

# Patterson function and $\delta$ recycling: derivation of the phasing equations

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Two phasing equations based on the Fourier syntheses  $\delta_P = T^{-1}[(E^2 - \langle E^2 \rangle) \exp(i\varphi)]$  and  $\delta_M = T^{-1}[(E - \langle E \rangle) \exp(i\varphi)]$  were recently described [Rius (2012). *Acta Cryst.* **A68**, 77–81] ( $E$  is the quasi-normalized structure factor and  $\langle E \rangle$  is the average over all reflections). These equations were found by comparison with the direct methods origin-free modulus sum function and constitute the core of the ‘ $\delta$  recycling’ phasing procedure. The derivation of these phasing equations from the minimization of a residual ( $R_P$ ) between two differently calculated density functions (one of them including the positivity constraint) is shown.

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## 1. Introduction

In Rius (2012), an alternative expression for calculating the  $\rho$  density function in terms of the set of phases  $\Phi = \{\dots, \varphi_{\mathbf{H}}, \dots\}$  of the quasi-normalized structure factors ( $\mathbf{E}$ ) was described. For an equal-atom structure,  $\rho$  in terms of  $\Phi$  is normally computed with the Fourier synthesis

$$\rho(\mathbf{r}, \Phi) = \frac{1}{V} \sum_{\mathbf{H}} E_{\mathbf{H}} \exp(i\varphi_{\mathbf{H}}) \exp(-i2\pi\mathbf{H}\mathbf{r}). \quad (1)$$

The alternative expression, based on the  $\delta_P$  function,

$$\delta_P(\mathbf{r}, \Phi) = \frac{1}{V} \sum_{\mathbf{H}} (E_{\mathbf{H}}^2 - \langle E^2 \rangle) \exp(i\varphi_{\mathbf{H}}) \exp(-i2\pi\mathbf{H}\mathbf{r}) \quad (2)$$

is defined by

$$\rho_P(\mathbf{r}, \Phi) = \frac{\delta_P(\mathbf{r}, \Phi)}{\langle E \rangle} m(\mathbf{r}, \Phi), \quad (3)$$

where  $m$  is a mask which is equal to zero in the whole unit cell except for those  $\mathbf{r}$  points for which  $\delta_P(\mathbf{r}) \geq \Delta = t\sigma(\delta_P)$ , where  $m$  is equal to one ( $t \sim 2.5$ ). An important fact is that the standard deviation  $\sigma(\delta_P)$  used for fixing the  $\Delta$  threshold limit is phase independent, *i.e.* it only depends on the structure-factor moduli derived from experiment. Multiplication by  $m$  ensures that  $\rho_P$  is positive definite. By making  $\delta_{P,\Delta} = \delta_P m$ , the recursive phasing formula

$$\varphi_{\mathbf{H}}^{\text{new}} = \text{phase of } \left\{ \int_V \delta_{P,\Delta}(\mathbf{r}, \Phi) \exp(i2\pi\mathbf{H}\mathbf{r}) dV \right\} \quad (4)$$

was also established by comparison with the direct methods origin-free modulus sum function (Rius, 1993; Rius *et al.*, 2007). The purpose of this contribution is to derive the  $\delta_P$  phasing formula [equation (4)] from the minimization of the  $R_P$  residual [equation (6)]. In this derivation the existing proportionality between  $\delta_P$  and  $\delta_M$  shown in Appendix A is used,  $\delta_M = T^{-1}[(E - \langle E \rangle) \exp(i\varphi)]$ .

## 2. The $R_P$ residual and the $\delta_P$ ( $\delta_M$ ) phasing formula

If  $\rho(\mathbf{r})$  represents a positive definite density function of the crystal, *e.g.* the electron density or even the electrostatic potential (for structure-determination purposes), let us assume that the condition

$$\rho(\mathbf{r}, \Phi) = \rho_P(\mathbf{r}, \Phi) = \rho(\mathbf{r}), \quad \forall \mathbf{r} \in V \quad (5)$$

is only fulfilled for the true  $\Phi$ 's. The discrepancy between  $\rho(\Phi)$  and  $\rho_P(\Phi)$  can be measured through the residual

$$R_P(\Phi) = \int_V [\rho(\mathbf{r}, \Phi) - \rho_P(\mathbf{r}, \Phi)]^2 d\mathbf{r} \quad (6)$$

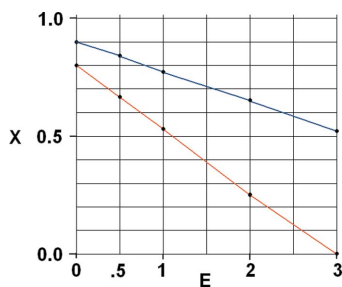
extended over the whole unit cell of  $V$  volume. To find the set of phases minimizing  $R_P$ , the above integral must be simplified. By omitting the  $\mathbf{r}$  and  $\Phi$  symbols in the integrand, it follows

$$\begin{aligned} R_P(\Phi) &= \int_V (\rho - \rho_P)^2 dV = \int_V \left( \rho - \frac{\delta_P m}{\langle E \rangle} \right)^2 dV \\ &= \int_V \rho^2 dV - \frac{1}{\langle E \rangle^2} \int_V (2\rho \langle E \rangle \delta_P m - \delta_P^2 m^2) dV = I_C - I_P. \end{aligned} \quad (7)$$

Integral  $I_C$  corresponds to the value of the Patterson function at the origin, *i.e.* it is equal to  $1/V \sum_{\mathbf{H}} E_{\mathbf{H}}^2$  and hence is phase independent. In integral  $I_P$ , the squared mask  $m^2$  (which is made of zeros and ones) is equal to  $m$ . In view of this property and after replacing  $\delta_P m$  by  $\delta_{P,\Delta}$ , integral  $I_P$  becomes

$$I_P = \frac{1}{\langle E \rangle^2} \int_V (2\langle E \rangle \rho - \delta_P) \delta_{P,\Delta} dV. \quad (8)$$

The physical meaning of the quantity inside the parentheses can best be understood by taking into account equation (19),  $\delta_P = k\delta_M$ , and by considering the definition of  $\delta_M$ , *i.e.*  $\delta_M = \rho - \langle E \rangle \rho_{\varphi}$ . The quantity inside the parentheses then becomes



**Figure 1**  
Plot of the linear dependence of  $X$  upon  $E$  for  $P1$  (upper line) and  $\bar{P1}$  (lower line).

$$\begin{aligned} 2\langle E \rangle \rho - \delta_P &= 2\langle E \rangle \rho - k\delta_M \\ &= k \left[ \langle E \rangle \rho_\varphi - \left( 1 - \frac{2\langle E \rangle}{k} \right) \rho \right] \\ &= k\rho_X \end{aligned} \quad (9)$$

where  $\rho_X$  (like  $\rho$  and the phase synthesis  $\rho_\varphi$ ) is a density function with the strongest peaks at the atomic positions. The Fourier coefficients of  $\rho_X$  are given by

$$\mathbf{X}_H = \left[ \langle E \rangle - \left( 1 - \frac{2\langle E \rangle}{k} \right) E_H \right] \exp i\varphi_H. \quad (10)$$

Replacement of  $(2\langle E \rangle \rho - \delta_P)$  by  $k\rho_X$  in equation (8) yields

$$I_P = \frac{k}{\langle E \rangle^2} \int_V \rho_X \delta_{P,\Delta} dV. \quad (11)$$

By introducing  $\rho_X$  in the form of a Fourier synthesis in equation (11),

$$\begin{aligned} I_P(\Phi) &= \frac{k}{\langle E \rangle^2 V} \sum_H \left[ X_{-H} \exp(i\varphi_{-H}) \int_V \delta_{P,\Delta}(\mathbf{r}, \Phi) \right. \\ &\quad \left. \times \exp(i2\pi\mathbf{H}\mathbf{r}) d\mathbf{r} \right]. \end{aligned} \quad (12)$$

Subsequent substitution of the complex integral (*i.e.* the  $\mathbf{H}$  Fourier transform of  $\delta_{P,\Delta}$ ) by  $A_H + iB_H$ , under consideration that in the sum there is a  $-\mathbf{H}$  reflection for each  $\mathbf{H}$  one (both with opposite phase values), leads to

$$I_P(\Phi) = \frac{2k}{\langle E \rangle^2 V} \sum'_H X_H [\cos \varphi_H A_H(\Phi) + \sin \varphi_H B_H(\Phi)] \quad (13)$$

where the prime above the summation symbol indicates that the sum only extends over one hemisphere of reciprocal space.

The necessary condition for an extremum of  $R_P$  is

$$\partial R_P / \partial \varphi_H = 0 \quad (14)$$

for every  $\mathbf{H}$ . Since  $R_P = I_C - I_P$ , and  $I_C$  is phase independent, equation (14) is equivalent to

$$\frac{\partial I_P}{\partial \varphi_H} = \frac{2kX_H}{\langle E \rangle^2 V} [-\sin \varphi_H A_H(\Phi) + \cos \varphi_H B_H(\Phi)] = 0. \quad (15)$$

Finally, this may be rearranged to give the  $\delta_P$  phasing formula of  $R_P$

$$\tan \varphi_H^{\text{new}} = \frac{B_H(\Phi)}{A_H(\Phi)}, \quad (16)$$

which corresponds to equation (4) but is now expressed as a tangent formula. Closely related to this tangent formula is the  $\delta_M$  phasing formula

$$\varphi_H^{\text{new}} = \text{phase of} \left\{ \int_V \delta_{M,\Delta}(\mathbf{r}, \Phi) \exp(i2\pi\mathbf{H}\mathbf{r}) dV \right\}, \quad (17)$$

which results from replacing  $\delta_{P,\Delta}$  by  $k\delta_{M,\Delta}$  in equation (11) and then by proceeding in parallel to the  $\delta_P$  case.

The linear dependence of  $X$  upon  $E$  is plotted for  $P1$  and  $\bar{P1}$  in Fig. 1. For both, the presence of  $X$  causes a decrease in the relative weight of the strong reflections in integral  $I_P$ . For the  $P1$  case, the negative slope is low. For  $\bar{P1}$ , the negative slope is higher but here the proportion of weak  $E$  values is also much higher than for  $P1$ .

## APPENDIX A

### Relationship between $\delta_P$ and $\delta_M$

It is known that the modulus function  $M$  is a Patterson-type function. The principal difference between  $M$  and the Patterson function  $P$  lies in the relative heights between the origin and non-origin peaks. If the respective origin peaks are removed, the resulting  $M'$  and  $P'$  functions will be essentially proportional, *i.e.*  $P' = kM'$ . Since  $\delta_P$  is defined by

$$\delta_P(\mathbf{r}) = \int_V \rho_\varphi(\mathbf{u}) P'(\mathbf{r} - \mathbf{u}) d\mathbf{u}, \quad (18)$$

substitution of  $P'$  by  $kM'$  in this integral leads to

$$\delta_P = k\delta_M, \quad (19)$$

*i.e.*  $\delta_P$  and  $\delta_M$  are also proportional. The best  $k$  value should correspond to the minimum of

$$R(k) = V \int_V (P' - kM')^2 dV \quad (20)$$

which, by applying the Fourier theory, is equivalent to

$$R(k) = \sum_H [(E_H^2 - \langle E^2 \rangle) - k(E_H - \langle E \rangle)]^2. \quad (21)$$

It is straightforward to show that the least-squares estimate of  $k$  is

$$k = \frac{\sum_H (E_H^2 - \langle E^2 \rangle)(E_H - \langle E \rangle)}{\sum_H (E_H - \langle E \rangle)^2} \quad (22)$$

and, after some algebraic manipulation, it simplifies to

$$k = \frac{\langle E^3 \rangle - \langle E \rangle \langle E^2 \rangle}{\langle E^2 \rangle - \langle E \rangle^2}. \quad (23)$$

The value of  $k$  for  $P1$  can be obtained by introducing the moments of the theoretical distribution of the  $E$ 's for the acentric case in equation (23) ( $\langle E^3 \rangle = 1.329$ ,  $\langle E^2 \rangle = 1$  by definition and  $\langle E \rangle = 0.886$ ). For  $\bar{P1}$  the moments for the centric case should be used ( $\langle E^3 \rangle = 1.596$ ,  $\langle E^2 \rangle = 1$  and  $\langle E \rangle = 0.798$ ). The resulting  $k$  values are 2.06 for  $P1$  and 2.20 for  $\bar{P1}$ .

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