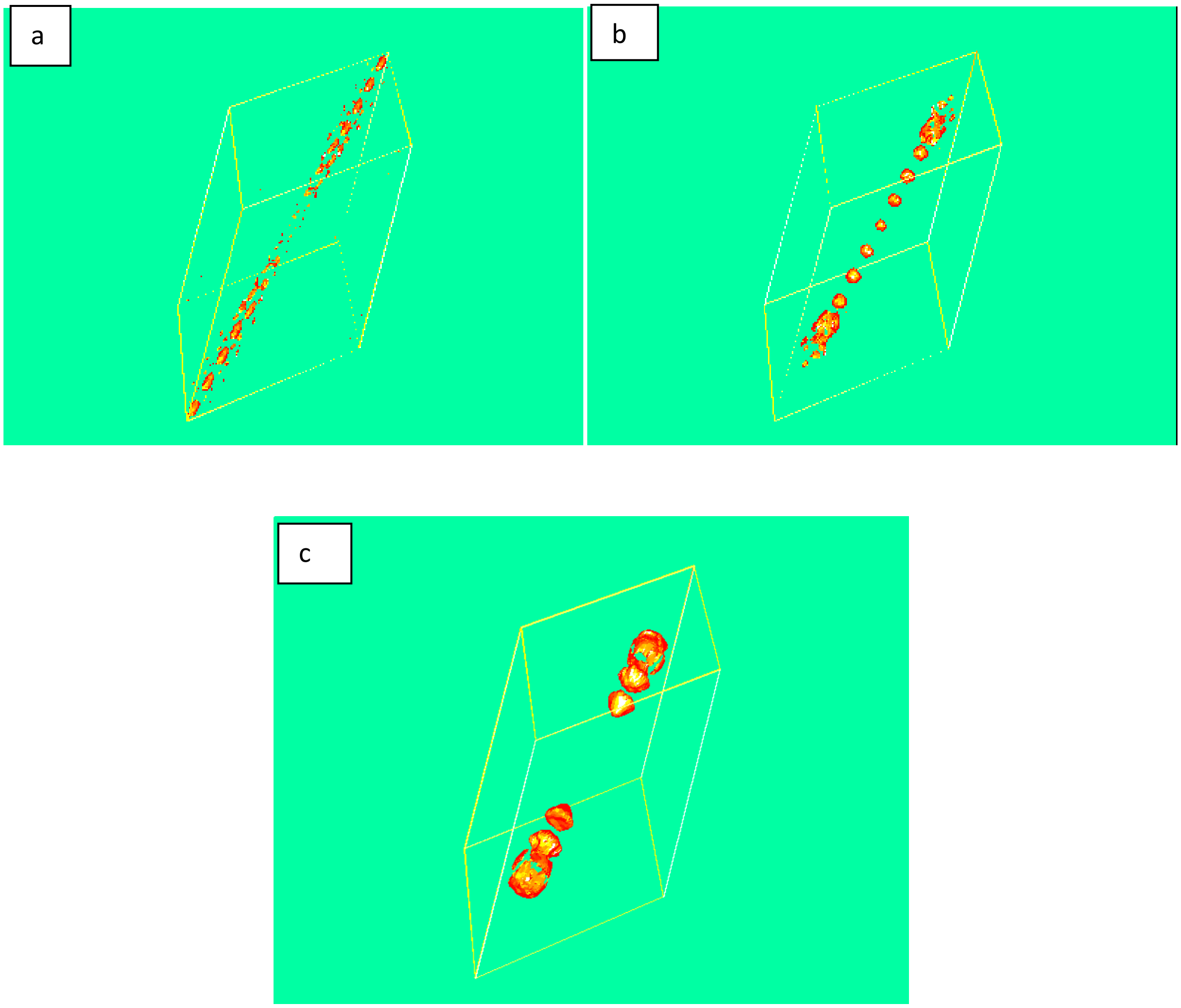

Figure 5: Electron densities obtained after a) 1000 cycles, contour 0.385e^-/Å^3 b) 10000 cycles, contour 0.08e^-/Å^3 c) 200000 cycles, contour 0.02e^-/Å^3, contour 0.04e^-/Å^3 using flat prior density.

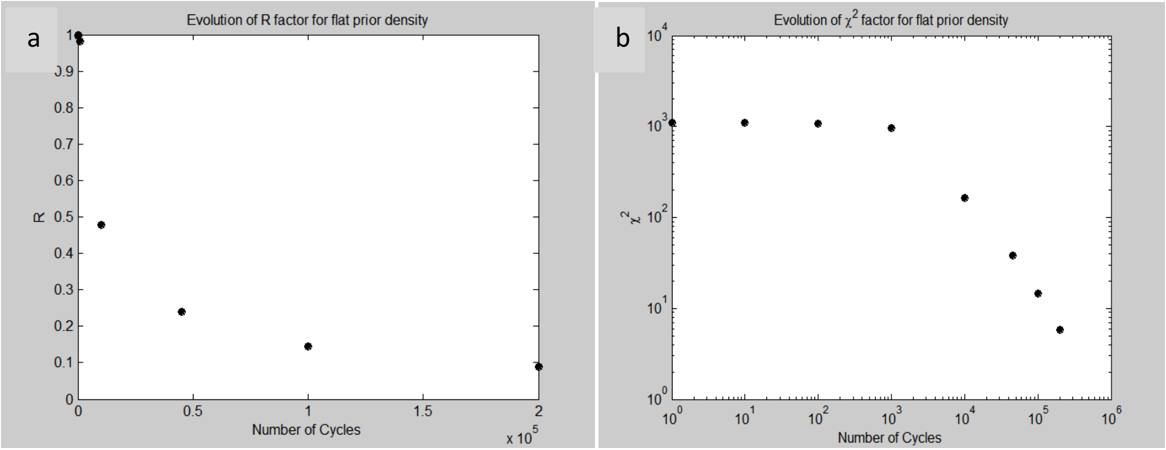

Figure 4: Graphical representation of a) *R*-factor, b) χ^2 , for flat prior density.

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