

# FULLPROF as a new tool for flipping ratio analysis

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## Abstract

We have added to FULLPROF new facilities to analyze flipping ratio (FR) data. The subroutines developed describe the total magnetization density as the sum of monoatomic contributions. Each monoatomic magnetization density ( $m_s$ ) can be described by two different approaches. The first one (density approach) assumes that  $m_s$  can be described by a development on real spherical harmonics truncated at  $l = 4$ . In the second one (orbital approach) unpaired electrons are assumed to have a well-defined angular quantum number  $l$ . The case of a hybrid s–p orbital has also been implemented. Different models can be used for the radial dependence of monoatomic magnetization densities. This includes, in the orbital approach, the use of hydrogen-like functions or Slater-type functions.

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PACS: 29.85.+c; 61.12.Ld

Keywords: Flipping ratio; Scientific software

## 1. Introduction

The use of flipping-ratio (FR) measurements has been long used to determine the magnetization density in a wide variety of compounds in quite different scientific branches. Analyzing the results, specially when the space group describing the structure is non-centrosymmetric, requires the use of adequate computer programs. However, the tools available to analyze data are, in general, difficult to use for non-specialized users. The main goal of the work done has been the development of

a user-friendly application able to analyze FR in both centrosymmetric and non-centrosymmetric cases in terms of the refinement by least-squares minimization of the magnetization density.

In order to deal with this goal, we have decided to implement in the FULLPROF program [1] the calculation of the magnetic form factors to analyzing FR data. The use of the FULLPROF program presents a number of advantages. One of them is that the use of FULLPROF input (PCR) files allows introducing initial data with great clarity. Another one is the use of the same tool to analyze nuclear and magnetic data. The nuclear contribution to increase and decrease intensities is calculated from the structural details provided in PCR files. It must also be mentioned that there exists the facility to draw Fourier maps from

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FULLPROF output with the use of GFOURIER program. This implementation has been checked by re-analyzing existing FR data on Metrz-Nit ( $\text{C}_{10}\text{H}_{16}\text{N}_5\text{O}_2$ ) compound [2].

## 2. Implementation details

FULLPROF program calculates the nuclear form factor  $F_N(\vec{h})$  from the structural model provided by the user. Afterwards, the scalar magnetic structure factor,  $M(\vec{h})$ , is calculated as the sum of the contributions of each atom multiplied by the appropriate phase factor. Each of these individual contributions are calculated following one of the two classical approaches.

### 2.1. Density approach

In this case, the spin density of each atom is approached as a development using real spherical harmonics (defined as in Ref. [3]), truncated at  $l = 4$ . Such a development reads

$$m(\vec{r}) = \sum_{l=0}^4 R_l^{\text{dens}}(r) \sum_{m,p} \beta_l^{m,p} \mathcal{Y}_l^{m,p}(\hat{r}), \quad (1)$$

where  $0 \leq m \leq l$  and  $p = \pm 1$ . So,  $M(\vec{h})$  can be expressed in the following way:

$$M(\vec{h}) = \sum_{l=0}^4 i^l \langle j_l \rangle (2\pi h) \sum_{m,p} \beta_l^m \mathcal{Y}_l^{m,p}(\hat{h}), \quad (2)$$

where  $\langle j_l \rangle(s)$  is the Fourier–Bessel transform of the radial function  $r^2 R_l^{\text{dens}}$ ,

$$\langle j_l \rangle(s) = \int_0^\infty dr r^2 R_l^{\text{dens}}(r) j_l(sr), \quad (3)$$

where  $j_l$  is the spherical Bessel function.  $\beta_l^{m,p}$  are adjustable occupancies of the different spherical harmonics. Radial density functions are taken to be Slater-type functions:

$$R_l^{\text{dens}}(r) = \frac{\zeta_l^{n_l+3}}{(n_l+2)!} r^{n_l} \exp\{-\zeta_l r\}. \quad (4)$$

The volume factor  $\zeta_l$  in the previous expression can also be adjusted.

### 2.2. Orbital approach

In this approach the contribution to the magnetization density arising from each ion is described in terms of an orbital centered on the ion. This orbital is taken to have a well-defined orbital moment (except in the case of a hybrid s–p orbital). Thus, in general,  $m(\vec{r}) = \alpha |\phi_l(\vec{r})|^2$ . Where  $\phi_l$  can be chosen to be a (normalized) p, d, or f orbital expressed in terms of the real spherical harmonics,

$$\phi_l(\vec{r}) = \frac{R_l(r)}{\sqrt{\sum_{m,p} |\mathcal{A}_l^{m,p}|^2}} \sum_{m,p} \mathcal{A}_l^{m,p} \mathcal{Y}_l^{m,p}(\hat{r}). \quad (5)$$

In general,  $\mathcal{A}_l^{m,p}$  are taken to be complex numbers. Each type of orbital (p, d or f) leads to a magnetization density that can be expressed in a way similar to Eq. (1),

$$\begin{aligned} M(\vec{r}) &= \alpha |\phi_l(\vec{r})|^2 \\ &= \alpha \left| \frac{R_l(r)}{\sqrt{\sum_{m,p} |\mathcal{A}_l^{m,p}|^2}} \sum_{m,p} \mathcal{A}_l^{m,p} \mathcal{Y}_l^{m,p}(\hat{r}) \right|^2 \\ &= R_l(r)^2 \sum_{l'=0,2,\dots,2l} \beta_{l'}^{m,p} \mathcal{Y}_{l'}^{m,p}(\hat{r}). \end{aligned} \quad (6)$$

Obviously,  $\beta_{l'}^{m,p}$  (which are all real numbers) are related to  $\mathcal{A}_l^{m,p}$  and  $\alpha$  (the specific relations implemented will be documented elsewhere [4]). From expression (6) the magnetic form factor of each magnetic ion can be expressed as

$$M(\vec{h}) = \sum_{l'=0,2,\dots,2l} (i)^{l'} \langle j_{l'} \rangle (2\pi h) \sum_{m,p} \beta_{l'}^m \mathcal{Y}_{l'}^{m,p}(\hat{h}), \quad (7)$$

where, in this case,  $\langle j_{l'} \rangle(s) \equiv \int_0^\infty dr r^2 R_{l'}^2(r) j_{l'}(sr) dr$ .

FULLPROF can handle three different treatments for the radial part [ $\langle j_{l'} \rangle(s)$ ]. The first one calculates the values of  $\langle j_{l'} \rangle(s)$  from the expression,

$$\begin{aligned} \langle j_{l'} \rangle(s) &= A_{l'} s^2 \exp\{-a_{l'} s^2\} + B_{l'} s^2 \exp\{-b_{l'} s^2\} \\ &\quad + C_{l'} s^2 \exp\{-b_{l'} s^2\} + D_{l'} s^2 \end{aligned}$$

for  $l' = 2, 4, 6$  and

$$\langle j_0 \rangle(s) = A_0 \exp\{-a_0 s^2\} + B_0 \exp\{-b_0 s^2\} + C_0 \exp\{-c_0 s^2\} + D_0; \quad (8)$$

the values of the constants,  $a_{l'}$ ,  $A_{l'}$ , ... can be found in the International Tables of Crystallography for many magnetic ions [5].

The second approach takes  $R_l$  as a Slater-type function [Eq. (4)], where  $n_l$  must be provided and  $\zeta_l$  can be refined, conveniently normalized ( $\int_0^\infty R_l^2(r) r^2 dr = 1$ ):

$$R_l(r) = \left[ \frac{(2\zeta_l)^{2n_l+3}}{(2n_l+2)!} \right]^{1/2} r^{n_l} \exp\{-\zeta_l r\}. \quad (9)$$

The third approach takes  $R_l$  as a hydrogen-like radial function with principal quantum number  $n$  ( $R_{n,l}$ ). The form of such function can be found in several text books. In this approach,  $n$  must be chosen by the user (with the obvious restriction  $n \geq l+1$ ) and the effective atomic number ( $Z_{\text{eff}}$ )

can be refined. In addition to pure p, d, and f orbitals, the case of a hybrid s-p and spherical orbitals can also be treated. For a hybrid s-p orbital, it is

$$\phi_{s-p}(\vec{r}) = R_p(r) \sum_{m,p} \mathcal{A}_1^{m,p} \mathcal{Y}_1^{m,p}(\hat{r}) + R_s(r) \mathcal{A}_0^{0+} \mathcal{Y}_0^{0+}(\hat{r}). \quad (10)$$

In this case, an expression for the magnetization density similar to that of Eq. (6), but with  $l' = 0, 1, 2$ , is recovered. If this type of orbital is chosen,  $\langle j_{l'} \rangle(s)$  only can be calculated by assuming that  $R_p$  and  $R_s$  are hydrogen-like functions with the same principal quantum number  $n$ .

Orbitals with spherical symmetry can be treated using the density approach and taking  $\beta_l^{m,p} = 0$  for  $l \neq 0$  [in Eq. (1)]. In addition to this, FULLPROF can take the magnetic form factor from

$$M(\vec{h}) = W_0 \langle j_0 \rangle(2\pi h) + W_2 \langle j_2 \rangle(2\pi h) + W_4 \langle j_4 \rangle(2\pi h) + W_6 \langle j_6 \rangle(2\pi h). \quad (11)$$

Table 1

Comparison of results from Ref. [2] and those obtained using FULLPROF implementation on Metrz-Nit data.

|                              | Spherical approximation |            | 2p NO approximation |            |
|------------------------------|-------------------------|------------|---------------------|------------|
|                              | FULLPROF                | Ref. [2]   | FULLPROF            | Ref. [2]   |
| $R_w^{\text{FR}} (\%)$       | 19                      | 19         | 16                  | 16         |
| $\zeta_N (\text{a.u.})^{-1}$ | 4.43 (21)               | 4.95 (16)  | 4.12 (32)           | 4.72 (12)  |
| $\zeta_O (\text{a.u.})^{-1}$ | 6.70 (32)               | 6.43 (27)  | 4.70 (10)           | 5.44 (13)  |
| O1                           | 0.248 (13)              | 0.285 (5)  | 0.265 (13)          | 0.276 (4)  |
| O2                           | 0.228 (17)              | 0.246 (7)  | 0.241 (17)          | 0.243 (5)  |
| N1                           | 0.006 (17)              | 0.008 (7)  | -0.038 (17)         | 0.002 (5)  |
| N2                           | -0.053 (15)             | -0.023 (5) | -0.017 (15)         | -0.005 (5) |
| N3                           | -0.036 (14)             | -0.027 (5) | -0.010 (14)         | -0.014 (4) |
| N4                           | 0.269 (26)              | 0.299 (8)  | 0.225 (26)          | 0.258 (6)  |
| N5                           | 0.274 (25)              | 0.295 (8)  | 0.262 (25)          | 0.275 (6)  |
| C1                           | 0.015 (17)              | -0.019 (8) | 0.016 (17)          | -0.014 (6) |
| C2                           | 0.016 (18)              | 0.015 (7)  | 0.054 (18)          | 0.018 (5)  |
| C3                           | -0.036 (20)             | 0.005 (8)  | 0.003 (21)          | 0.008 (6)  |
| C4                           | -0.055 (23)             | -0.106 (8) | -0.089 (23)         | -0.084 (6) |
| C5                           | 0.042 (17)              | 0.037 (8)  | 0.030 (17)          | 0.040 (6)  |
| C6                           | -0.065 (26)             | -0.012 (9) | -0.099 (26)         | -0.024 (7) |
| C7                           | 0.027 (13)              | 0.001 (8)  | 0.007 (13)          | 0.001 (6)  |
| C8                           | 0.037 (16)              | -0.007 (8) | 0.054 (16)          | 0.008 (6)  |
| C9                           | 0.028 (18)              | -0.007 (8) | 0.052 (18)          | 0.006 (6)  |
| C10                          | 0.056 (14)              | 0.007 (8)  | 0.043 (14)          | 0.005 (6)  |

The table shows the agreement factors, refined Slater exponents of N and O and magnetic densities of each atom normalized to  $1\mu_B/\text{molecule}$ . The standard deviations provided by FULLPROF are multiplied by  $\chi^2$  (approximately by a factor of 4).

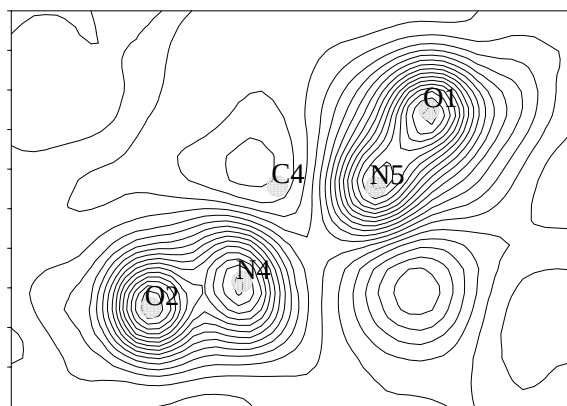


Fig. 1. Magnetization density refined using FULLPROF when 2p-orbitals for O1, O2, N4 and N5 atoms are used. The magnetization has been plotted in the plane defined by O1, O2 and N4.

The values of  $\langle j_i \rangle$  are taken from Eq. (8) and  $W_i$  are adjustable parameters.

### 3. Comparative results

In order to check the correctness of the implementation done, we have analyzed data on Metrz-Nit compound (2-{3-[4-methyl-1,2,4-triazolyl]}-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). Three different models are used in Ref. [2]. We have tried to reproduce two of them. The first one assumes that magnetic densities of N, O and C have spherical symmetry. In the second one, the shape of the spin density on O atoms and two N atoms (namely N4 and N5 in Ref. [2]) is described in terms of 2p-orbitals. In both cases, the radial part of the magnetization densities are described in

terms of a Slater-type function [Eq. (4)] with  $n_l = 2$  and refined  $\zeta$  for N and O and  $n_l = 0$  and fixed  $\zeta$  for the other atoms.

Table 1 presents the results obtained using FULLPROF for both cases (for comparison, results reported in Ref. [2] are also printed). The agreement between both sets of results must be highlighted and ensures the correctness of the implementation done. Fig. 1 shows the obtained magnetization density in the plane containing O1, O2, N4 and N5 atoms. This can be fairly compared with Fig. 4 in Ref. [2].

### Acknowledgements

C. Frontera thanks financial support from the ESF (through a Short Time Fellowship), from DRFMC/SPSMS/MDN and from Institut Laue Langevin. His gratitude for the hospitality of DRFMC/SPSMS/MDN is also expressed. The authors thank Dr. Gillon for providing them data on Metrz-Nit.

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