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Profile function for Vega/Sirius and its derivatives with respect to refinable parameters

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This document was written while developing a Rietveld-refinement program, RIETAN-9001T for the time-of-flight (TOF) neutron powder diffractometers Vega and Sirius at the KENS pulsed neutron source. We are very proud that both Vega/Sirius and RIETAN-2001T have been developed quite independently of predecessors in the United States and Europe. In general, the profile shape in the time-of-flight (TOF) neutron powder diffraction pattern is most complex, depending on the shape, temperature, and material of the moderator, the flight path, and the geometry of the diffractometer. This is also the case for Vega/Sirius. Without such a detailed document, we would forget its details, in particular, derivation of partial derivatives of the profile function with respect to profile parameters, conversion parameters, and elements of the metric tensor. Two intense pulsed neutron sources are expected to be built in Japan in future. This document must be used conveniently when developing a Rietveld-refinement program optimized for powder diffractometers which will be installed in these neutron sources.

1. Profile function

$$F(\Delta t_{0i}) = (1-R)F_1(\Delta t_{0i}) + RF_2(\Delta t_{0i})$$

$$\Delta t_{0i} = t_i - t_0$$

In what follows, variable names are attatched with three different symbols showing subroutines where they are calculated:

★: SUBROUTINE UPDATE in update.f

○: SUBROUTINE DERREF in ran3.f

●: SUBROUTINE DPRFL in ran3.f

1.1 Profile in the region of λ shorter than the peak position ($F = F_1 = F_2$)

Pseudo-Voigt function (= Lorentz function + Gauss function No. 1)
Note that the FWHM's of the Lorentz and Gauss components differ from each other.

$$t_i \le t_0 \qquad F(\Delta t_{0i}) = A\left[\eta\left(1 + \frac{\Delta t_{0i}^2}{2\sigma_0^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}^2}{2\sigma_1^2}\right)\right]$$

1.2 Profile in the region of λ longer than the peak position

Gauss function No. 2

$$t_0 \le t_i \le t_0 + \gamma_1\sigma_2^2 \qquad F_1(\Delta t_{0i}) = A\exp\left(-\frac{\Delta t_{0i}^2}{2\sigma_2^2}\right)$$

Exponential function No. 1

$$t_i \ge t_0 + \gamma_1\sigma_2^2 \qquad F_1(\Delta t_{0i}) = A\exp\left(\frac{\gamma_1^2\sigma_2^2}{2} - \gamma_1\Delta t_{0i}\right) = A_1\exp(-\gamma_1\Delta t_{0i})$$

$$A_1 = A\exp\left(\frac{\gamma_1^2\sigma_2^2}{2}\right)$$

Gauss function No. 2

$$t_0 \le t_i \le t_0 + \gamma_2\sigma_2^2 \qquad F_2(\Delta t_{0i}) = A\exp\left(-\frac{\Delta t_{0i}^2}{2\sigma_2^2}\right)$$

Exponential function No. 2

$$t_i \ \geq \ t_0 \ + \ \gamma_2 \sigma_2{}^2 \qquad F_2(\Delta t_{0i}) \ = \ A\exp\left(\frac{\gamma_2{}^2\sigma_2{}^2}{2} - \gamma_2 \Delta t_{0i}\right) \ = \ A_2 \exp(-\gamma_2 \Delta t_{0i})$$

$$A_2 \ = \ A\exp\left(\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right)$$

1.3 Normalization factor

★ FNORM

$$\begin{aligned} A^{-1} &= B \\ &= \eta \frac{\pi}{\sqrt{2}} \sigma_0 + (1-\eta)\sqrt{\frac{\pi}{2}}\,\sigma_1 \\ &\quad + \sqrt{\frac{\pi}{2}}(1-R)\sigma_2 \operatorname{erf}\left(\frac{\gamma_1\sigma_2}{\sqrt{2}}\right) + (1-R)\frac{1}{\gamma_1}\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) \\ &\quad + \sqrt{\frac{\pi}{2}}R\sigma_2 \operatorname{erf}\left(\frac{\gamma_2\sigma_2}{\sqrt{2}}\right) + R\frac{1}{\gamma_2}\exp\left(-\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right) \end{aligned}$$

1.4 Dependence of primary profile parameters on *d*

The following equations representing primary profile parameters versus d were determined using TableCurve 2D (Jandel Scientific).

★ SIGMA0 (Lorentz function)

$$\sigma_0 = \exp\left(\sigma_{01} + \sigma_{02} d^{2.5} + \sigma_{03}\sqrt{d}\right)$$

★ SIGMA1 (Gauss function No. 1)

$$\sigma_1 = \exp\left(\sigma_{11} + \sigma_{12}\frac{\ln d}{d} + \frac{\sigma_{13}}{d^{1.5}}\right)$$

★ ETA (Lorentz fraction)

$$\eta = \eta_1 + \eta_2 d$$

★ SIGMA2 (Gauss function No. 2)

$$\sigma_2 = \exp\left(\sigma_{21} + \sigma_{22}\sqrt{d}\right)$$

★ GAMMA1 (exponential function No. 1)

$$\gamma_1 = \gamma_{11} + \gamma_{12} \exp\left(-\gamma_{13} d^{1.5}\right)$$

★ GAMMA2 (exponential function No. 2)

$$\gamma_2 = \gamma_{21} + \gamma_{22} \exp\left(-\gamma_{23} d\right)$$

★ R (fraction of the Cole-Windsor function)

$$R = R_1 + \frac{R_2}{1 + \left(\frac{d}{R_3}\right)^{R_4}}$$

At present, σ_{02} and γ_{22} are fixed at 0 and 0.01, respectively.

TOF (µs) at the peak position of a Bragg reflection

$$t_0 = c_0 + c_1 d + c_2 d^2 + c_3 d^3 + c_4 d^4$$

2. Derivatives of the profile function with respect to parameters contained in it

(1) For $\Delta t_0 < 0$

$$\frac{\partial F}{\partial x} = (1-R)\frac{\partial F_1}{\partial x} + R\frac{\partial F_2}{\partial x}$$

where $x = t_0,\ d,\ \sigma_0,\ \sigma_1,\ \eta, \sigma_2,\ \gamma_1,\ \gamma_2,$ and R

(2) For $\Delta t_0 > 0$, $\partial F/\partial x$ can be calculated directly.

Derivatives with respect to d are approximated to be $(\partial F/\partial t_0)(\partial t_0/\partial d)$. The dependence of the primary profile parameters upon d is neglected to make the derivatives much simpler.

Derivative of the error function

$$\frac{\mathrm{d}}{\mathrm{d}x}\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\exp\left(-x^2\right)$$

2.1 t_0

○ DT0DD

$$\frac{\partial t_0}{\partial d} = c_1 + 2c_2 d + 3c_3 d^2 + 4c_4 d^3$$

2.2 A

$$\frac{\partial A}{\partial x} = \frac{\partial}{\partial x}\left(B^{-1}\right) = -B^{-2}\frac{\partial B}{\partial x} = -A^2\frac{\partial B}{\partial x}$$

○ DADS0

$$\frac{\partial A}{\partial \sigma_0} = -A^2\frac{\partial B}{\partial \sigma_0} = -A^2\eta\frac{\pi}{\sqrt{2}}$$

○ DADS1

$$\frac{\partial A}{\partial \sigma_1} = -A^2 \frac{\partial B}{\partial \sigma_1} = -A^2 (1 - \eta)\sqrt{\frac{\pi}{2}}$$

○ DADET

$$\frac{\partial A}{\partial \eta} = -A^2 \frac{\partial B}{\partial \eta} = -A^2 \left(\frac{\pi}{\sqrt{2}} \sigma_0 - \sqrt{\frac{\pi}{2}}\, \sigma_1 \right)$$

○ DADS2

$$\frac{\partial A}{\partial \sigma_2} = -A^2 \frac{\partial B}{\partial \sigma_2}$$

$$= -A^2 \left[\begin{array}{l} \sqrt{\frac{\pi}{2}}(1-R)\mathrm{erf}\left(\frac{\gamma_1 \sigma_2}{\sqrt{2}}\right) + \sqrt{\frac{\pi}{2}}(1-R)\sigma_2 \frac{\gamma_1}{\sqrt{2}} \frac{2}{\sqrt{\pi}} \exp\left(-\frac{\gamma_1{}^2 \sigma_2{}^2}{2}\right) \\ + (1-R)\frac{1}{\gamma_1}\left(-\frac{2\gamma_1{}^2\sigma_2}{2}\right)\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) \\ + \sqrt{\frac{\pi}{2}} R\mathrm{erf}\left(\frac{\gamma_2\sigma_2}{\sqrt{2}}\right) + \sqrt{\frac{\pi}{2}} R\sigma_2 \frac{\gamma_2}{\sqrt{2}} \frac{2}{\sqrt{\pi}} \exp\left(-\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right) \\ + R\frac{1}{\gamma_2}\left(-\frac{2\gamma_2{}^2\sigma_2}{2}\right)\exp\left(-\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right) \end{array} \right]$$

$$= -A^2 \sqrt{\frac{\pi}{2}} \left[(1-R)\mathrm{erf}\left(\frac{\gamma_1\sigma_2}{\sqrt{2}}\right) + R\mathrm{erf}\left(\frac{\gamma_2\sigma_2}{\sqrt{2}}\right) \right]$$

○ DADG1

$$\frac{\partial A}{\partial \gamma_1} = -A^2 \frac{\partial B}{\partial \gamma_1}$$

$$= -A^2 \left[\begin{array}{l} \sqrt{\frac{\pi}{2}}(1-R)\sigma_2 \frac{\sigma_2}{\sqrt{2}} \frac{2}{\sqrt{\pi}} \exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) \\ + (1-R)\left(-\frac{1}{\gamma_1{}^2}\right)\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) (1-R)\frac{1}{\gamma_1}\left(-\frac{2\gamma_1\sigma_2{}^2}{2}\right)\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) \end{array} \right]$$

$$= A^2 (1-R) \frac{1}{\gamma_1{}^2} \exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

○ DADG2

$$\frac{\partial A}{\partial \gamma_2} = -A^2 \frac{\partial B}{\partial \gamma_2} = A^2 R \frac{1}{\gamma_2{}^2} \exp\left(-\frac{\gamma_2{}^2 \sigma_2{}^2}{2}\right)$$

○ DADR

$$\frac{\partial A}{\partial R} = -A^2 \frac{\partial B}{\partial R}$$

$$= -A^2\left[-\sqrt{\frac{\pi}{2}}\sigma_2 \mathrm{erf}\left(\frac{\gamma_1\sigma_2}{\sqrt{2}}\right) - \frac{1}{\gamma_1}\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) + \sqrt{\frac{\pi}{2}}\sigma_2 \mathrm{erf}\left(\frac{\gamma_2\sigma_2}{\sqrt{2}}\right) + \frac{1}{\gamma_2}\exp\left(-\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right)\right]$$

$$= A^2\left\{\sqrt{\frac{\pi}{2}}\sigma_2\left[\mathrm{erf}\left(\frac{\gamma_1\sigma_2}{\sqrt{2}}\right) - \mathrm{erf}\left(\frac{\gamma_2\sigma_2}{\sqrt{2}}\right)\right] + \frac{1}{\gamma_1}\exp\left(-\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) - \frac{1}{\gamma_2}\exp\left(-\frac{\gamma_2{}^2\sigma_2{}^2}{2}\right)\right\}$$

2.3 Pseudo-Voigt function

$$t_i \le t_0 \qquad F(\Delta t_{0i}) = A\left[\eta\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

● DFDT0

$$\frac{\partial F}{\partial t_0} = \frac{\partial \Delta t_{0i}}{\partial t_0}\frac{\partial F}{\partial \Delta t_{0i}}$$

$$= -A\left[-\eta\frac{\Delta t_{0i}}{\sigma_0{}^2}\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-2} + (1-\eta)\left(-\frac{\Delta t_{0i}}{\sigma_1{}^2}\right)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

$$= A\Delta t_{0i}\left[\eta\frac{1}{\sigma_0{}^2}\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-2} + (1-\eta)\frac{1}{\sigma_1{}^2}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

● DFDD

$$\frac{\partial F}{\partial d} = \frac{\partial F}{\partial t_0}\frac{\partial t_0}{\partial d}$$

● DFDS0

$$\frac{\partial F}{\partial \sigma_0} = \frac{\partial A}{\partial \sigma_0}\left[\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)\right]$$

$$+ A\frac{\partial}{\partial \sigma_0}\left[\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)\right]$$

$$= \frac{\partial A}{\partial \sigma_0}\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + \frac{\partial A}{\partial \sigma_0}(1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)$$

$$+ A\eta\left(\frac{\Delta t_{0i}^{\,2}}{\sigma_0^{\,3}}\right)\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-2}$$

$$= \left[\frac{\partial A}{\partial \sigma_0} + A\frac{\Delta t_{0i}^{\,2}}{\sigma_0^{\,3}}\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1}\right]\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + \frac{\partial A}{\partial \sigma_0}(1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)$$

● DFDS1

$$\frac{\partial F}{\partial \sigma_1} = \frac{\partial A}{\partial \sigma_1}\left[\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)\right]$$

$$+ A\frac{\partial}{\partial \sigma_1}\left[\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)\right]$$

$$= \frac{\partial A}{\partial \sigma_1}\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + \frac{\partial A}{\partial \sigma_1}(1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)$$

$$+ A(1-\eta)\frac{\Delta t_{0i}^{\,2}}{\sigma_1^{\,3}}\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)$$

$$= \frac{\partial A}{\partial \sigma_1}\eta\left(1 + \frac{\Delta t_{0i}^{\,2}}{2\sigma_0^{\,2}}\right)^{-1} + \left(\frac{\partial A}{\partial \sigma_1} + A\frac{\Delta t_{0i}^{\,2}}{\sigma_1^{\,3}}\right)(1-\eta)\exp\left(-\frac{\Delta t_{0i}^{\,2}}{2\sigma_1^{\,2}}\right)$$

● DFDET

$$\frac{\partial F}{\partial \eta} = \left(\frac{\partial A}{\partial \eta}\eta + A\right)\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + \left[\frac{\partial A}{\partial \eta}(1-\eta) - A\right]\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)$$

● DFDS2

$$\frac{\partial F}{\partial \sigma_2} = \frac{\partial A}{\partial \sigma_2}\left[\eta\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

● DFDG1

$$\frac{\partial F}{\partial \gamma_1} = \frac{\partial A}{\partial \gamma_1}\left[\eta\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

● DFDG2

$$\frac{\partial F}{\partial \gamma_2} = \frac{\partial A}{\partial \gamma_2}\left[\eta\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

● DFDR

$$\frac{\partial F}{\partial R} = \frac{\partial A}{\partial R}\left[\eta\left(1 + \frac{\Delta t_{0i}{}^2}{2\sigma_0{}^2}\right)^{-1} + (1-\eta)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_1{}^2}\right)\right]$$

2.4 Gauss function No. 2 (multiplied by $1 - R$)

$$t_0 \le t_i \le t_0 + \gamma_1\sigma_2{}^2 \qquad F_1(\Delta t_{0i}) = A\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DT0

$$\frac{\partial F_1}{\partial t_0} = \frac{\partial \Delta t_{0i}}{\partial t_0}\frac{\partial F_1}{\partial \Delta t_{0i}} = -A\left(-\frac{\Delta t_{0i}}{\sigma_2{}^2}\right)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

$$= A\frac{\Delta t_{0i}}{\sigma_2{}^2}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DD

$$\frac{\partial F_1}{\partial d} = \frac{\partial F_1}{\partial t_0}\frac{\partial t_0}{\partial d}$$

● DF1DS0

$$\frac{\partial F_1}{\partial \sigma_0} = \frac{\partial A}{\partial \sigma_0}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DS1

$$\frac{\partial F_1}{\partial \sigma_1} = \frac{\partial A}{\partial \sigma_1}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DET

$$\frac{\partial F_1}{\partial \eta} = \frac{\partial A}{\partial \eta}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DS2

$$\frac{\partial F_1}{\partial \sigma_2} = \left(\frac{\partial A}{\partial \sigma_2} + A\frac{\Delta t_{0i}{}^2}{\sigma_2{}^3}\right)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DG1

$$\frac{\partial F_1}{\partial \gamma_1} = \frac{\partial A}{\partial \gamma_1}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DG2

$$\frac{\partial F_1}{\partial \gamma_2} = \frac{\partial A}{\partial \gamma_2}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

● DF1DR

$$\frac{\partial F_1}{\partial R} = \frac{\partial A}{\partial R}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

2.5 Exponential function No. 1

$$t_i \geq t_0 + \gamma_1\sigma_2{}^2 \qquad F_1(\Delta t_{0i}) = A\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2} - \gamma_1\Delta t_{0i}\right) = A_1\exp(-\gamma_1\Delta t_{0i})$$

$$A_1 = A\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

● DF1DT0

$$\frac{\partial F_1}{\partial t_0} = \frac{\partial \Delta t_{0i}}{\partial t_0}\frac{\partial F_1}{\partial \Delta t_{0i}} = -A_1(-\gamma_1)\exp(-\gamma_1\Delta t_{0i}) = A_1\gamma_1\exp(-\gamma_1\Delta t_{0i})$$

● DF1DD

$$\frac{\partial F_1}{\partial d} = \frac{\partial F_1}{\partial t_0}\frac{\partial t_0}{\partial d}$$

● DF1DS0

$$\frac{\partial F_1}{\partial \sigma_0} = \frac{\partial A_1}{\partial \sigma_0}\exp(-\gamma_1\Delta t_{0i})$$

● DF1DS1

$$\frac{\partial F_1}{\partial \sigma_1} = \frac{\partial A_1}{\partial \sigma_1}\exp(-\gamma_1\Delta t_{0i})$$

● DF1DET

$$\frac{\partial F_1}{\partial \eta} = \frac{\partial A_1}{\partial \eta}\exp(-\gamma_1\Delta t_{0i})$$

● DF1DS2

$$\frac{\partial F_1}{\partial \sigma_2} = \frac{\partial A_1}{\partial \sigma_2} \exp(-\gamma_1 \Delta t_{0i})$$

● DF1DG1

$$\frac{\partial F_1}{\partial \gamma_1} = \left(\frac{\partial A_1}{\partial \gamma_1} - A_1 \Delta t_{0i} \right) \exp(-\gamma_1 \Delta t_{0i})$$

● DF1DG2

$$\frac{\partial F_1}{\partial \gamma_2} = \frac{\partial A_1}{\partial \gamma_2} \exp(-\gamma_1 \Delta t_{0i})$$

● DF1DR

$$\frac{\partial F_1}{\partial R} = \frac{\partial A_1}{\partial R} \exp(-\gamma_1 \Delta t_{0i})$$

$$A_1 = A \exp\left(\frac{\gamma_1{}^2 \sigma_2{}^2}{2} \right)$$

○ DA1DS0

$$\frac{\partial A_1}{\partial \sigma_0} = \frac{\partial A}{\partial \sigma_0} \exp\left(\frac{\gamma_1{}^2 \sigma_2{}^2}{2} \right)$$

○ DA1DS1

$$\frac{\partial A_1}{\partial \sigma_1} = \frac{\partial A}{\partial \sigma_1} \exp\left(\frac{\gamma_1{}^2 \sigma_2{}^2}{2} \right)$$

○ DA1DET

$$\frac{\partial A_1}{\partial \eta} = \frac{\partial A}{\partial \eta} \exp\left(\frac{\gamma_1{}^2 \sigma_2{}^2}{2} \right)$$

○ DA1DS2

$$\frac{\partial A_1}{\partial \sigma_2} = \frac{\partial A}{\partial \sigma_2}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) + A\frac{\partial}{\partial \sigma_2}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

$$= \frac{\partial A}{\partial \sigma_2}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) + A\gamma_1{}^2\sigma_2\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

$$= \left(\frac{\partial A}{\partial \sigma_2} + A\gamma_1{}^2\sigma_2\right)\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

○ DA1DG1

$$\frac{\partial A_1}{\partial \gamma_1} = \frac{\partial A}{\partial \gamma_1}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) + A\frac{\partial}{\partial \gamma_1}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

$$= \frac{\partial A}{\partial \gamma_1}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right) + A\gamma_1\sigma_2{}^2\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

$$= \left(\frac{\partial A}{\partial \gamma_1} + A\gamma_1\sigma_2{}^2\right)\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

○ DA1DG2

$$\frac{\partial A_1}{\partial \gamma_2} = \frac{\partial A}{\partial \gamma_2}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

○ DA1DR

$$\frac{\partial A_1}{\partial R} = \frac{\partial A}{\partial R}\exp\left(\frac{\gamma_1{}^2\sigma_2{}^2}{2}\right)$$

2.6 Gauss function No. 2 (multiplied by R)

$t_0 \le t_i \le t_0 + \gamma_2\sigma_2{}^2$ $\qquad F_2(\Delta t_{0i}) = A\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$

● DF2DT0

$$\frac{\partial F_2}{\partial t_0} = \frac{\partial \Delta t_{0i}}{\partial t_0}\frac{\partial F_2}{\partial \Delta t_{0i}} = -A\left(-\frac{\Delta t_{0i}}{\sigma_2{}^2}\right)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

$$= A\frac{\Delta t_{0i}}{\sigma_2{}^2}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DD

$$\frac{\partial F_2}{\partial d} = \frac{\partial F_2}{\partial t_0}\frac{\partial t_0}{\partial d}$$

- DF2DS0

$$\frac{\partial F_2}{\partial \sigma_0} = \frac{\partial A}{\partial \sigma_0}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DS1

$$\frac{\partial F_2}{\partial \sigma_1} = \frac{\partial A}{\partial \sigma_1}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DET

$$\frac{\partial F_2}{\partial \eta} = \frac{\partial A}{\partial \eta}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DS2

$$\frac{\partial F_2}{\partial \sigma_2} = \left(\frac{\partial A}{\partial \sigma_2} + A\frac{\Delta t_{0i}{}^2}{\sigma_2{}^3}\right)\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DG1

$$\frac{\partial F_2}{\partial \gamma_1} = \frac{\partial A}{\partial \gamma_1}\exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2}\right)$$

- DF2DG2

$$\frac{\partial F_2}{\partial \gamma_2} = \frac{\partial A}{\partial \gamma_2} \exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2} \right)$$

● DF2DR

$$\frac{\partial F_2}{\partial R} = \frac{\partial A}{\partial R} \exp\left(-\frac{\Delta t_{0i}{}^2}{2\sigma_2{}^2} \right)$$

2.7 Exponential function No. 2

$$t_i \geq t_0 + \gamma_2 \sigma_2{}^2 \qquad F_2(\Delta t_{0i}) = A \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} - \gamma_2 \Delta t_{0i} \right) = A_2 \exp(-\gamma_2 \Delta t_{0i})$$

$$A_2 = A \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

● DF2DT0

$$\frac{\partial F_2}{\partial t_0} = \frac{\partial \Delta t_{0i}}{\partial t_0} \frac{\partial F_2}{\partial \Delta t_{0i}} = -A_2(-\gamma_2) \exp(-\gamma_2 \Delta t_{0i}) = A_2 \gamma_2 \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DD

$$\frac{\partial F_2}{\partial d} = \frac{\partial F_2}{\partial t_0} \frac{\partial t_0}{\partial d}$$

● DF2DS0

$$\frac{\partial F_2}{\partial \sigma_0} = \frac{\partial A_2}{\partial \sigma_0} \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DS1

$$\frac{\partial F_2}{\partial \sigma_1} = \frac{\partial A_2}{\partial \sigma_1} \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DET

$$\frac{\partial F_2}{\partial \eta} = \frac{\partial A_2}{\partial \eta} \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DS2

$$\frac{\partial F_2}{\partial \sigma_2} = \frac{\partial A_2}{\partial \sigma_2} \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DG1

$$\frac{\partial F_2}{\partial \gamma_1} = \frac{\partial A_2}{\partial \gamma_1} \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DG2

$$\frac{\partial F_2}{\partial \gamma_2} = \left(\frac{\partial A_2}{\partial \gamma_2} - A_2 \Delta t_{0i} \right) \exp(-\gamma_2 \Delta t_{0i})$$

● DF2DR

$$\frac{\partial F_2}{\partial R} = \frac{\partial A_2}{\partial R} \exp(-\gamma_2 \Delta t_{0i})$$

$$A_2 = A \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DS0

$$\frac{\partial A_2}{\partial \sigma_0} = \frac{\partial A}{\partial \sigma_0} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DS1

$$\frac{\partial A_2}{\partial \sigma_1} = \frac{\partial A}{\partial \sigma_1} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DET

$$\frac{\partial A_2}{\partial \eta} = \frac{\partial A}{\partial \eta} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DS2

$$\frac{\partial A_2}{\partial \sigma_2} = \frac{\partial A}{\partial \sigma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right) + A \frac{\partial}{\partial \sigma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

$$= \frac{\partial A}{\partial \sigma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right) + A \gamma_2{}^2 \sigma_2 \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

$$= \left(\frac{\partial A}{\partial \sigma_2} + A \gamma_2{}^2 \sigma_2 \right) \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DG1

$$\frac{\partial A_2}{\partial \gamma_1} = \frac{\partial A}{\partial \gamma_1} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DG2

$$\frac{\partial A_2}{\partial \gamma_2} = \frac{\partial A}{\partial \gamma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right) + A \frac{\partial}{\partial \gamma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

$$= \frac{\partial A}{\partial \gamma_2} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right) + A \gamma_2 \sigma_2{}^2 \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

$$= \left(\frac{\partial A}{\partial \gamma_2} + A \gamma_2 \sigma_2{}^2 \right) \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

○ DA2DR

$$\frac{\partial A_2}{\partial R} = \frac{\partial A}{\partial R} \exp\left(\frac{\gamma_2{}^2 \sigma_2{}^2}{2} \right)$$

2.8 Derivatives of *R*

Derivatives of R with respect to R_j (j = 1–4) are described because of the difficulty in deriving them.

$$R = R_1 + \frac{R_2}{1+\left(\frac{d}{R_3}\right)^{R_4}} = R_1 + \frac{R_2}{1+y}$$

$$\frac{\partial R}{\partial y} = -R_2 \frac{1}{(1+y)^2}$$

$$\frac{\partial y}{\partial R_3} = R_4\left(\frac{d}{R_3}\right)^{R_4-1} d(-R_3{}^{-2}) = -\frac{R_4}{R_3}\left(\frac{d}{R_3}\right)^{R_4} = -\frac{R_4}{R_3} y$$

$$\frac{\partial R}{\partial R_3} = \frac{\partial R}{\partial y}\frac{\partial y}{\partial R_3} = \frac{R_2 R_4 y}{R_3(1+y)^2}$$

$$\frac{\partial y}{\partial R_4} = \frac{\partial y}{\partial(\ln y)}\frac{\partial(\ln y)}{\partial R_4} = y\ln\left(\frac{d}{R_3}\right)$$

$$\frac{\partial R}{\partial R_4} = \frac{\partial R}{\partial y}\frac{\partial y}{\partial R_4} = -R_2 y \ln\left(\frac{d}{R_3}\right)\frac{1}{(1+y)^2}$$

2.9 Derivatives with respect to the elements of the metric tensor

$$\frac{\partial F}{\partial X_j} = \frac{\partial F}{\partial t_0}\frac{\partial t_0}{\partial d}\frac{\partial d}{\partial X_j} = \frac{\partial F}{\partial d}\frac{\partial d}{\partial X_j}$$

○ YPEAK(I) * $\partial d/\partial X_j$ is calculated in SUBROUTINE DERREF

$$\frac{1}{d^2} = X_1 h^2 + X_2 k^2 + X_3 l^2 + 2X_4 kl + 2X_5 hl + 2X_6 hk$$

$$d = \left(X_1 h^2 + X_2 k^2 + X_3 l^2 + 2X_4 kl + 2X_5 hl + 2X_6 hk\right)^{-1/2}$$

Elements of the metric tensor

$$X_1 = a^{*2}$$

$$X_2 = b^{*2}$$

$$X_3 = c^{*2}$$

$$X_4 = b^* c^* \cos\alpha^*$$

$$X_5 = a^* c^* \cos\beta^*$$

$$X_6 = a^* b^* \cos\gamma^*$$

$$\frac{\partial d}{\partial X_1} = -\frac{d^3 h^2}{2}$$

$$\frac{\partial d}{\partial X_2} = -\frac{d^3 k^2}{2}$$

$$\frac{\partial d}{\partial X_3} = -\frac{d^3 l^2}{2}$$

$$\frac{\partial d}{\partial X_4} = -d^3 kl$$

$$\frac{\partial d}{\partial X_5} = -d^3 hl$$

$$\frac{\partial d}{\partial X_6} = -d^3 hk$$

3.0 Functions calculated in SUBROUTINE UPDATE

★ GS12

$$GS12 = \gamma_1 \sigma_2^{\,2}$$

★ EXP12

$$EXP12 = \exp\left(\frac{\gamma_1^{\,2} \sigma_2^{\,2}}{2}\right)$$

★ ERF12

$$ERF12 = \mathrm{erf}\left(\frac{\gamma_1 \sigma_2}{\sqrt{2}}\right)$$

★ GS22

$$GS22 = \gamma_2 \sigma_2^{\,2}$$

★ EXP22

$$EXP22 = \exp\left(\frac{\gamma_2^{\,2} \sigma_2^{\,2}}{2}\right)$$

★ ERF22

$$ERF22 = \mathrm{erf}\left(\frac{\gamma_2 \sigma_2}{\sqrt{2}}\right)$$

A primary profile parameter, p', for a reflection whose profile is relaxed because of its anisotropic broadening is given by

$$p' = p + \Delta p,$$

where p is a primary profile parameter calculated from secondary profile parameters, and Δp is the difference between actual and 'observed' primary profile parameters. Not p but Δp is refined in Rietveld analysis.

A partial derivative of the profile function, $F(p')$, with respect to Δp can be calculated easily:

$$\frac{\partial F(p')}{\partial \Delta p} = \frac{\partial F(p')}{\partial p'} \frac{\partial p'}{\partial \Delta p} = \frac{\partial F(p')}{\partial p'}$$

The derivatives of $F(p')$ with respect to p' are calculated in the same way as those of $F(p)$ with respect to p for reflections whose primary profile parameters are constrained by empirical equations.