DRAFT: May 29, 2003

RAINS

Refinement Application for Inelastic Neutron Scattering

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CONTENTS

Introduction

RAINS is a new application included in the DAVE software package that gives users the power to analyze their inelastic neutron spectra by fitting models of $S(Q,\omega)$ to their entire data set. In contrast to another analysis application in DAVE called PAN (Peak Analysis), RAINS is not limited to fitting a single model to individual detector groups. Rather RAINS fits a parametrized surface given by a theoretical scattering law $S(Q,\omega)$ to the entire data set. Moreover users can fit <u>different</u> models to the <u>same</u> data set and compare the least-squares goodness-of-fit metric χ^2 for instance thus facilitating the model selection process. Of course this is not a *black-box* type program so model selection based solely on χ^2 can be fraught with peril. *Caveat emptor*! This document summarizes the features and functionality of the RAINS program.

Overview of the RAINS environment

RAINS is launched from the main DAVE interface from the menu item labeled Data Analysis $\mapsto$ RAINS. Two detached panels should appear as shown below in Fig. 1. You can move these panels around independent of one another and resize them at any stage during your data analysis. The panel on the left contains three regions as shown below. This panel contains a tree hierarchy for ease of file and model navigation through the fit process and two vertically stacked windows that display the data and the residual difference between the model and the data. The right panel contains two vertically stacked windows that display a particular cut or Q value of the data as well as the overall fit. The residuals are displayed in the bottom window.
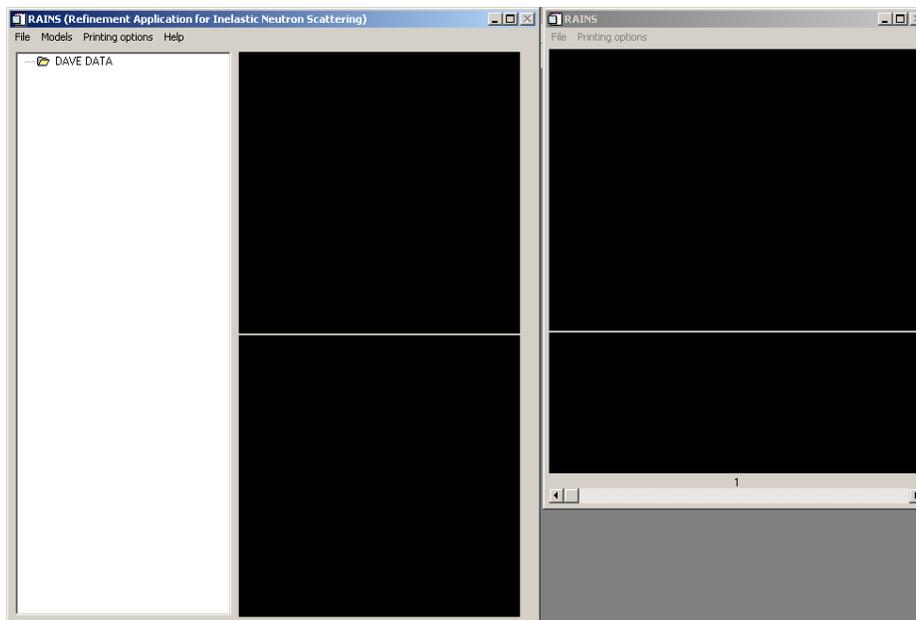
Fig. 1 Two-panels in the RAINS fitting environment. See text for an explanation.

The menus in the left panel consist of FILE, MODEL, PRINTING OPTIONS, and HELP selections. At the moment the PRINTING OPTIONS menu has no items under it as it is a work-in-progress. The FILE menu contains options to LOAD DAVE (i.e. load a DAVE file) or QUIT. The MODELS menu

item contains selections that allow the user to ADD NEW MODEL or select from a further list of DIFFUSION FUNCTIONS, TUNNELING FUNCTIONS, and/or MISCELLANEOUS FUNCTIONS. A comprehensive list of these individual functions is shown at the end of this document.

This environment has been designed to enable users to test different models for the same data set in order to aid in the model selection process. To that end a tree hierarchy has been selected as the main navigation tool. For each data set users can have as many models as they wish. A single model can be composed of as many $S(Q,\omega)$ functions as desired. The functions in one model are added together to form the overall model. The details will be discussed later in this document but a simple example showing the organization of the functions, models, and data files are shown in Fig. 2. In this figure the data set labeled 20010621_02dyn.dave has two models associated with it. The first model is composed of two functions: a background function and a 3-fold jump diffusion model. The second model is composed of just a 2-fold jump diffusion model. These two models can be fit to the same data set independently and the goodness-of-fit can be compared.
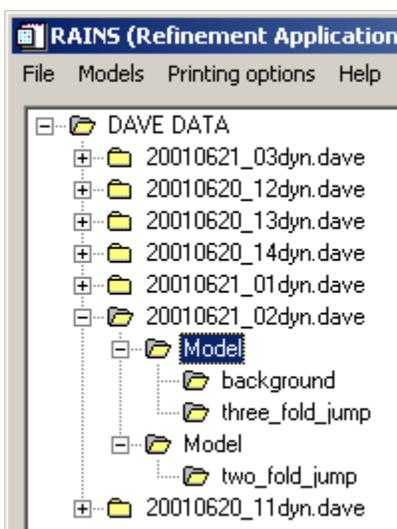
Fig. 2 Overview of the navigation tool for the function/model/file tree hierarchy.

Loading DATA in RAINS

Any number of existing DAVE files can be loaded into the workspace by selecting the FILE $\mapsto$ LOAD DAVE FILE menu item. Note that the data file must be a function of two variables (Q,E). In general it is expected that the independent variables are wavevector transfer Q and energy transfer E. In addition it is expected that the data are uniformly spaced on a regular grid in E. This is checked when the data file is loaded. Upon successfully loading the files into RAINS new folders will appear on the tree hierarchy under the DAVE DATA folder and the name of the folders will match the file names. Moreover a folder labeled MODEL will appear under the new data folder. In addition an image representation (also called a *spectrogram* in time-frequency lingo) of the data associated with the currently selected data folder will appear in the top window of the left panel. An example of a data file collected on the High Flux Backscattering Spectrometer and reduced using DAVE is shown in Fig. 3. Note that the cut showing Q=1.51 Å^{-1} is displayed in the right panel.
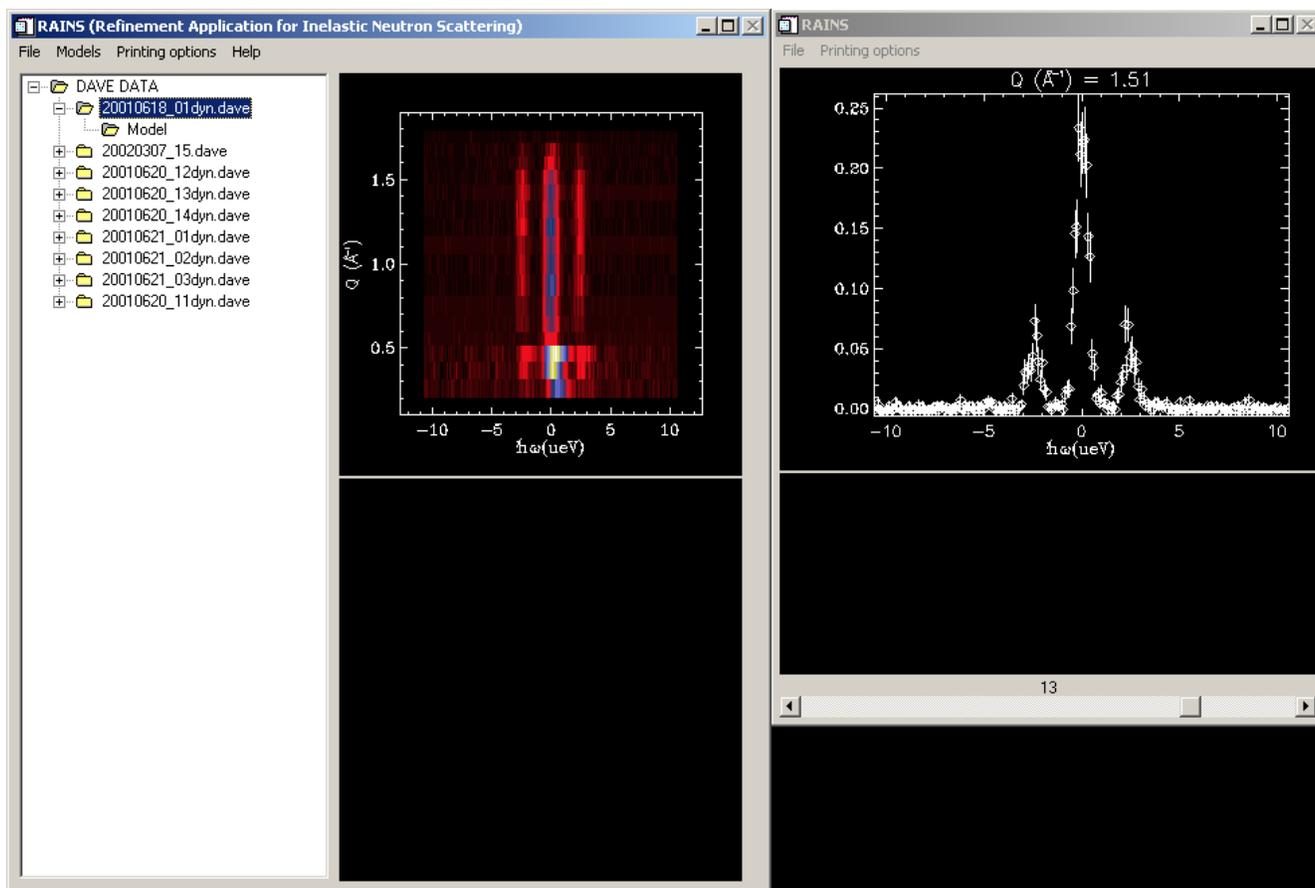
Fig. 3 Display resulting from loading a data set collected on HFBS.

You can use the mouse to zoom into the top window of either panel in order to get a magnified view of your data. This is a standard rubber-band type operation in which you simply drag the cursor over the plot while holding the left mouse button down. Releasing the left mouse button will execute the magnification operation. Note that there is an upper bound on the magnification limit.

Data operations/functions

The operations performed within this application are accessible primarily via context-sensitive menus. These are simply menus that appear when the user presses the right mouse button when the cursor is on top of one of the folders displayed in the left panel. For instance, when you put the cursor over the data file folder currently selected and press the right mouse button, you should see the context sensitive menu like the one shown in Fig. 4.
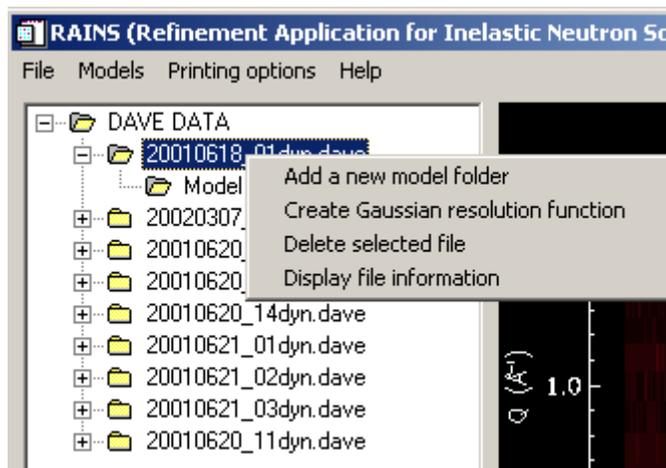
Fig. 4 Context-sensitive menu that appears when user right-clicks the mouse and the cursor is over the data file folder.

Selecting the first choice, ADD A NEW MODEL FOLDER, results in a new folder appearing after the existing one. You should note that all of the data folders have a single default folder associated with them. The second choice allows the user to create a Gaussian resolution function based on the data binning and grouping. Selecting this option launches a utility allowing the user to parameterize the Q dependence of the full-width-at-half-maximum (FWHM) and the center of the function. This application is shown in Fig. 5. Note that the user can type in any expression in IDL syntax as a function of y. Note Y is used in place of Q. The surface is actually represented internally as a function of the independent variables x and y. Examples of expressions you might put in for the Y-dependence for the FWHM or center are listed below:

Examples:		
Algebraic expression	IDL syntax	Comment
0.25	0.25+0.0*y	Must include 0.0
$0.5+1.05Q^2$	0.5+1.05*y^2	
$j_o(3.0Q)$	sph_bessel(3.0*y,0)	
$J_o(3.0Q)$	beselj(3.0*y,0)	
$e^{-0.5q}$	exp(-0.5*y)	

When you are satisfied with the resolution function you can press the ACCEPT button and the resolution function will be present *for that data set* for the rest of the session. Note that you can create a new resolution function at any time thereafter by repeating this operation.
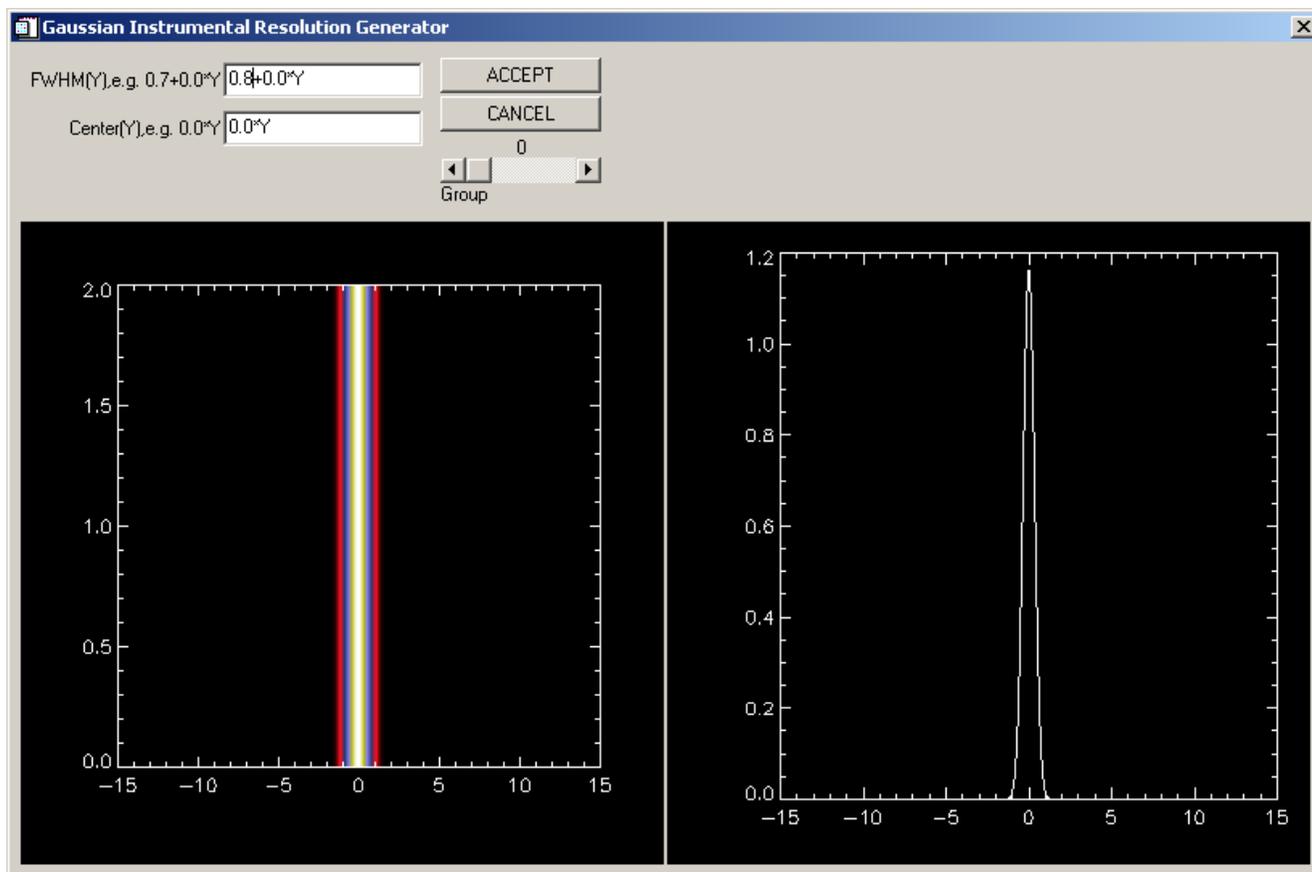
Fig. 5 Gaussian instrumental resolution function generator application.

Users may also delete any number of data files from memory by selecting the next item in the menu context-sensitive menu labeled DELETE SELECTED FILE. Finally the user may display descriptive information related to a particular data file by selecting DISPLAY FILE INFORMATION. The exact content displayed depends on the instrument from which the data was collected and how the data were reduced.

Model operations/functions

Another context-sensitive menu appears by left-clicking on the MODEL menu as shown in Fig. 6. There is a further drop-down menu on this one labeled FITTING (selected in Fig. 6) which contains a number of selections germane to the fitting process. The first is algorithm selection. For the moment only the least-squares algorithm is present but work is in progress on incorporating a genetic algorithm for more difficult fitting problems. The next item in FITTING is SELECT FIT RANGE(S) in which the user can enter the indices to include in both the Q and E variables for fitting.
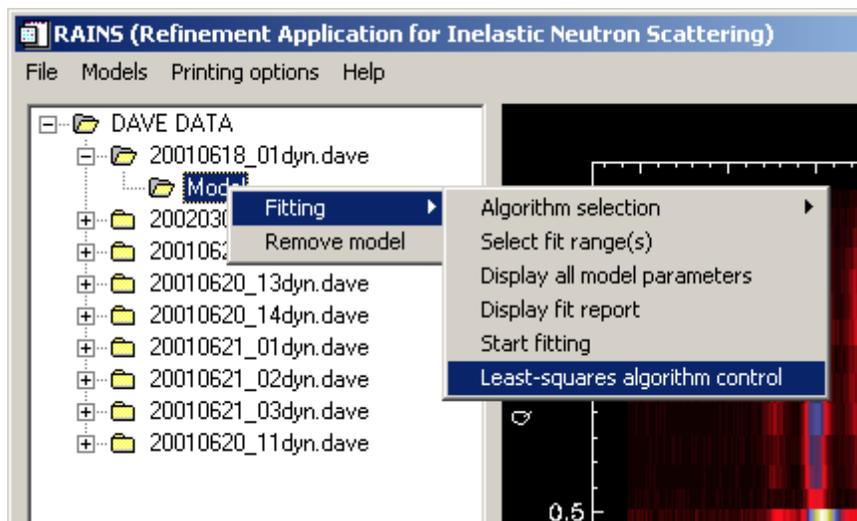
Fig. 6 Model context-sensitive menu.

Data Fitting Example

In this section we present a demonstration of fitting a tunneling model to real data. The data loaded into the RAINS environment in Fig. 6 is from the High Flux Backscattering Spectrometer. This instrument has an approximate Gaussian-like resolution function with a full-width at half maximum of about 0.8 meV. Therefore we create a resolution function by selecting CREATE GAUSSIAN RESOLUTION FUNCTION from the data context-sensitive menu as discussed in the section on **Data operations/functions**. In the Resolution Function Generator application type 0.8+0.0*y in the field labeled FWHM (Y) *and press carriage return*. It is important to press the carriage return so that the display in the application updates (you should see this update). Next press the ACCEPT button.

Next select the MODEL folder below the data set labeled 20010618_01dyn.dave. Select the MODELS menu item from the application menu bar, select TUNNELING FUNCTIONS, then 3-FOLD TUNNELING. A new element labeled 3-FOLD TUNNELING will appear below the MODEL folder for that data set. Next select the MODEL folder and you should see both the spectrogram and the cuts windows show the model superposed on the data. RAINS actually tries to guess model parameters without fitting anything so the resulting plots should look close. An example of what you should see is shown in Fig. 7.
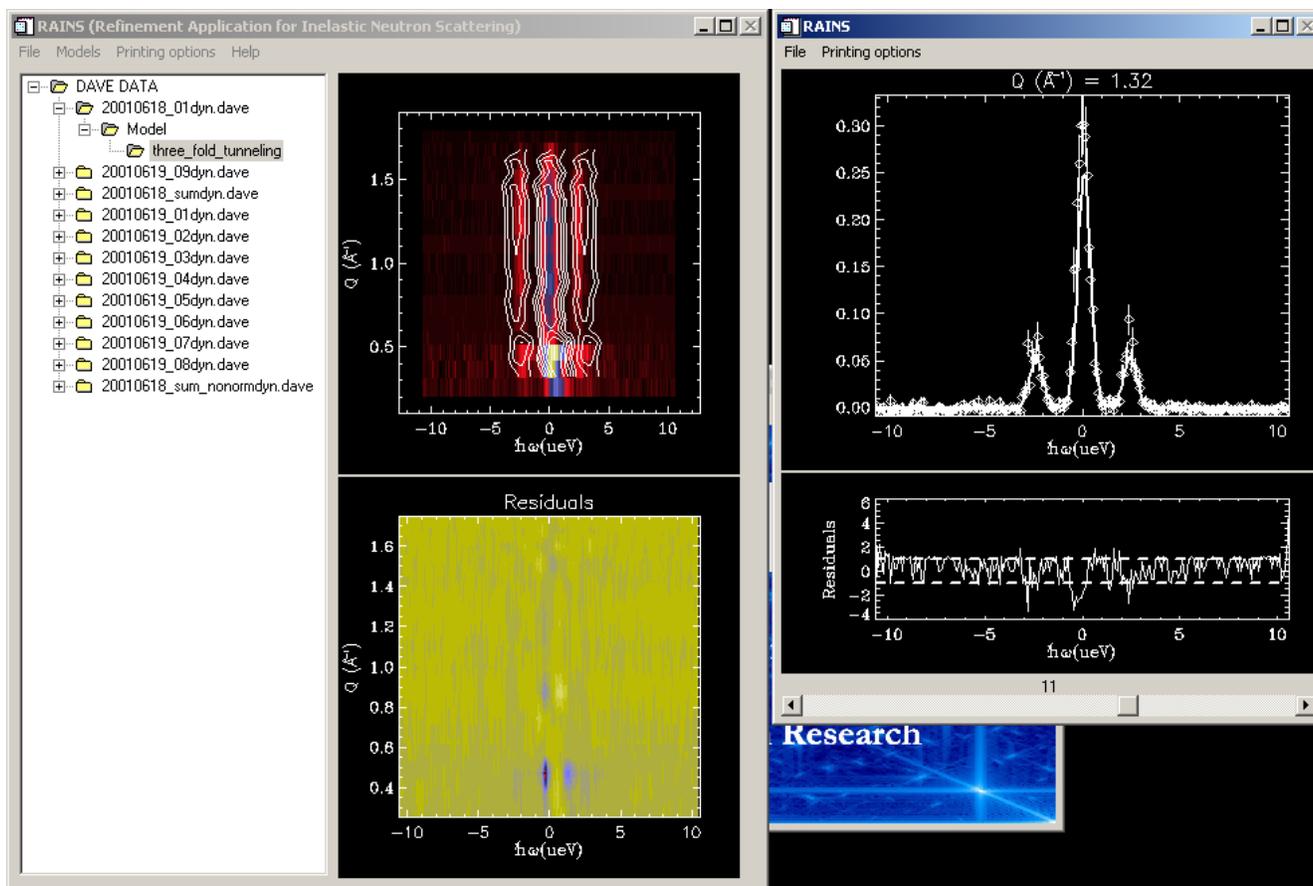
Fig. 7 Initial guess for the model fit.

The next step is to set up the fit range. This is accomplished by selecting the MODEL folder and launching the context-sensitive menu. Select FITTING ↦ SELECT FIT RANGE(S) and you will see a dialog shown in fig. 8. The existing values for this file are 0-217 for the x-range (energy transfer) and 0-15 for the y-range (wavevector transfer). Note that these ranges are zero-based indices into the arrays for each of the independent variables. So in this case there are 218 energy channels and 16 wavevector transfer values. For our purposes we will include all energy transfers in the fit (0-217) but limit the wavevector transfer to wavevectors with indices between 3 and 14 inclusive. Note that this dialog supports comma delimited specifications as well. For instance if you wanted to include only wavevectors 0, 9,10,11,12, and 15 you could type: `0,9-12,15`. Press ACCEPT and DISMISS when you are finished.
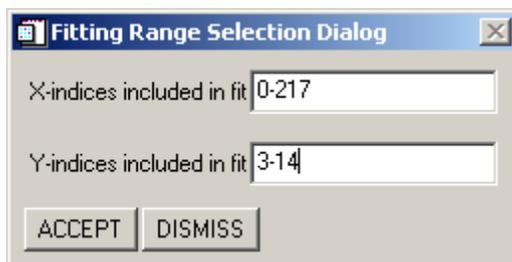
Fig. 8 Fit range entry dialog.

Now you are ready to fit the model to the data. From the MODEL context-sensitive menu select FITTING ↦START FITTING. As RAINS fits the data a new dialog display appears that tells the user how the fit is progressing in terms of the fit iteration, the c2 value, and also provides an interrupt button which will pause the fit and save the current best-fit parameters at this iteration. This dialog display is shown in Fig. 9.
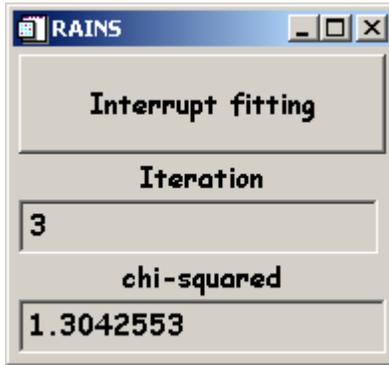
Fig. 9 Fit progress dialog.

Once the fit has completed this dialog will disappear. You can examine the resulting fit visually by looking at individual spectra with the best-fit model superposed as well as view the image-representation of the fit and data. You may examine the parametric results of the fit by selecting FITTING↦DISPLAY FIT REPORT which launches a dialog that displays the parameters and the uncertainties based on the fit.

Current models included in RAINS
Tunneling functions

3-fold rotational tunneling

Analytic expression:

$$S(Q,E) = I(Q)\left[A_o(Q)\delta(E - E_c(Q)) + \left(\frac{1 - A_o(Q)}{2}\right)\left(\delta(E - E_t - E_c(Q)) + \delta(E + E_t - E_c(Q))\right)\right]$$

where the EISF (elastic-incoherent structure factor) is given by

$$A_o(Q) = \frac{5 + 4j_o(Qr\sqrt{3})}{9}$$

and jo is the zeroth-order spherical Bessel function.
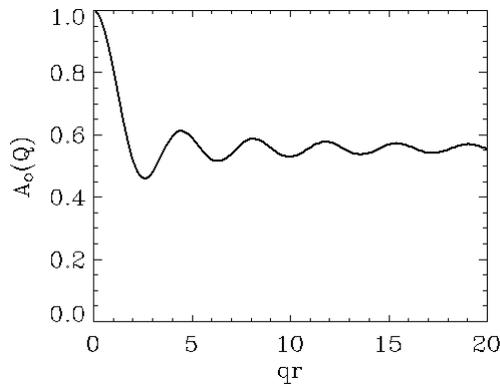
Model parameters:

I(Q): group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
E_t: tunnel splitting
r: tunnel circle radius (Å)

Broadened 3-fold rotational tunneling

Analytic expression:

$$S(Q, E) = I(Q) \times$$
$$\Big[A_o(Q)\delta(E - E_c(Q)) +$$
$$\left(\frac{1 - A_o(Q)}{3}\right)\Big(L(E - E_c(Q); \Gamma_q) + L(E - E_t - E_c(Q); \Gamma_t) + L(E + E_t - E_c(Q); \Gamma_t)\Big)\Big]$$

where the EISF (elastic-incoherent structure factor) is given by

$$A_o(Q) = \frac{1 + 2j_o(Qr\sqrt{3})}{3}$$

jo is the zeroth-order Bessel function, and the Lorentzian broadened components are given by

$$L(E; \Gamma) = \frac{\Gamma}{\pi}\frac{1}{E^2 + \Gamma^2} .$$

Model parameters:

$I(Q)$:   group/detector-dependent overall intensity
$E_c(Q)$:   group/detector-dependent center of scattering function
E_t: tunnel splitting
Γ_t: broadening of the tunnel lines
Γ_q: broadening of the elastic line
r: tunnel circle radius (Å)

Diffusion functions

2-fold jump diffusion

Analytic expression:

$$S(Q,E) = I(Q)\left[A_o(Q)\delta(E - E_c(Q)) + (1 - A_o(Q))\frac{\Gamma}{\pi}\frac{1}{(E - E_c(Q))^2 + \Gamma^2}\right]$$

where the EISF (elastic-incoherent structure factor) is given by

$$A_o(Q) = \frac{1 + j_o(Qd)}{2}$$
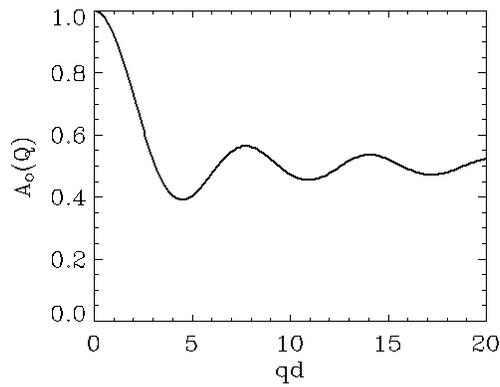
Model parameters:

I(Q):   group/detector-dependent overall intensity
Γ: half-width at half-maximum of Lorentzian component
$E_c(Q)$: group/detector-dependent center of scattering function
d: jump distance (Å)

3-fold jump diffusion on a circle

Analytic expression:

$$S(Q,E) = I(Q)\left[A_o(Q)\delta(E - E_c(Q)) + (1 - A_o(Q))\frac{\Gamma}{\pi}\frac{1}{(E - E_c(Q))^2 + \Gamma^2} \right]$$

where the EISF (elastic-incoherent structure factor) is given by

$$A_o(Q) = \frac{1 + 2j_o(Qr\sqrt{3})}{3}$$
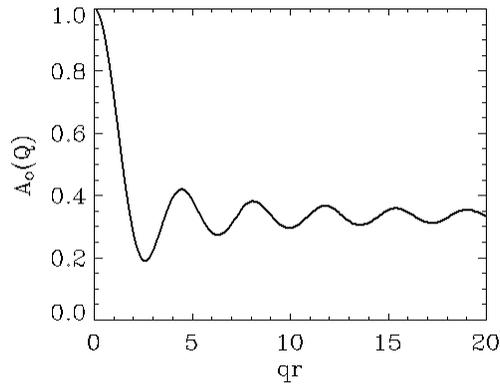
Model parameters:

I(Q): group/detector-dependent overall intensity
Γ: half-width at half-maximum of Lorentzian component
$E_c(Q)$: group/detector-dependent center of scattering function
r: jump circle radius (Å)

Translational diffusion

Analytic expression:

$$S(Q,E) = I(Q) \frac{\hbar D Q^2}{\pi} \frac{1}{\left(E - E_c(Q)\right)^2 + (\hbar D Q^2)^2}$$

Model parameters:

I(Q): group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
D: diffusion constant (cm^2/s)

N-fold jump diffusion on a circle

Analytic expression:

$$S(Q,E) = I(Q) \left[A_o(Q)\delta(E - E_c(Q)) + \sum_{\ell=1}^{N-1} A_\ell(Q) \frac{\left(\hbar / \tau_\ell\right)}{\pi} \frac{1}{\left(E - E_c(Q)\right)^2 + \left(\hbar / \tau_\ell\right)^2} \right]$$

where the structure factors are given by

$$A_\ell(Q) = \frac{1}{N} \sum_{n=1}^{N} j_o(Q r_n) \cos\left(\frac{2\ell n \pi}{N}\right),$$

the jump distances are given by

$$r_n = 2r \sin\left(\frac{n\pi}{N}\right),$$

and the inverse correlation times are given by

$$\tau_\ell^{-1} = 2\tau^{-1} \sin^2\left(\frac{\pi\ell}{N}\right)$$

Model parameters:

I(Q): group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
N: number of equivalent sites upon which the particle jumps
τ: inverse correlation time (ns^{-1} for [E]=μeV and ps^{-1} for [E]=meV)
r: jump circle radius (Å)

Isotropic Rotational Diffusion

<u>Analytic expression</u>:

$$S(Q,E) = I(Q)\left[A_o(Q)\delta(E - E_c(Q)) + \sum_{i=1}^{\infty} \frac{A_i(Q)}{\pi} \frac{\left(\hbar/\tau_i\right)}{\left(\hbar/\tau_i\right)^2 + \left(E - E_c(Q)\right)^2}\right]$$

where
$\tau_i^{-1} = i(i+1)D_R$, and the structure factors are given by

$A_o(Q) = j_o^2(Qr)$ and $A_i(Q) = (2i+1)j_i^2(Qr)$.
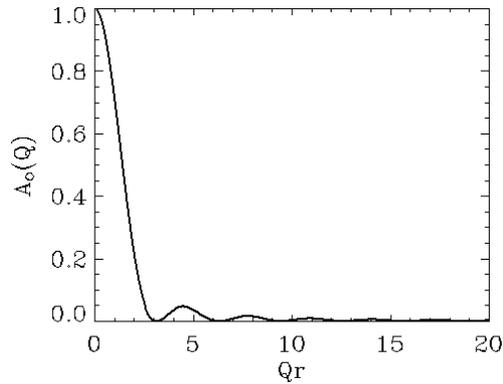
The $j_\ell(x)$ are the spherical Bessel functions of the first kind of order ℓ.

<u>Model parameters</u>:

I(Q):   group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
D_R: rotational diffusion constant (ns^{-1} for [E] in μeV and ps^{-1} for [E] in meV).
r: radius of sphere (Å)

Diffusion in a Sphere
(F. Volino and A.J. Dianoux, Molecular Physics **41**, 271-279 (1980))

Analytic expression:

$$S(Q,E) = I(Q)\left[A_0^0(Q)\delta(E - E_c(Q)) + \sum_{\{l,n\}\neq\{0,0\}} \frac{(2\ell+1)}{\pi} A_n^\ell(Q) \frac{\left(x_n^\ell\right)^2 \hbar D \big/ a^2}{\left(\left(x_n^\ell\right)^2 \hbar D \big/ a^2\right)^2 + \left(E - E_c(Q)\right)^2} \right]$$

where the structure factors are given by

$$A_0^0(Q) = \left[\frac{3j_1(Qa)}{Qa}\right]^2,$$

$$A_n^\ell(Q) = \frac{3}{2} j_\ell^2(x_n^\ell) \frac{\left(x_n^\ell\right)^2 - \ell(\ell+1)}{\left(x_n^\ell\right)^2}, \quad Qa = x_n^\ell$$

$$A_n^\ell(Q) = \frac{6\left(x_n^\ell\right)^2}{\left(x_n^\ell\right)^2 - \ell(\ell+1)}\left[\frac{Qa j_{\ell+1}(Qa) - \ell j_\ell(Qa)}{(Qa)^2 - \left(x_n^\ell\right)^2}\right], \quad Qa \neq x_n^\ell$$
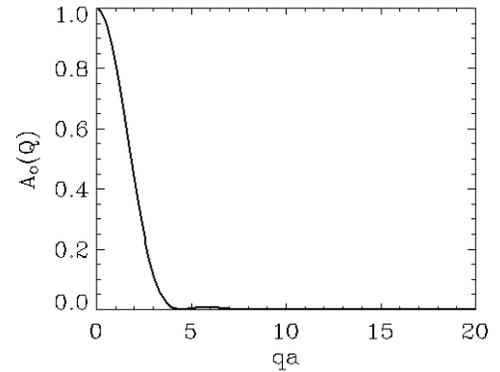
the x_n^ℓ are found as described in the reference above and

the $j_\ell(x)$ are the spherical Bessel functions of the first kind of order ℓ.

Model parameters:

I(Q): group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
a: radius of sphere (Å)
D: diffusion constant (cm^2/s).

Bounded Jump Diffusion
(P.L. Hall and D. K. Ross, Molecular Physics **42**, 673-682 (1981))

<u>Analytic expression</u>:

$$S(Q,E) = I(Q)\left[A_o(Q)\delta(E - E_c(Q)) + \sum_{n=1}^{\infty} \frac{A_n(Q)}{\pi} \frac{\Gamma_n}{\Gamma_n^2 + (E - E_c(Q))^2} \right]$$

where

$$\Gamma_n = \Gamma\left[1 - \exp\left(-\frac{1}{2}(n\pi r_o / L)^2 \right) \right],$$ and the structure factors are given by

$$A_o(Q) = j_o^2(QL/2) \text{ and } A_n(Q) = \frac{(2QL)^2}{\left[(QL)^2 - (n\pi)^2 \right]^2}\left[1 - (-1)^n \cos(QL) \right].$$
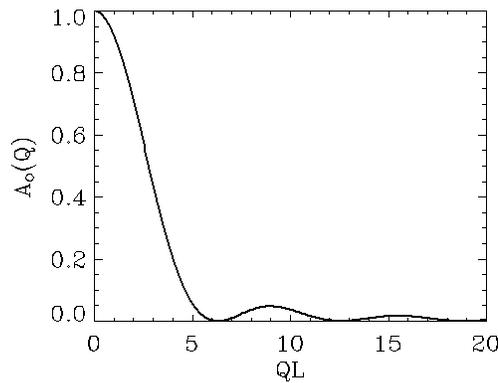
<u>Model parameters</u>:

$I(Q)$:   group/detector-dependent overall intensity
$E_c(Q)$: group/detector-dependent center of scattering function
Γ: half-width at half-maximum
r_o: jump distance (Å)
L: confinement distance

Miscellaneous functions

Background

Analytic expression:

$$S(Q, E) = M(Q, E)E + B(Q, E)$$

Model parameters:

M(Q,E):   slope of the background
B(Q,E):   offset

Gaussian

Analytic expression:

$$S(Q, E) = \frac{I(Q)}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2}\left(\frac{E - E_c(Q)}{\sigma}\right)\right)^2$$

Model parameters:

I(Q):   group/detector-dependent overall intensity
E_c(Q): group/detector-dependent center of scattering function
F(Q):   full-width at half-maximum (= 2.354σ(Q))

Lorentzian

Analytic expression:

$$S(Q, E) = \frac{I(Q)\Gamma(Q)}{\pi} \frac{1}{(E - E_c(Q))^2 + \Gamma(Q)^2}$$

Model parameters:

I(Q):   group/detector-dependent overall intensity
E_c(Q): group/detector-dependent center of scattering function
F(Q):   full-width at half-maximum (= 2Γ(Q))