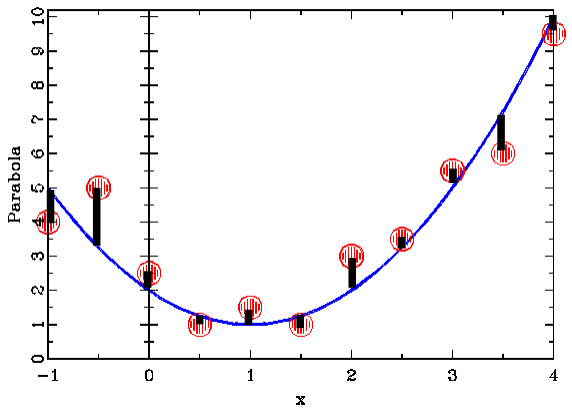
tutorial session VII

refinement



- experimental data

Model: $y = a x^2 + bx + c$

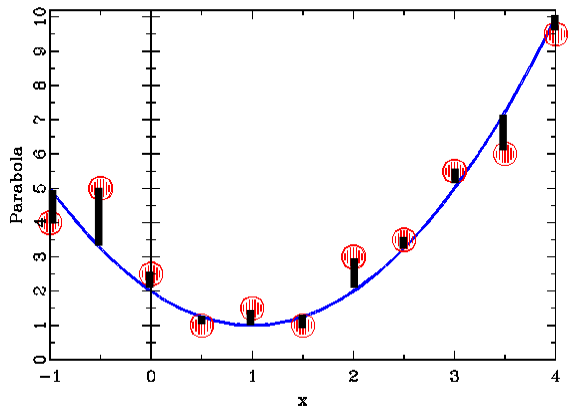
what are **best** a, b, c ?

smallest deviations between data and model

$$R_w = \sqrt{\frac{\sum_j w_j (y_{j,obs} - y_{j,calc})^2}{\sum_j w_j y_{j,obs}^2}}$$

weighted Residual

$y_{j,obs}$	observed values
$y_{j,calc}$	calculated values
w_j	weight = $1/\sigma_j^2$



- experimental data

Model: $y = a x^2 + bx + c$

what are **best** a, b, c ?

least squares fit start with estimates a, b, c

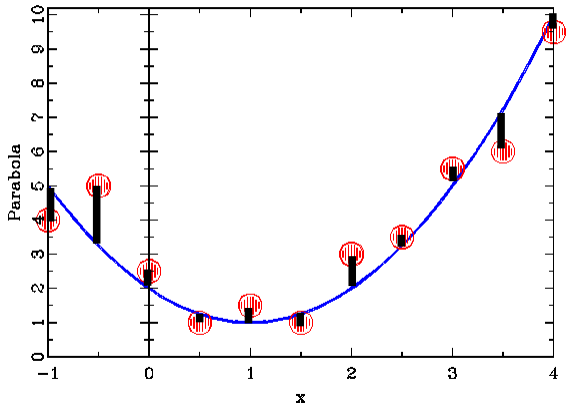
calculate derivatives:

$$\begin{cases} \partial y/\partial a = x^2 \\ \partial y/\partial b = x \\ \partial y/\partial c = 1 \end{cases}$$

obtain better estimates of a, b, c

derive lattice constants, atom positions ...

powder pattern calculated analytically ==> Rietveld



● experimental data

Model: $y = a x^2 + bx + c$

what are **best** a, b, c ?

Monte Carlo techniques
simulated annealing
Reverse Monte Carlo

start with estimates a, b, c

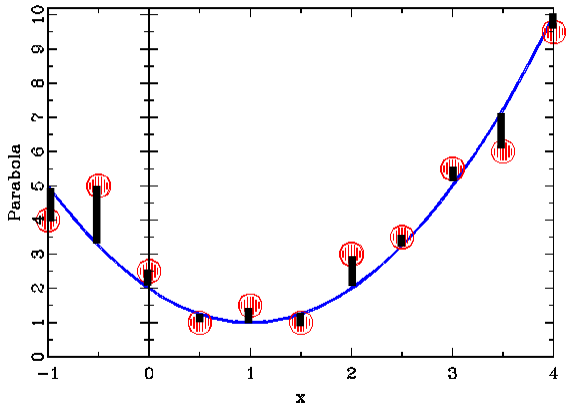
"randomly" vary a, b, c until a good fit is obtained

create list of atom positions

"randomly" modify atom positions within crystal

shift atoms, switch two atoms ...

refine by comparing calculated powder pattern to experimental pattern



- experimental data

Model: $y = a x^2 + bx + c$

what are **best** a, b, c ?

Genetic Algorithms
Evolutionary Algorithms

start with **N sets** of estimates a, b, c; calculate R

derive M (M ≥ N) new sets of parameters a, b, c

compare fit of new sets to old sets

keep better parameter sets

create parameter sets: lattice constants, atom positions, defects...

build crystal

refine by comparing
calculated powder pattern
to experimental pattern

least squares fit

requires analytical derivable expression
$I(\mathbf{h}) = G(a,b,c, \alpha, \beta, \gamma, \mathbf{r}_j, B_j, N_j, \text{strain, size, profile})$

fastest algorithm

defects, very small size difficult

Monte Carlo techniques
simulated annealing
Reverse Monte Carlo

slow algorithm

requires modification of an existing crystal

structural parameters derived from model

Genetic Algorithms
Evolutionary Algorithms

slow algorithm

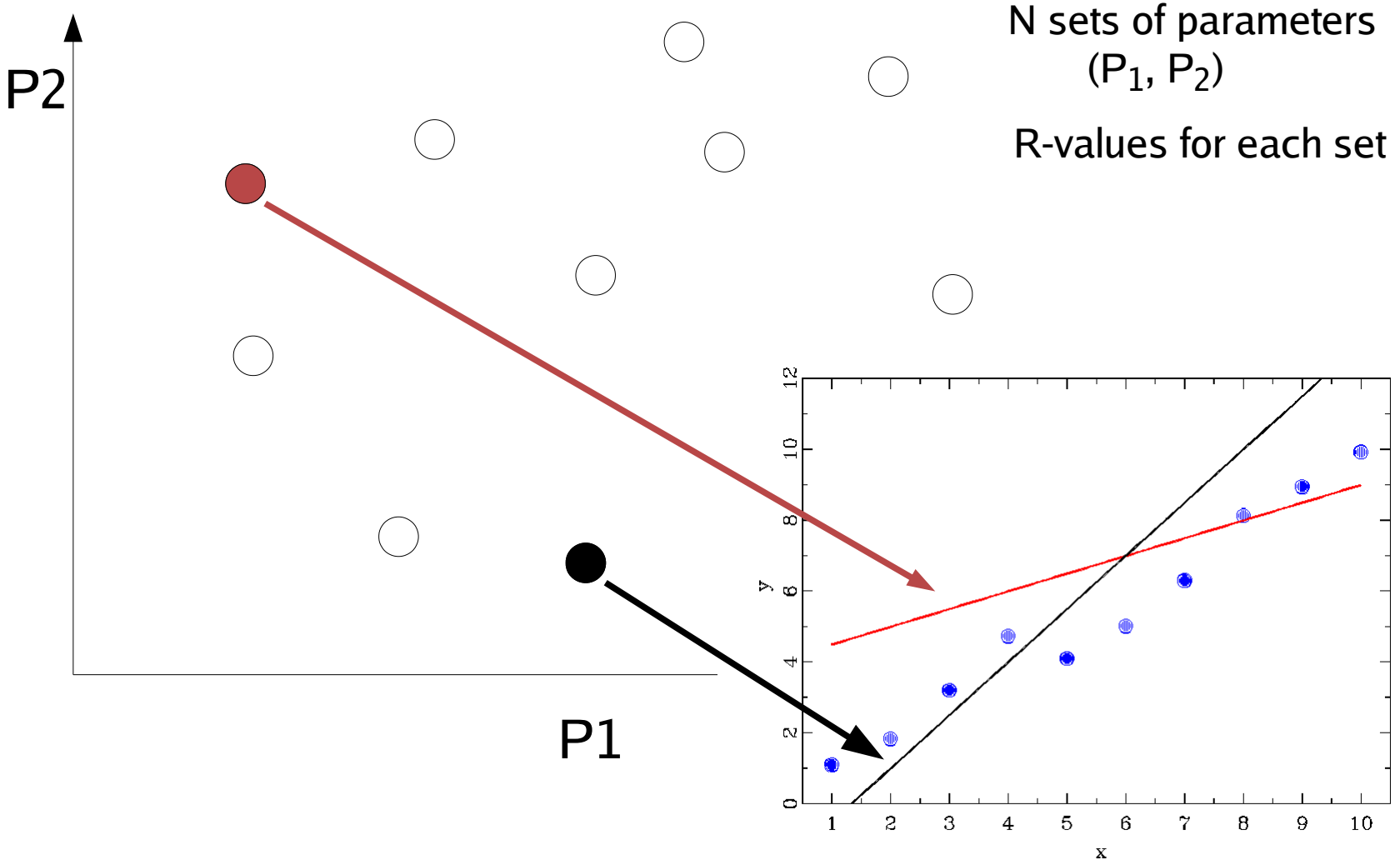
model derived from structural parameters

rough concept must exist

$y = P_1x + P_2$

N sets of parameters
(P_1, P_2)

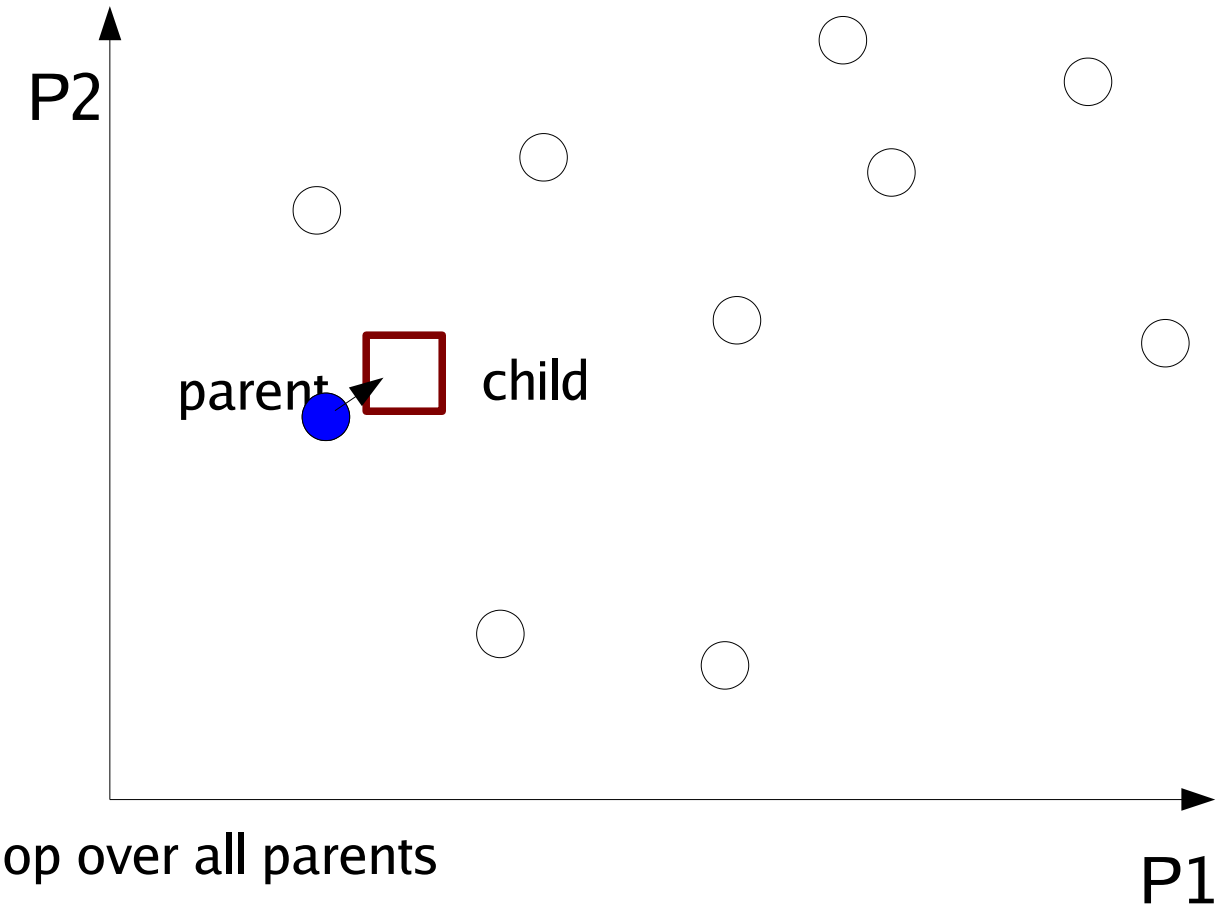
R-values for each set



$y = P_1x + P_2$

N sets of parameters
(P_1, P_2)

R-values for each set



loop over all parents

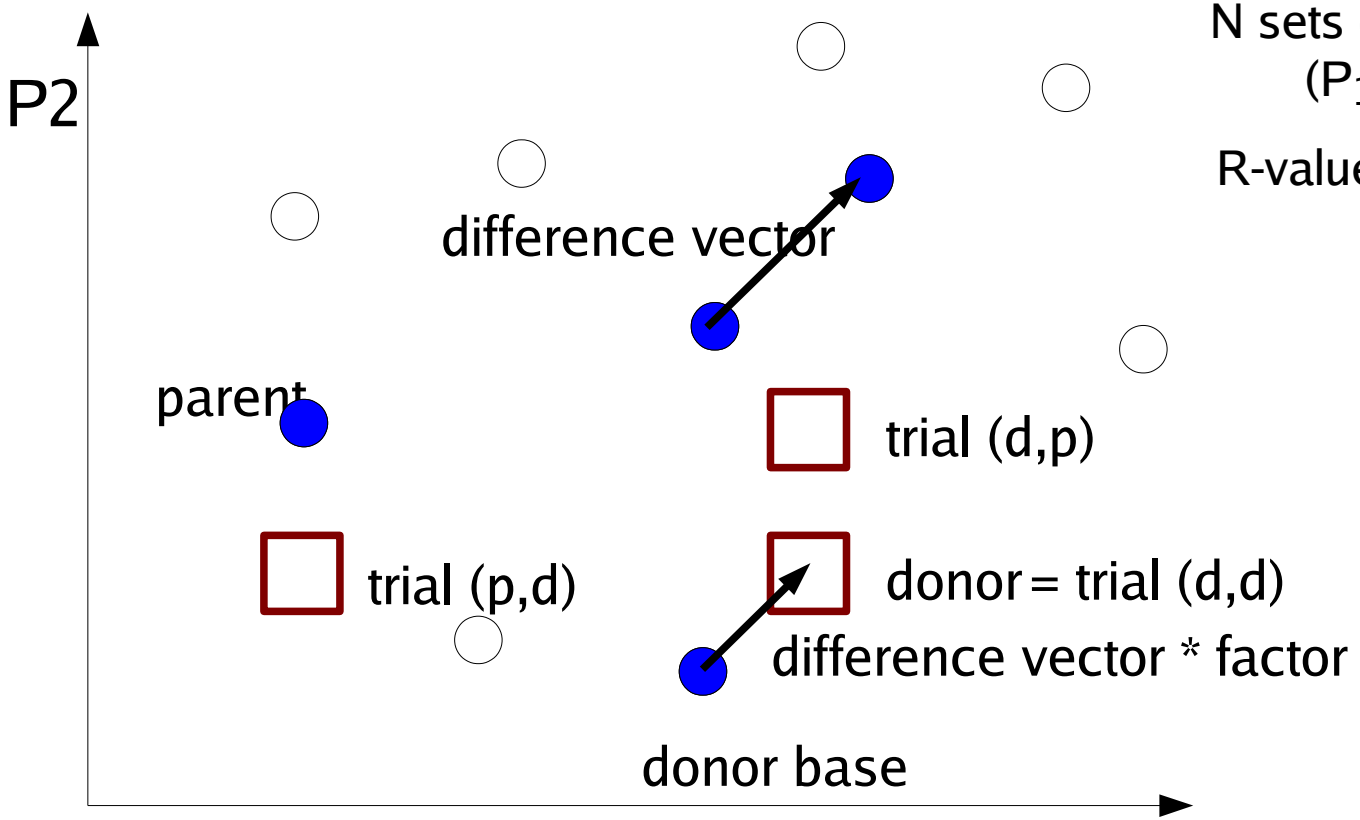
"randomly" modify parameter values

compute cost function for all children, keep better of parent(s)/child(ren)

$y = P_1x + P_2$

N sets of parameters
(P_1, P_2)

R-values for each set



choose parent
choose difference vector
add to donor base to get donor
cross-over between parent and donor

generic refinement program; part of discus_suite

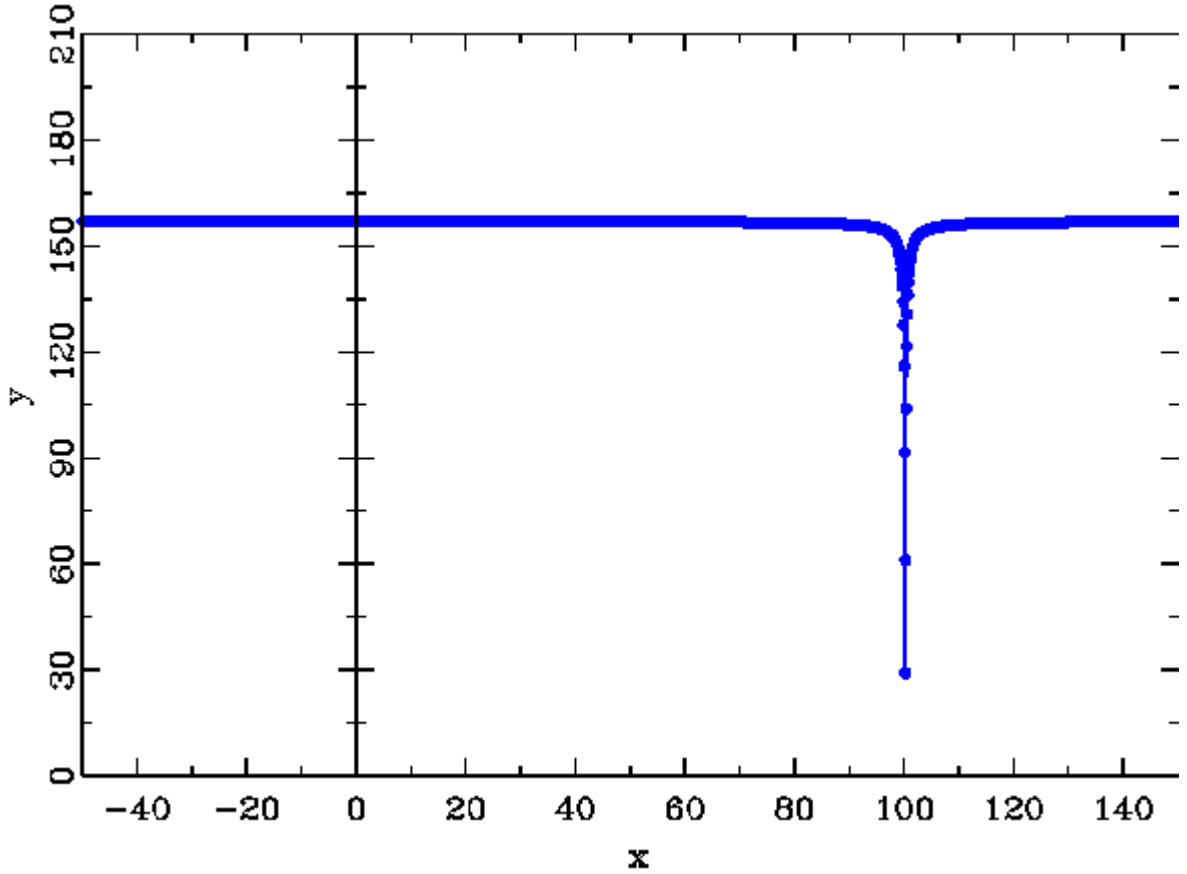
identical command language as DISCUS/KUPLOT

initialization commands

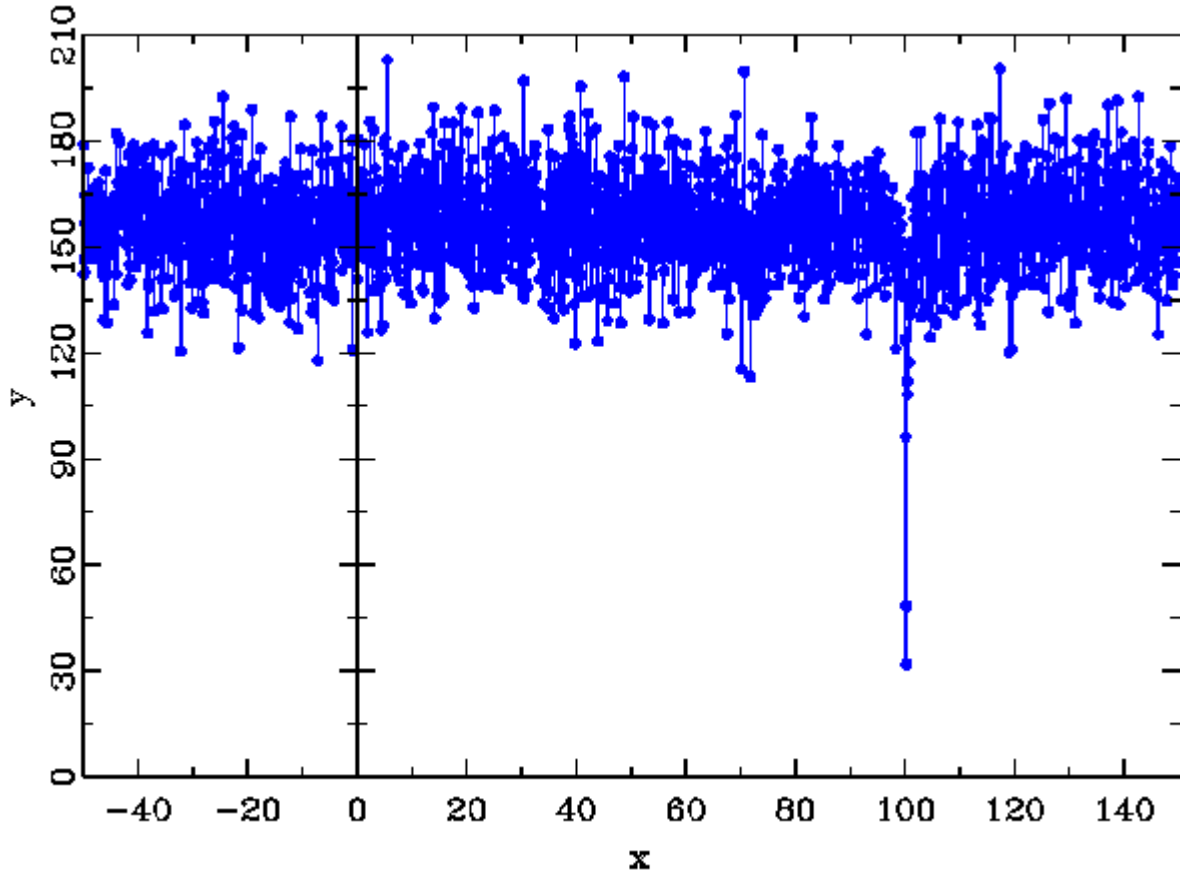
loop

system external calculation

compare



$$100 * \arctan\left(\frac{|\ x - 100.23\ |}{0.05}\right)$$



$$100 * \arctan\left(\frac{|\ x - 100.23\ |}{0.05}\right)$$

GENERATION	fixed filename, contains current generation number, refinement size
DIFFEV/Parameter.*	contains the complete refinement history,
DIFFEV/Parameter.Rvalue	Development of R-value
DIFFEV/Parameter.P_length	Development of Parameter named P_length path/name is set by user, extension fixed
	contains a refinement summary,
DIFFEV/Summary.Rvalue	Development of R-value
DIFFEV/Summary.P_length	Development of Parameter named P_length path/name is set by user, extension fixed

kpara Rvalue — plots changes of parameters 0 to... as function of refinement cycle

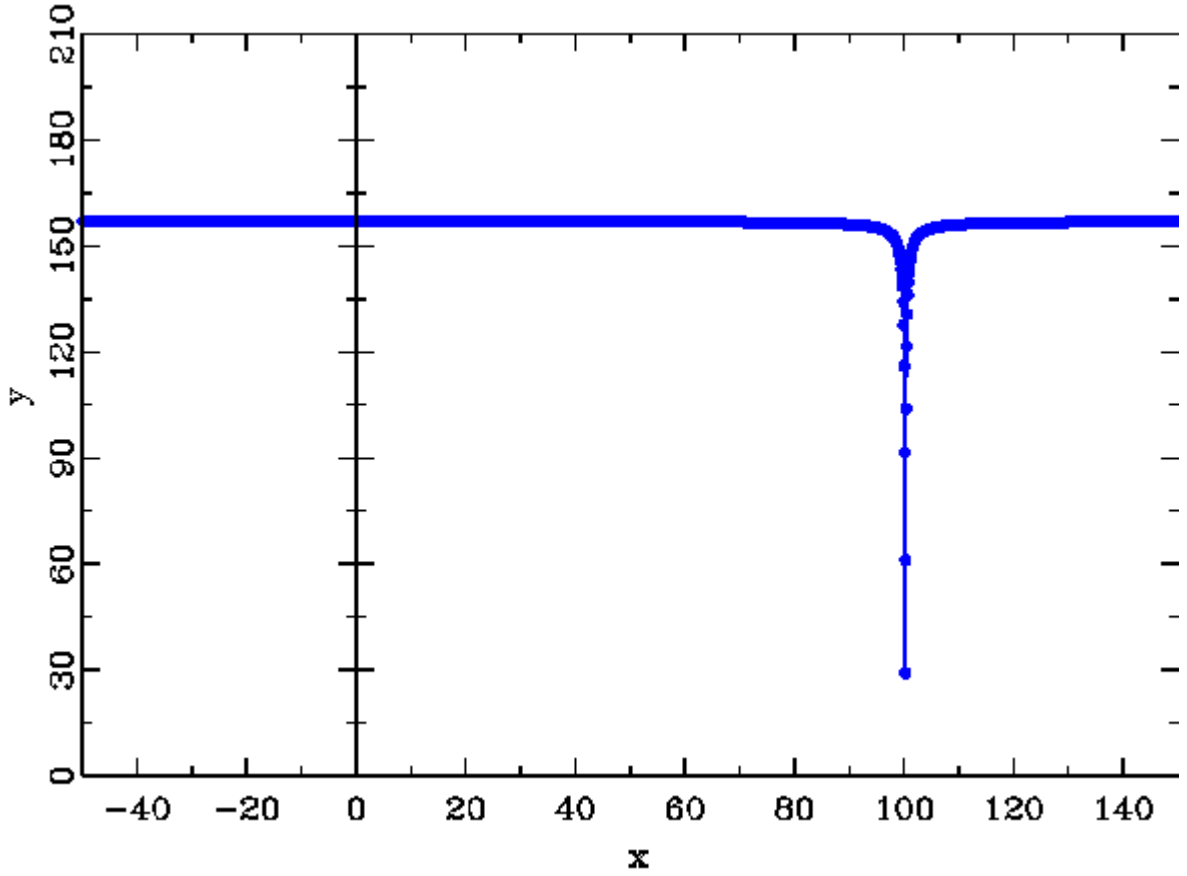
parameter Rvalue
or actual parameter names

@ksingle.mac 1 — plots the current best match to the data; or the 2nd ...

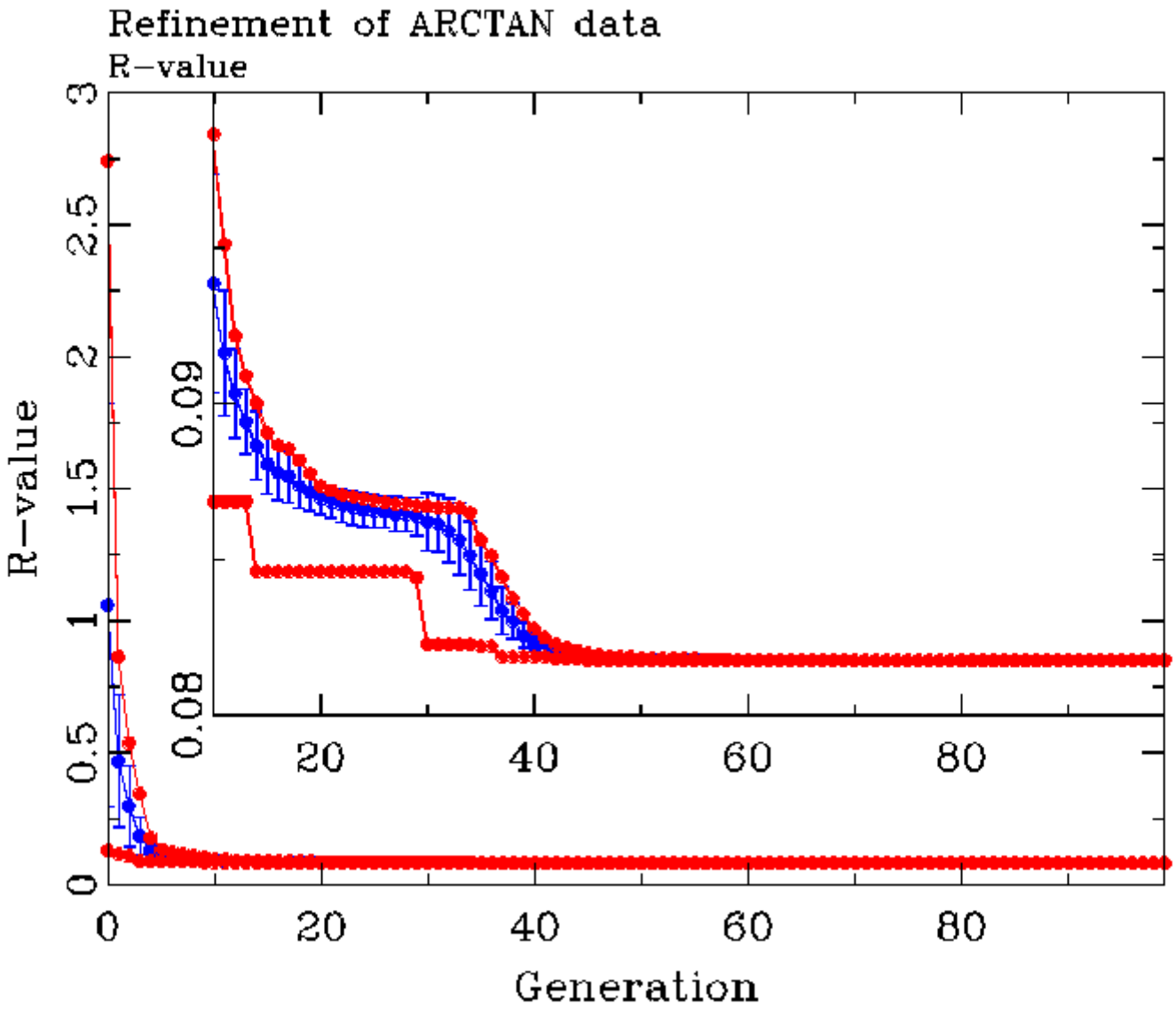
kpar_par -1,1,0 — plots parameters 1 versus R-value for the current generation

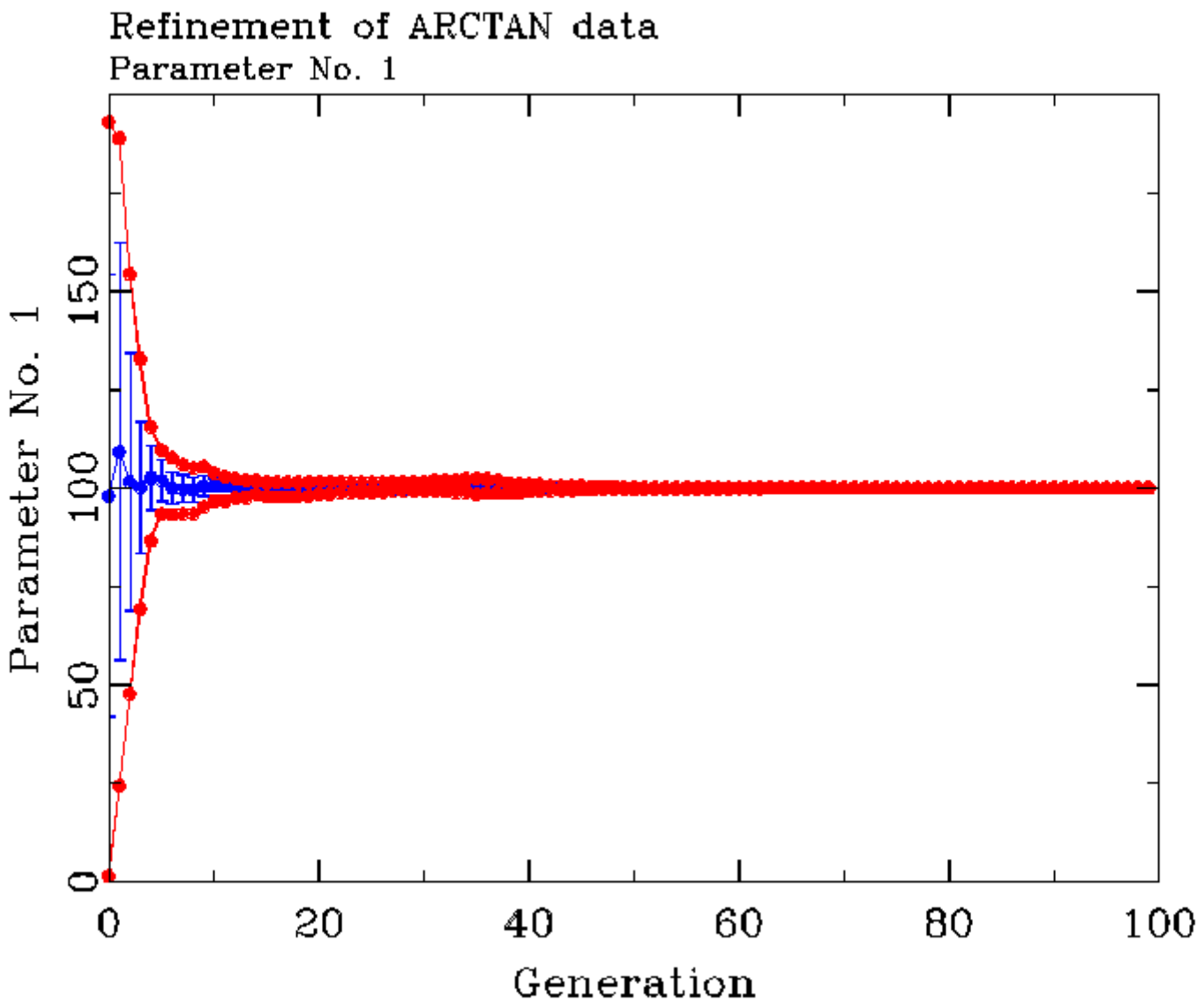
1st argument:	generation number	-1 for latest
2nd argument:	parameter name along y-axis	
3rd argument:	parameter name along x-axis	
	0 = R-value	
	1,... actual parameter names	
	-1 = number of the child in the population	

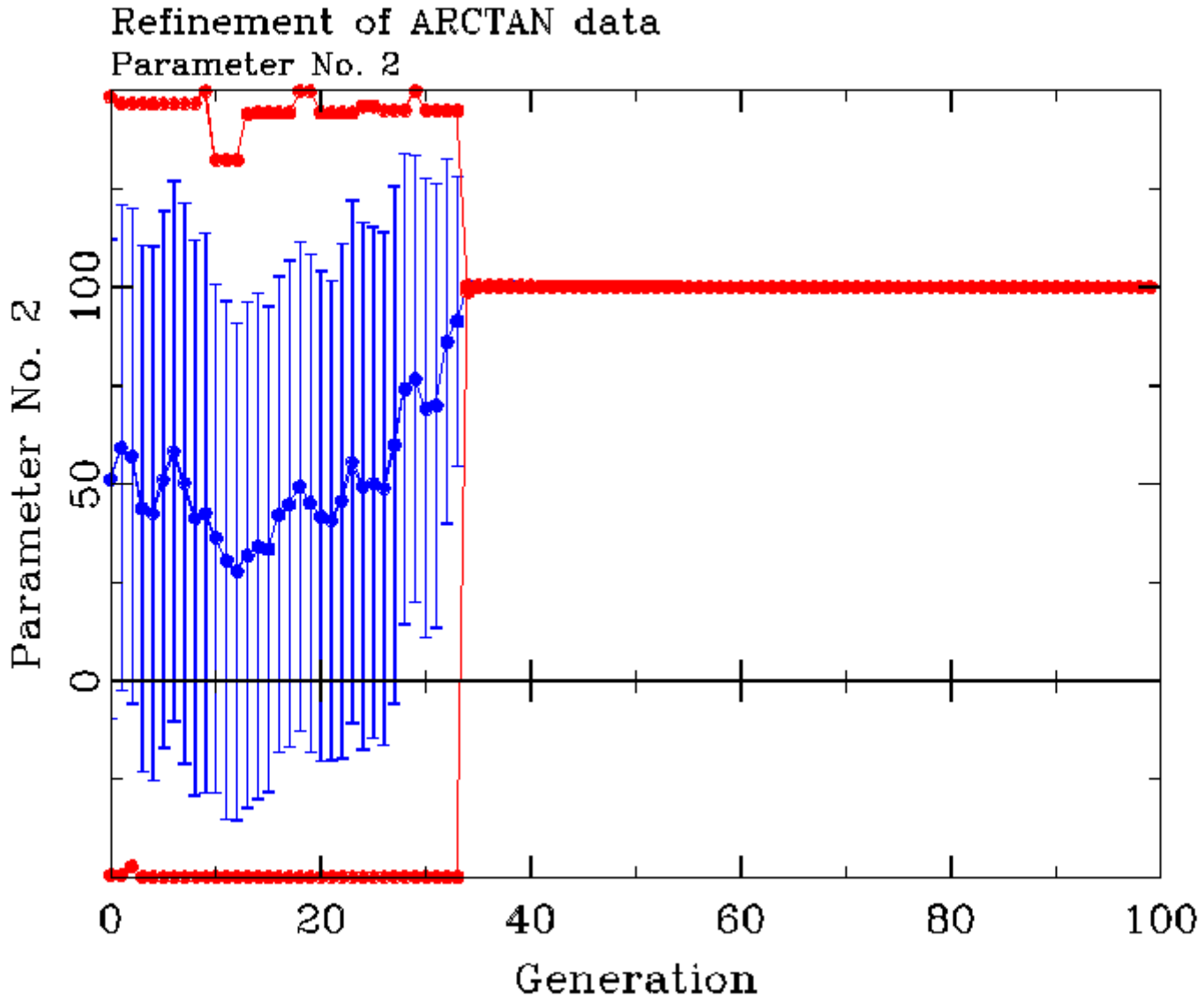
Sample function

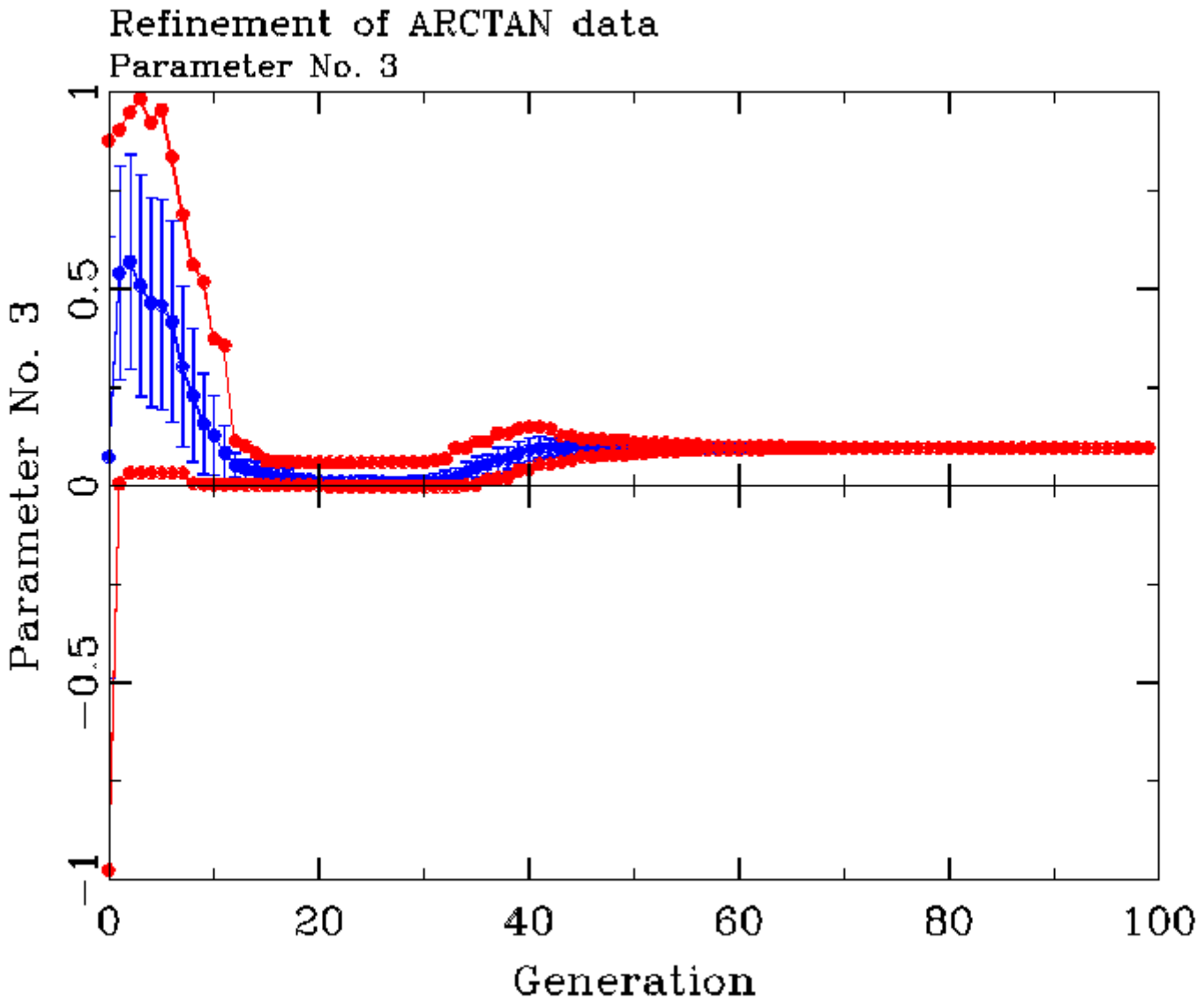


$$150 * \arctan\left(\frac{|\ x - 100.23\ |}{0.05}\right)$$

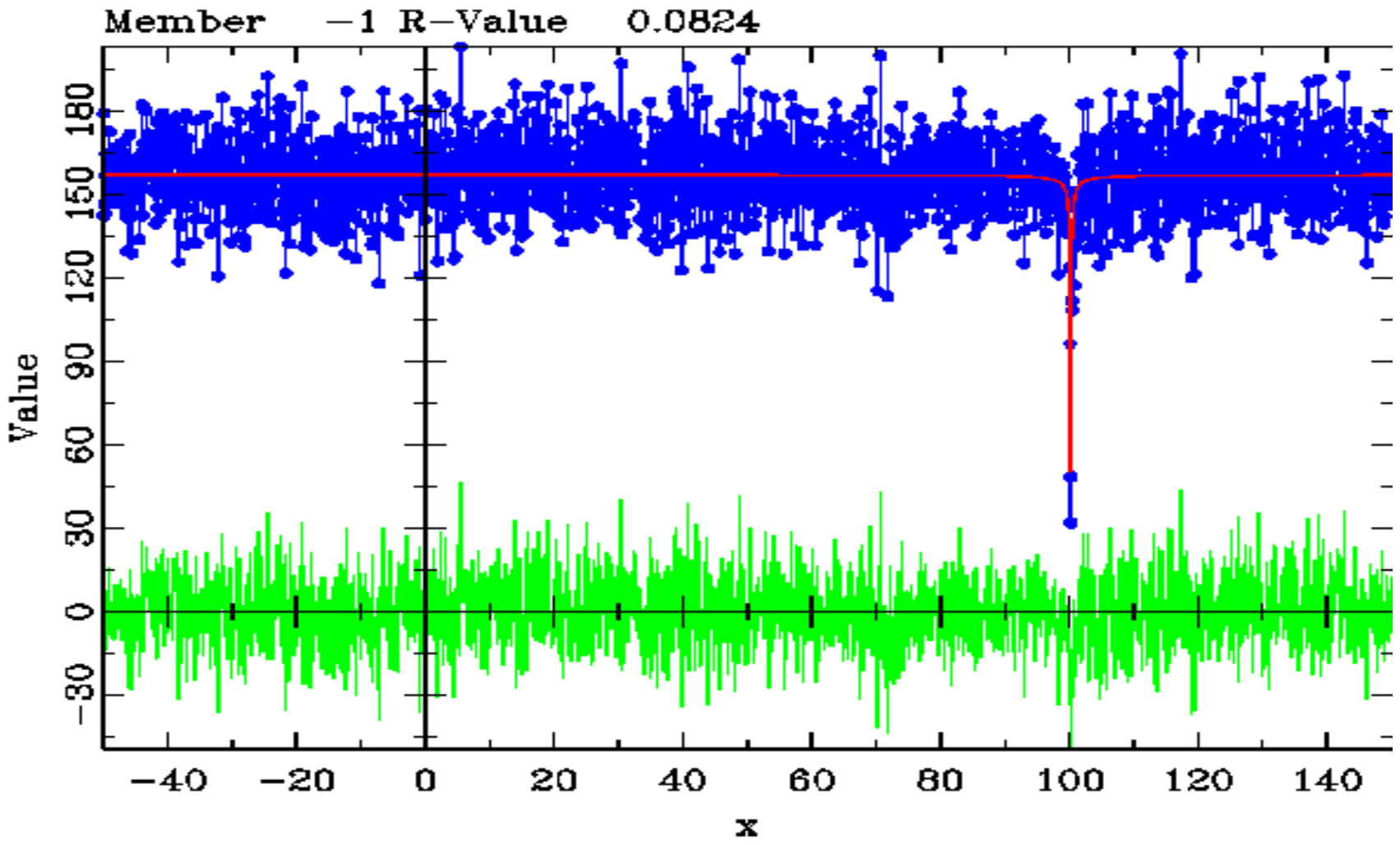

Refinement of ARCTAN data
R−value
R−value
Generation
0
0.5
1
1.5
2
2.5
3
0.08
0.09
20
40
60
80


Refinement of ARCTAN data
Parameter No. 1
Parameter No. 1
0
50
100
150
0
20
40
60
80
100
Generation


Refinement of ARCTAN data
Parameter No. 2
Parameter No. 2
0
50
100
0
20
40
60
80
100
Generation


Refinement of ARCTAN data
Parameter No. 3
Parameter No. 3
1
0.5
0
−0.5
−1
0
20
40
60
80
100
Generation

Sample function



$$99.93 * \arctan\left(\frac{|\, x - 100.23 \,|}{0.049}\right)$$