SHORT COMMUNICATIONS

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A generalized *n*-dimensional inverse Fourier transform incorporating experimental error bars.

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Abstract

The inverse Fourier transform is a most prominent and widely used tool in crystallography. Used to retrieve Patterson densities and densities from measured intensities or phased structure factors, it is well known to suffer from major drawbacks among which is the neglect of known error bars. In this paper, it is shown how to incorporate measured experimental error bars in the computation of the Fourier syntheses. This simple novel procedure should be useful when a proper maximum-entropy analysis proves infeasible, due to either a high dynamical range of the data or a high dimension of the direct space in which the density is sought (at least five or six dimensions for quasicrystallography).

Introduction

It is first shown that the standard procedure to retrieve $\rho(\mathbf{r})$ from a noiseless finite set of structure factors minimizes the functional $\int \rho^2(\mathbf{r})\,\mathrm{d}\mathbf{r}$ subject to two types of constraints: the N given independent structure factors and the symmetry requirements. When the structure factors are known within error bars, the constraints on the structure factors are turned very naturally into the weaker constraint (or restraint) that χ^2 be less than or equal to N. An example is given.

Notations and definitions

Let $\mathcal{G}$ be the space group of a given crystal X, $\mathcal{T}$ the pure translation group, $G = \mathcal{G}/\mathcal{T}$ the related factor group of order g. In the case of Patterson-density retrievals, the space group of the vector set of the crystal has to be considered instead (Buerger, 1959). Let $\hat{R} = (\hat{\alpha}, \boldsymbol{\beta})$ represent an element $\mathcal{R} = (\hat{\alpha}, \boldsymbol{\beta})\mathcal{T}$ of $\mathcal{G}$, so that $\hat{R}\mathbf{r} = \hat{\alpha}\mathbf{r} + \boldsymbol{\beta}$, where $\mathbf{r}$ belongs to direct space, of dimension n. Let the volume V of the n-dimensional unit cell be divided into M pixels p_j ($j = 1, \ldots, M$) of volume $\Delta = V/M$. Let the value of the sought density $\rho(\mathbf{r})$ be ρ_j in pixel p_j centered at $\mathbf{r}_j$.

Moreover, let N symmetrically independent data points (D_k, σ_k) be related to the scattering vectors $\mathbf{K}_k$ where $k = 1, \ldots, N$, D_k stands either for a phased structure factor F_k or for the square $|F_k|^2$ of its modulus, and σ_k is the corresponding measured or estimated error bar.

For the sake of simplicity, the validity of Friedel's law will be assumed throughout this paper, namely that $F^*(\mathbf{K}) = F(-\mathbf{K})$ holds for any scattering vector $\mathbf{K}$. Hence, only $F(\mathbf{K})$ or $F(-\mathbf{K})$ must be considered for each $\mathbf{K}$. This assumption, which rules out X-ray anomalous scattering, is certainly well justified for neutron nuclear or magnetic diffraction. Next, let $g(\mathbf{K})$ be the degeneracy factor associated with the star of $\mathbf{K}$. This degeneracy factor is the number of symmetry operations (rotations) in Fourier space which leave $\mathbf{K}$ invariant.

Finally, let the computed structure factor F_k^c be defined by

$$F_k^c = F(\mathbf{K}_k) = \int \exp\{2\pi i \mathbf{K}_k \cdot \mathbf{r}\}\rho(\mathbf{r})\,\mathrm{d}\mathbf{r} = \sum_{j=1}^{M} \exp\{2\pi i \mathbf{K}_k \cdot \mathbf{r}_j\}\rho(\mathbf{r}_j)\Delta = \sum_{j=1}^{M} A_{k,j}\rho_j.$$

Without loss of generality, we shall limit ourselves to the retrieval of the density $\rho(\mathbf{r})$ from a finite set of complex structure factors F_k in what follows.

The standard inverse Fourier transform as the result of a constrained minimization procedure

Minimizing a functional under constraints or restraints is done *via* the use of a Lagrangian and Lagrange multipliers. In order to allow for numerical computations, the quadratic functional $\int \rho^2(\mathbf{r})\,\mathrm{d}\mathbf{r}$ mentioned above must be replaced by its discretized form $\sum_{j=1}^{M} \rho_j^2$. In this case, our proposed Lagrangian reads

$$\mathcal{L} = \sum_j \rho_j^2 + \sum_k \lambda_k |F_k^c - F_k|^2 + \sum_{j_0} \sum_j \mu_{j_0,j}(\rho_j - \rho_{j_0}). \qquad (1)$$

The first term on the right-hand side is the functional to be minimized.

Why minimize $\int \rho^2(\mathbf{r})\,\mathrm{d}\mathbf{r}$? Besides its practicality, this choice is reasonable since, making use of Parseval's theorem, minimizing the proposed functional amounts to minimizing the integrated power spectrum of the sought density $\rho(\mathbf{r})$. Among all possible densities compatible with the constraints, we look for the most featureless one in some sense.

The second term ensures that the structure factors F_k^c computed from the solution $\rho(\mathbf{r})$ will be equal to the measured known structure factors F_k. The third term ensures that the symmetry constraints are obeyed: the value ρ_j of the density must be the same in all pixels p_j which are related to a given pixel p_{j_0} by a symmetry operation. Hence, the last term in the above expression involves the double sum over symmetrically independent pixels p_{j_0} inside the unit cell, and then over all pixels p_j symmetrically related to p_{j_0}. Let $\mathcal{O}_{j_0}$ be the set of the latter. At the minimum, one obtains for each pixel p_j belonging to $\mathcal{O}_{j_0}$:

$$\frac{\partial \mathcal{L}}{\partial \rho_j} = 2\rho_j + \sum_k \lambda_k [A_{k,j}^*(F_k^c - F_k) + A_{k,j}(F_k^{c*} - F_k^*)] + \mu_{j_0,j} - \delta_{j,j_0} \sum_{p_i \in \mathcal{O}_{j_0}} \mu_{j_0,j} = 0 \qquad (2)$$

where δ_{j,j_0} is a Kronecker delta and has value 1 or 0. The

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next step is to average the above equality over all p_j belonging to $\mathcal{O}_{j_0}$ to eliminate the $\mu_{j_0,j}$. This procedure yields averaged $A_{k,j}$, which are in fact equal to averages $\langle A_{k,j}\rangle$ over the g symmetry operations of the factor group G:

$$\langle A_{k,j}\rangle = \frac{1}{g}\sum_{s=1}^{g}\exp\{2\pi i\mathbf{K}_k(\hat{\alpha}_s\mathbf{r}_j+\boldsymbol{\beta}_s)\}\Delta. \tag{3}$$

The N Lagrange multipliers λ_k are determined by the N conditions $F_k^c = F_k$.

$$\begin{aligned}
&\sum_j A_{k_0,j}\langle A_{k,j}^*\rangle \\
&\quad=(1/g)\sum_{s=1}^{g}\sum_{j=1}^{M}\exp\{2\pi i\mathbf{K}_{k_0}\cdot\mathbf{r}_j\} \\
&\qquad\times\exp\{-2\pi i\mathbf{K}_k(\hat{\alpha}_s\mathbf{r}_j+\boldsymbol{\beta}_s)\}\Delta^2 \\
&\quad=(\Delta^2/g)\sum_{s=1}^{g}\exp\{-2\pi i\mathbf{K}_k\cdot\boldsymbol{\beta}_s\} \\
&\qquad\times\sum_{j=1}^{M}\exp\{2\pi i(\mathbf{K}_{k_0}-\hat{\alpha}_s^{-1}\mathbf{K}_k)\cdot\mathbf{r}_j\} \\
&\quad=(V\cdot\Delta)/g)\sum_{s=1}^{g}\exp\{-2\pi i\mathbf{K}_k\cdot\boldsymbol{\beta}_s\}\delta_{\hat{\alpha}_s\mathbf{K}_{k_0},\mathbf{K}_k} \\
&\quad=(V\cdot\Delta/g)\sum_{s=1}^{g}\exp\{-2\pi i\hat{\alpha}_s\mathbf{K}_{k_0}\cdot\boldsymbol{\beta}_s\}\delta_{\hat{\alpha}_s\mathbf{K}_{k_0},\mathbf{K}_k}.
\end{aligned} \tag{4}$$

Because only symmetrically independent scattering vectors are considered, the above expression is zero unless $k = k_0$.

It has been known for some time (Waser, 1955) that, in our notation,

$$F(\hat{\alpha}\mathbf{K}) = \exp\{2\pi i\hat{\alpha}\mathbf{K}\cdot\boldsymbol{\beta}\}F(\mathbf{K}). \tag{5}$$

Consequently, if $\mathbf{K}$ is not forbidden by extinction rules, $\exp\{2\pi i\hat{\alpha}\mathbf{K}\cdot\boldsymbol{\beta}\}=1$ for all $\hat{R}$ for which $\hat{\alpha}\mathbf{K}=\mathbf{K}$. Finally,

$$\sum_j A_{k_0,j}\langle A_{k,j}^*\rangle = V\Delta[g(\mathbf{K}_{k_0}/g)]\delta_{k_0,k} \tag{6a}$$

and, for the acentric case,

$$\sum_j A_{k_0,j}\langle A_{k,j}\rangle = V\Delta[g(\mathbf{K}_{k_0})/g]\delta_{k_0,k}\varepsilon_{k_0} \tag{6b}$$

where $\varepsilon_{k_0}=\varepsilon(\mathbf{K}_{k_0})$ is equal to 1 if $-\mathbf{K}_{k_0}$ belongs to the star of $\mathbf{K}_{k_0}$, and is equal to zero otherwise. The λ_k are determined by

$$\begin{aligned}
F_k = F_k^c &= \sum_{j=1}^{M} A_{k,j}\rho_j \\
&= -V\Delta[g(\mathbf{K}_k)/g](F_k^c-F_k)\lambda_k[(1+\varepsilon_k)/2]
\end{aligned}$$

for the acentric case; (7a)

$$= -V\Delta[g(\mathbf{K}_k)/g](F_k^c-F_k)\lambda_k$$

for the centrosymmetric case. (7b)

The final result reads

$$\begin{aligned}
\rho_j &= (1/V)\sum_{k=1}^{N}[g/g(\mathbf{K}_k)] \\
&\quad\times[(\langle A_{k,j}\rangle^*/\Delta)F_k+(\langle A_{k,j}\rangle/\Delta)F_k^*]/(1+\varepsilon_k)
\end{aligned}$$

for the acentric case; (8a)

$$= (1/V)\sum_{k=1}^{N}[g/g(\mathbf{K}_k)](\langle A_{k,j}\rangle/\Delta)F_k$$

for the centrosymmetric case. (8b)

We have shown in a previous paper (Papoular, 1991) that the inverse Fourier transform can be expressed using averaged exponentials over all symmetry operations of the relevant space group.

Remark 1: From (7*a*) or (7*b*) all the λ_k are infinite, so that the products $(F_k^c - F_k)\lambda_k$ should be finite and non-zero.

Remark 2: In (1), as many Lagrange multipliers were introduced as there are rigid *linear* constraints (noiseless structure factors or symmetry relations). The constraints over the structure factors were chosen to be nonlinear *via* the square of the moduli of the deviates in order to keep the Lagrangian $\mathcal{L}$ real, which ensures that Friedel's rule is automatically satisfied. A second reason to use this formulation is its obvious similarly to χ^2.

Remark 3: The linearity of the constraints relative to the structure factors could have been preserved through the introduction of two real Lagrange multipliers for each independent scattering vector: one, λ_k^r, for the real part of the deviate $\mathrm{Re}\,(F_k^c - F_k)$, and a second one, λ_k^i, for the imaginary part of the deviate $\mathrm{Im}\,(F_k^c - F_k)$. After introduction of the complex Lagrange multiplier $\lambda_k = \lambda_k^r + i\lambda_k^i$ and its conjugate λ_k^*, the related term of $\mathcal{L}$ now reads: $\sum[\lambda_k(F_k^{c*} - F_k^*) + \lambda_k^*(F_k^c - F_k)]$. Elementary algebra yields exactly the same result (8*a*) and (8*b*) as already obtained above, albeit with finite Lagrange multipliers.

Generalization of the variational procedure to include the experimental error bars

The generalization is straightforward: let us simply replace the constraints over the F_k by a single restraint over χ^2 which we require to be less than or equal to N, the number of independent data points.

Our proposed Lagrangian now reads:

$$\mathcal{L} = \sum_j \rho_j^2 + \lambda\left[\sum_k |(F_k^c - F_k)/\sigma_k|^2 - N\right] + \sum_{j_0}\sum_j \mu_{j_0,j}(\rho_j - \rho_{j_0}). \tag{9}$$

The computations run almost identically to the previous noiseless case, yielding:

$$\begin{aligned}
F_k^c &= \sum_{j=1}^{M} A_{k,j}\rho_j \\
&= -V\Delta[g(\mathbf{K}_k)/g][(F_k^c - F_k)/\sigma_k^2]\lambda[(1+\varepsilon_k)/2]
\end{aligned}$$

for the acentric case; (10a)

$$= -V\Delta[g(\mathbf{K}_k)/g][(F_k^c - F_k)/\sigma_k^2]\lambda$$

for the centrosymmetric case. (10b)

Finally, one arrives at:

$$[(F_k^c - F_k)/\sigma_k] = -F_k\sigma_k\{\sigma_k^2 + Ug(\mathbf{K}_k)[(1+\varepsilon_k)/2]\}^{-1} \tag{11}$$

where $U = \lambda(V\Delta/g)$ for both the centrosymmetric and the acentric cases.

Note that $U = 0$ corresponds to the constant density $\rho(\mathbf{r})$ which is equal to 0 everywhere, whereas $U = \infty$ corresponds to the standard inverse Fourier density which ignores the error bars. U is derived from the restraint $\chi^2 = N$, or $\chi_N^2 \equiv \chi^2 - N = 0$, *i.e.*

$$\chi_N^2(U) = \sum_{k=1}^{N} |F_k|^2\sigma_k^2\{\sigma_k^2 + Ug(\mathbf{K}_k)[(1+\varepsilon_k)/2]\}^{-2} - N = 0. \tag{12}$$

Solving for U. The procedure is iterative. Set $U_0 = 0$.

Note that if $\chi^2_N(0) \leq 0$ the measured Fourier components are smaller than their error bars on average. In this case, since it obeys all the constraints/restraints and minimizes $\int \rho^2(\mathbf{r})\,\mathbf{dr}$, the preferred density ρ is constant and equal to zero unless N is replaced by a smaller number, closer to the number of 'good' independent data measurements (Gull, 1989). Conversely, if $\chi^2_N(0) > 0$, then, due to both the convexity of the functional $\int \rho^2(\mathbf{r})\,\mathbf{dr}$ and that of $\chi^2[\{\rho(\mathbf{r})\}]$, the solution $\rho(\mathbf{r})$ exists, is unique and is such that $\chi^2 = N$.

Assuming now that $\chi^2_N(0) > 0$, find the smallest $U_1 = 2^p$, where p is a positive integer and for which $\chi^2_N(U_1) < 0$. Then dichotomize between the bracketing values U_0 and U_1 towards the unique positive solution U_∞.

Let us consider the acentric case first. Now that U and hence λ are known, the final result reads:

$$\begin{aligned}\rho_j &= -(\lambda/2)\sum_{k=1}^{N}\{A^*_{k,j}[(F^c_k - F_k)/\sigma^2_k] \\ &\quad + A_{k,j}[(F^c_k - F_k)^*/\sigma^2_k]\} \\ &= (1/V)\sum_{k=1}^{N}[g/g(\mathbf{K}_k)] \\ &\quad \times\{[(\langle A_{k,j}\rangle^*/\Delta)F_k + (\langle A_{k,j}\rangle/\Delta)F^*_k]/(1+\varepsilon_k)\} \\ &\quad \times(1-\sigma^2_k\{\sigma^2_k + Ug(K_k)[(1+\varepsilon_k)/2]\}^{-1}) \qquad (13a)\end{aligned}$$

The following similar formula holds for the centrosymmetric case:

$$\begin{aligned}\rho_j &= -\lambda\sum_{k=1}^{N}A_{k,j}[F^c_k - F_k]/\sigma^2_k \\ &= (1/V)\sum_{k=1}^{N}[g/g(\mathbf{K}_k)](\langle A_{k,j}\rangle/\Delta)F_k \\ &\quad \times\{1-\sigma^2_k[\sigma^2_k + Ug(\mathbf{K}_k)]^{-1}\}. \qquad (13b)\end{aligned}$$

Discussion and example

From Parseval's theorem, minimizing the functional $\int \rho^2(\mathbf{r})\,\mathbf{dr}$ amounts to minimizing the integrated power spectrum of the density $\rho(\mathbf{r})$, *i.e.* the sum of the squares of the moduli of all structure factors. Our generalized formulation is thus to minimize the latter, given the knowledge at hand: experimental data, symmetry, Friedel's law and so on. As a result of our procedure, unknown Fourier components are taken to be zero. Thus, our procedure does not take care of truncation effects. The expression of the density in the noisy case is very similar to the noiseless case except that each measured Fourier component is now multiplied by a positive correcting factor, which is close to unity if the related error bar is small and close to zero otherwise. The practical effect of our procedure is to remove the inaccurate components from the standard Fourier synthesis.

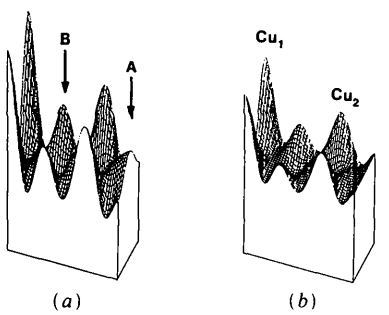

Fig. 1. $YBa_2Cu_3O_7$ at 30 K: comparison of the spin density projected along the $[1\bar{1}0]$ direction (*a*) by standard Fourier inversion and (*b*) by our suggested procedure, which incorporates experimental error bars. Note the disappearance of the spurious peak at *A*.

Table 1. *Data set for* $YBa_2Cu_3O_7$ *used in example*

h	k	l	g_K	σ_K	F^{meas}_K	F^{calc}_K
0	0	1	4	0.000231	0.000482	0.000430
0	0	2	4	0.000240	0.001422	0.001257
0	0	3	4	0.000246	0.001862	0.001636
0	0	4	4	0.000381	0.000489	0.000367
0	0	5	4	0.000378	0.001046	0.000789
0	0	6	4	0.000407	0.001831	0.001328
0	0	7	4	0.000468	0.000366	0.000244
0	0	8	4	0.000587	0.001030	0.000576
1	1	0	4	0.000460	0.002123	0.001431
1	1	1	2	0.000597	0.000998	0.000380
1	1	2	2	0.000658	−0.000215	−0.000072
1	1	3	2	0.000486	0.001697	0.000816
1	1	4	2	0.000804	−0.000456	−0.000115
1	1	5	2	0.000702	0.000886	0.000272
1	1	6	2	0.000487	0.001932	0.000927
2	2	0	4	0.001049	−0.000126	−0.000036

Consider the following example, pertaining to the projected magnetization density along $[1\bar{1}0]$ of $YBa_2Cu_3O_7$ at 30 K, taken from the work of Boucherle *et al.* (1990). The data set consists of 16 independent Fourier components (see Table 1). We neglect twinning effects and assume that the pseudosymmetry belongs to the centrosymmetric case (space group $P4/mmm$). Only eight symmetry operations are compatible with the projection, namely xyz, $\bar{x}\bar{y}\bar{z}$, $xy\bar{z}$, $\bar{x}\bar{y}z$, yxz, $\bar{y}\bar{x}z$, $yx\bar{z}$ and $\bar{y}\bar{x}\bar{z}$. U is equal to 0.10944×10^{-6}. The volume V of (13*b*) must be replaced by the projected surface S of the unit cell. The assumed noiseless (*a*) and the noisy (*b*) Fourier syntheses are shown in Fig. 1. Our procedure gets rid of the spurious peak at *A*. Nevertheless, truncation effects remain, in particular the peak at *B*. It is well established that maximum entropy eliminates truncation series effects. In the present example, it can and should be used, albeit at a much higher computing cost: maximum entropy wipes out the peak at *B* as well as all the remaining truncation effects (Papoular & Schweizer, 1991).

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References

BOUCHERLE, J. X., HENRY, J. Y., JURGENS, M. J., ROSSAT-MIGNOD, J., SCHWEIZER, J. & TASSET, F. (1990). *Physica (Utrecht)*, C**162–164**, 1285–1286.

BUERGER, M. J. (1959). *Vector space*, Ch. 9, Table 1, pp. 202–210. New York: Wiley.

GULL, S. F. (1989). In *Maximum Entropy and Bayesian Methods*, edited by J. SKILLING, pp. 53–71. Dordrecht: Kluwer Academic Publishers.

PAPOULAR, R. J. (1991). *Acta Cryst.* A**47**, 293–295.

PAPOULAR, R. J. & SCHWEIZER, J. (1991). In *Proc. VI International School on Neutron Physics, Alushta, USSR*, 1990 (Fig. 10). In the press.

WASER, J. (1955). *Acta Cryst.* **8**, 595.