SUPPLEMENTARY PUBLICATION MATERIAL

On integrating the techniques of direct methods and SIRAS: The probabilistic theory of doublets and its applications

Hongliang Xu* and Herbert A. Hauptman

Hauptman-Woodward Medical Research Institute and Department of Structural Biology, School of Medicine and Biomedical Sciences, State University of New York at Buffalo, 73 High Street, Buffalo, NY 14203, USA. E-mail: xu@hwi.buffalo.edu

Abstract

The mathematical formalism of direct methods is here applied to the SIRAS case. Specifically, the joint probability distribution of three structure factors, which plays the central role in the probabilistic theory of the two-phase structure invariants (doublets), is derived. This distribution leads directly to the conditional probability distribution of the two-phase structure invariants, given the values of selected sets of magnitudes. Furthermore, a probabilistic formula for estimating individual phases of the derivative structure is derived, provided that the heavy-atom substructure is assumed to be known. The formulas were tested for experimental SIRAS data and results are reported.

Appendix A.
Preliminary formulas

For convenient reference a number of frequently used formulas are listed here. First, from elementary trigonometry,

$$\sum_{i=1}^{n} A_i \cos(\varphi + \alpha_i) = X \cos(\varphi + \xi), \tag{1}$$

where

$$X \cos \xi = \sum_{i=1}^{n} A_i \cos \alpha_i, \tag{2}$$

$$X \sin \xi = \sum_{i=1}^{n} A_i \sin \alpha_i, \tag{3}$$

$$X^2 = \sum_{j=1}^{n} \sum_{i=1}^{n} A_i A_j \cos(\alpha_i - \alpha_j), \tag{4}$$

so that X and ξ are independent of φ.

Next, for $b > 0$

$$\int_{\rho=0}^{\infty} I_n(a\rho) exp(-b\rho^2)\rho^{n+1} d\rho = \frac{a^n}{(2b)^{n+1}} exp\left(\frac{a^2}{4b}\right), \tag{5}$$

where I_n is the modified Bessel function of degree n. In particular, when $n = 0$,

$$I_0(a\rho) = \frac{1}{2\pi} \int_{\theta=0}^{2\pi} exp\Big[a\rho \cos(\theta - \alpha)\Big] d\theta. \tag{6}$$

Substitute (6) into (5). We have the final formula

$$\int_{\rho=0}^{\infty} \int_{\theta=0}^{2\pi} \rho exp\Big[-b\rho^2 - a\rho \cos(\theta - \alpha)\Big] d\rho d\theta = \frac{\pi}{b} exp\left(\frac{a^2}{4b}\right). \tag{7}$$

Appendix B.
Derivation of $q_j(\sigma, \rho, \bar{\rho}, \gamma, \theta, \bar{\theta})$ and $\prod_{j=1}^{N} q_j(\sigma, \rho, \bar{\rho}, \gamma, \theta, \bar{\theta})$

Denote by $P_6 = P(R, S, \bar{S}; \varphi, \psi, \bar{\psi})$ the joint probability distribution of the three magnitudes R, S, $\bar{S}$ and the three phases φ, ψ, $\bar{\psi}$ of the normalized structure factors

E_H, G_H, $G_{\bar{H}}$. Then the joint probability distribution is given by the sixfold integral

$$P_6 = P(R,S,\bar{S};\varphi,\psi,\bar{\psi}) = \frac{1}{(2\pi)^6} RS\bar{S} \int_{\sigma,\rho,\bar{\rho}=0}^{\infty} \int_{\gamma,\theta,\bar{\theta}=0}^{2\pi} \sigma\rho\bar{\rho} \times \exp\Big\{-i\Big[R\sigma\cos(\gamma-\varphi) + S\rho\cos(\theta-\psi) + \bar{S}\bar{\rho}\cos(\bar{\theta}-\bar{\psi})\Big]\Big\} \times \prod_{j=1}^{N} q_j(\sigma,\rho,\bar{\rho},\gamma,\theta,\bar{\theta}) \;\; d\sigma d\rho d\bar{\rho} d\gamma d\theta d\bar{\theta}, \quad (8)$$

where

$$q_j(\sigma,\rho,\bar{\rho},\gamma,\theta,\bar{\theta}) = \Big\langle \exp\Big\{ i(f_{jH}\alpha_H^{-1/2})\sigma\cos(2\pi\mathbf{H}\cdot\mathbf{r}_j-\gamma) + i(|g_{jH}|\beta_H^{-1/2}) \Big[\rho\cos(\delta_{jH}+2\pi\mathbf{H}\cdot\mathbf{r}_j-\theta) + \bar{\rho}\cos(\delta_{jH}-2\pi\mathbf{H}\cdot\mathbf{r}_j-\bar{\theta})\Big]\Big\}\Big\rangle_{\mathbf{r}_j} \quad (9)$$

Using the approximation

$$\exp(x) \approx 1 + x + \frac{1}{2}x^2,$$

we have

$$q_j(\sigma,\rho,\bar{\rho},\gamma,\theta,\bar{\theta}) \approx 1 - \frac{f_{jH}^2}{4\alpha_H}\sigma^2 - \frac{|g_{jH}|^2}{4\beta_H}(\rho^2+\bar{\rho}^2) - \frac{f_{jH}|g_{jH}|}{2(\alpha_H\beta_H)^{1/2}}\sigma\rho\cos(\delta_{jH}+\gamma-\theta) - \frac{f_{jH}|g_{jH}|}{2(\alpha_H\beta_H)^{1/2}}\sigma\bar{\rho}\cos(\delta_{jH}-\gamma-\bar{\theta}) - \frac{|g_{jH}|^2}{2\beta_H}\rho\bar{\rho}\cos(2\delta_{jH}-\theta-\bar{\theta}), \quad (10)$$

Since

$$\log q_j \approx -1 + q_j,$$

then

$$\prod_{j=1}^{N} q_j = \exp\Big(\log\prod_{j=1}^{N} q_j\Big) = \exp\Big(\sum_{j=1}^{N}\log q_j\Big) \approx \exp\Big(\sum_{j=1}^{N}(-1+q_j)\Big)$$
$$= \exp\Big\{-\frac{1}{4}(\sigma^2+\rho^2+\bar{\rho}^2) - \frac{1}{2}\sigma\rho\sum_{j=1}^{N}\frac{f_{jH}|g_{jH}|}{(\alpha_H\beta_H)^{1/2}}\cos(\delta_{jH}+\gamma-\theta) - \frac{1}{2}\sigma\bar{\rho}\sum_{j=1}^{N}\frac{f_{jH}|g_{jH}|}{(\alpha_H\beta_H)^{1/2}}\cos(\delta_{jH}-\gamma-\bar{\theta}) - \frac{1}{2}\rho\bar{\rho}\sum_{j=1}^{N}\frac{|g_{jH}|^2}{\beta_H}\cos(2\delta_{jH}-\theta-\bar{\theta})\Big\}, \quad (11)$$

Define

$$C_{mn} = \frac{1}{(\alpha_H^m\beta_H^n)^{1/2}}\sum_{j=1}^{N} f_{jH}^m|g_{jH}|^n\cos(n\delta_{jH}), \quad (12)$$

$$S_{mn} = \frac{1}{(\alpha_H^m\beta_H^n)^{1/2}}\sum_{j=1}^{N} f_{jH}^m|g_{jH}|^n\sin(n\delta_{jH}), \quad (13)$$

and

$$X_{mn} \cos \xi_{mn} = C_{mn}, \tag{14}$$

$$X_{mn} \sin \xi_{mn} = -S_{mn}. \tag{15}$$

Substitute (12)-(15) into (11). We have

$$\prod_{j=1}^{N} q_j(\sigma, \rho, \bar{\rho}, \gamma, \theta, \bar{\theta}) \approx \exp\Big\{ -\frac{1}{4}(\sigma^2 + \rho^2 + \bar{\rho}^2) - \frac{1}{2}\sigma\rho X_{11} \cos(\theta - \gamma + \xi_{11}) \\ -\frac{1}{2}\sigma\bar{\rho}X_{11}\cos(\bar{\theta} + \gamma + \xi_{11}) - \frac{1}{2}\rho\bar{\rho}X_{02}\cos(\theta + \bar{\theta} + \xi_{02})\Big\}. \tag{16}$$

Appendix C.
Evaluation of the sixfold integral

Substitute (16) into (8). We have

$$P_6 \approx \frac{1}{(2\pi)^6} RS\bar{S} \int_{\sigma,\rho,\bar{\rho}=0}^{\infty} \int_{\gamma,\theta,\bar{\theta}=0}^{2\pi} \sigma\rho\bar{\rho} \exp\Big[-\frac{1}{4}(\sigma^2 + \rho^2 + \bar{\rho}^2)\Big] \\ \exp\Big\{ -i\Big[R\sigma\cos(\gamma - \varphi) + S\rho\cos(\theta - \psi) + \bar{S}\bar{\rho}\cos(\bar{\theta} - \bar{\psi})\Big] - \frac{1}{2}\sigma\rho X_{11}\cos(\theta - \gamma + \xi_{11}) \\ -\frac{1}{2}\sigma\bar{\rho}X_{11}\cos(\bar{\theta} + \gamma + \xi_{11}) - \frac{1}{2}\rho\bar{\rho}X_{02}\cos(\theta + \bar{\theta} + \xi_{02})\Big\} \; d\sigma d\rho d\bar{\rho} d\gamma d\theta d\bar{\theta}, \tag{17}$$

C.1. The (σ, γ) integration

Collect all terms in the second exponent of (17) involving σ and γ:

$$\begin{aligned} & -iR\sigma\cos(\gamma - \varphi) - \frac{1}{2}\sigma\rho X_{11}\cos(\gamma - \theta - \xi_{11}) - \frac{1}{2}\sigma\bar{\rho}X_{11}\cos(\gamma + \bar{\theta} + \xi_{11}) \\ = & -i\sigma\Big[R\cos(\gamma - \varphi) - \frac{i}{2}\rho X_{11}\cos(\gamma - \theta - \xi_{11}) - \frac{i}{2}\bar{\rho}X_{11}\cos(\gamma + \bar{\theta} + \xi_{11})\Big] \\ = & -i\sigma U\cos(\gamma - \alpha) \end{aligned} \tag{18}$$

where

$$U\cos\alpha = R\cos\varphi - \frac{i}{2}\rho X_{11}\cos(\theta + \xi_{11}) - \frac{i}{2}\bar{\rho}X_{11}\cos(\bar{\theta} + \xi_{11}), \tag{19}$$

$$U\sin\alpha = R\sin\varphi - \frac{i}{2}\rho X_{11}\sin(\theta + \xi_{11}) + \frac{i}{2}\bar{\rho}X_{11}\sin(\bar{\theta} + \xi_{11}). \tag{20}$$

It follows, in view of (4), that

$$U^2 = R^2 - \frac{1}{4}X_{11}^2(\rho^2 + \bar{\rho}^2) - iR\rho X_{11}\cos(\theta - \varphi + \xi_{11})$$
$$-iR\bar{\rho}X_{11}\cos(\bar{\theta} + \varphi + \xi_{11}) - \frac{1}{2}\rho\bar{\rho}X_{11}^2\cos(\theta + \bar{\theta} + 2\xi_{11}). \qquad (21)$$

The twofold integral of (σ, γ), in view of (7), becomes

$$\int_{\sigma=0}^{\infty}\int_{\gamma=0}^{2\pi}\sigma\exp\Big[-\frac{1}{4}\sigma^2 - i\sigma U\cos(\gamma - \alpha)\Big]d\sigma d\gamma = 4\pi\exp(-U^2). \qquad (22)$$

Substitute (21) and (22) into (17). We have

$$P_6 \approx \frac{4\pi}{(2\pi)^6}RS\bar{S}\exp(-R^2)\int_{\rho,\bar{\rho}=0}^{\infty}\int_{\theta,\bar{\theta}=0}^{2\pi}\rho\bar{\rho}\exp\Big[-\frac{1}{4}(1 - X_{11}^2)(\rho^2 + \bar{\rho}^2)\Big]$$
$$\exp\Big\{-i\Big[S\rho\cos(\theta - \psi) + \bar{S}\bar{\rho}\cos(\bar{\theta} - \bar{\psi}) - R\rho X_{11}\cos(\theta - \varphi + \xi_{11}) - R\bar{\rho}X_{11}\cos(\bar{\theta} + \varphi + \xi_{11})\Big]$$
$$-\frac{1}{2}\rho\bar{\rho}X_{02}\cos(\theta + \bar{\theta} + \xi_{02}) + \frac{1}{2}\rho\bar{\rho}X_{11}^2\cos(\theta + \bar{\theta} + 2\xi_{11})\Big\}\; d\rho d\bar{\rho}d\theta d\bar{\theta}. \qquad (23)$$

C.2. The (ρ, θ) integration

Collect all terms in the second exponent of (23) involving ρ and θ:

$$-iS\rho\cos(\theta - \psi) + iR\rho X_{11}\cos(\theta - \varphi + \xi_{11}) - \frac{1}{2}\rho\bar{\rho}X_{02}\cos(\theta + \bar{\theta} + \xi_{02}) + \frac{1}{2}\rho\bar{\rho}X_{11}^2\cos(\theta + \bar{\theta} + 2\xi_{11})$$
$$= -i\rho\Big[S\cos(\theta - \psi) - RX_{11}\cos(\theta - \varphi + \xi_{11}) - \frac{i}{2}\bar{\rho}X_{02}\cos(\theta + \bar{\theta} + \xi_{02}) + \frac{i}{2}\bar{\rho}X_{11}^2\cos(\theta + \bar{\theta} + 2\xi_{11})\Big]$$
$$= -i\rho V\cos(\theta - \beta) \qquad (24)$$

where

$$V\cos\beta = S\cos\psi - RX_{11}\cos(\varphi - \xi_{11}) - \frac{i}{2}\bar{\rho}X_{02}\cos(\bar{\theta} + \xi_{02}) + \frac{i}{2}\bar{\rho}X_{11}^2\cos(\bar{\theta} + 2\xi_{11}) \qquad (25)$$
$$V\sin\beta = S\sin\psi - RX_{11}\sin(\varphi - \xi_{11}) + \frac{i}{2}\bar{\rho}X_{02}\sin(\bar{\theta} + \xi_{02}) - \frac{i}{2}\bar{\rho}X_{11}^2\sin(\bar{\theta} + 2\xi_{11}) \qquad (26)$$

It follows, in view of (4) again, that

$$V^2 = S^2 + R^2X_{11}^2 - 2SRX_{11}\cos(\psi - \varphi + \xi_{11}) - \frac{1}{4}\bar{\rho}^2\Big[X_{11}^4 + X_{02}^2 - 2X_{11}^2X_{02}\cos(\xi_{02} - 2\xi_{11})\Big]$$
$$+i\bar{\rho}\Big[SX_{11}^2\cos(\psi + \bar{\theta} + 2\xi_{11}) - SX_{02}\cos(\psi + \bar{\theta} + \xi_{02})$$
$$+RX_{11}X_{02}\cos(\varphi + \bar{\theta} - \xi_{11} + \xi_{02}) - RX_{11}^3\cos(\varphi + \bar{\theta} + \xi_{11})\Big]. \qquad (27)$$

The twofold integral of (ρ, θ), in view of (7) again, becomes

$$\int_{\rho=0}^{\infty} \int_{\theta=0}^{2\pi} \rho \exp\Big[-\frac{1}{4}(1-X_{11}^2)\rho^2 - i\rho V \cos(\theta-\beta)\Big] d\rho d\theta = \frac{4\pi}{1-X_{11}^2} \exp(-\frac{V^2}{1-X_{11}^2}). \quad (28)$$

C.3. The $(\bar{\rho}, \bar{\theta})$ integration

Substitute (27) and (28) into (23). We have

$$\begin{aligned} P_6 &\approx \frac{(4\pi)^2}{(2\pi)^6(1-X_{11}^2)} RS\bar{S} \exp\Big\{-\frac{1}{1-X_{11}^2}\Big[R^2+S^2-2RSX_{11}\cos(\psi-\varphi+\xi_{11})\Big]\Big\} \\ &\quad \int_{\bar{\rho}=0}^{\infty} \int_{\bar{\theta}=0}^{2\pi} \bar{\rho} \exp\Big[-\frac{1}{4}(1-Z^2)\bar{\rho}^2 - i\bar{\rho} W \cos(\bar{\theta}-\mu)\Big] d\bar{\rho} d\bar{\theta} \\ &= \frac{(4\pi)^2}{(2\pi)^6(1-X_{11}^2)} RS\bar{S} \exp\Big\{-\frac{1}{1-X_{11}^2}\Big[R^2+S^2-2RSX_{11}\cos(\psi-\varphi+\xi_{11})\Big]\Big\} \\ &\quad \frac{4\pi}{1-Z^2} exp\Big(-\frac{W^2}{1-Z^2}\Big), \end{aligned} \quad (29)$$

where

$$Z^2 = \frac{X_{11}^2 + X_{02}^2 - 2X_{11}^2 X_{02}\cos(\xi_{02}-2\xi_{11})}{1-X_{11}^2}, \quad (30)$$

$$\begin{aligned} W\cos\mu &= \bar{S}\cos\bar{\psi} - \frac{RX_{11}}{1-X_{11}^2}\cos(\varphi+\xi_{11}) + \frac{RX_{11}X_{02}}{1-X_{11}^2}\cos(\varphi-\xi_{11}+\xi_{02}) \\ &\quad + \frac{SX_{11}^2}{1-X_{11}^2}\cos(\psi+2\xi_{11}) - \frac{SX_{02}}{1-X_{11}^2}\cos(\psi+\xi_{02}), \end{aligned} \quad (31)$$

$$\begin{aligned} W\sin\mu &= \bar{S}\sin\bar{\psi} + \frac{RX_{11}}{1-X_{11}^2}\sin(\varphi+\xi_{11}) - \frac{RX_{11}X_{02}}{1-X_{11}^2}\sin(\varphi-\xi_{11}+\xi_{02}) \\ &\quad - \frac{SX_{11}^2}{1-X_{11}^2}\sin(\psi+2\xi_{11}) + \frac{SX_{02}}{1-X_{11}^2}\sin(\psi+\xi_{02}). \end{aligned} \quad (32)$$

It follows from (31) and (32) that

$$\begin{aligned} W^2 &= \bar{S}^2 + \frac{R^2X_{11}^2 + R^2X_{11}^2X_{02}^2 + S^2X_{11}^4 + S^2X_{02}^2}{(1-X_{11}^2)^2} \\ &\quad - \frac{2R\bar{S}X_{11}}{1-X_{11}^2}\cos(\varphi+\bar{\psi}+\xi_{11}) + \frac{2R\bar{S}X_{11}X_{02}}{1-X_{11}^2}\cos(\varphi+\bar{\psi}-\xi_{11}+\xi_{02}) \\ &\quad + \frac{2S\bar{S}X_{11}^2}{1-X_{11}^2}\cos(\psi+\bar{\psi}+2\xi_{11}) - \frac{2S\bar{S}X_{02}}{1-X_{11}^2}\cos(\psi+\bar{\psi}+\xi_{02}) \\ &\quad - \frac{2(R^2+S^2)X_{11}^2X_{02}}{(1-X_{11}^2)^2}\cos(2\xi_{11}-\xi_{02}) - \frac{2RSX_{11}(X_{11}^2+X_{02}^2)}{(1-X_{11}^2)^2}\cos(\varphi-\psi-\xi_{11}) \\ &\quad + \frac{2RSX_{11}X_{02}}{(1-X_{11}^2)^2}\cos(\varphi-\psi+\xi_{11}-\xi_{02}) + \frac{2RSX_{11}^3X_{02}}{(1-X_{11}^2)^2}\cos(\varphi-\psi-3\xi_{11}+\xi_{02}) \end{aligned} \quad (33)$$

C.4. The joint probability distribution

Substitute (33) into (29). We have

$$P_6 \approx \frac{RS\bar{S}}{\pi^3(1-X_{11}^2)(1-Z^2)} \exp\left[-\frac{(1-X_{02}^2)R^2 + (1-X_{11}^2)(S^2+\bar{S}^2)}{(1-X_{11}^2)(1-Z^2)}\right]$$
$$\exp\left[W_1 RS\cos(\varphi-\psi+\lambda) + W_1 R\bar{S}\cos(\varphi+\bar{\psi}-\lambda) + W_2 S\bar{S}\cos(\psi+\bar{\psi}+\mu)\right], \qquad (34)$$

where

$$Z^2 = \frac{C_{11}^2 + S_{11}^2 + C_{02}^2 + S_{02}^2 - 2C_{11}^2 C_{02} + 2S_{11}^2 C_{02} - 4C_{11}S_{11}S_{02}}{1 - C_{11}^2 - S_{11}^2}, \qquad (35)$$

$$W_1 = \frac{2U}{(1-X_{11}^2)(1-Z^2)}, \qquad (36)$$

$$W_2 = \frac{2V}{(1-X_{11}^2)(1-Z^2)}, \qquad (37)$$

and

$$U\cos\lambda = C_{11} - C_{11}C_{02} - S_{11}S_{02}, \qquad (38)$$

$$U\sin\lambda = S_{11} + S_{11}C_{02} - C_{11}S_{02}, \qquad (39)$$

$$V\cos\mu = C_{02} - C_{11}^2 + S_{11}^2, \qquad (40)$$

$$V\sin\mu = 2C_{11}S_{11} - S_{02}. \qquad (41)$$