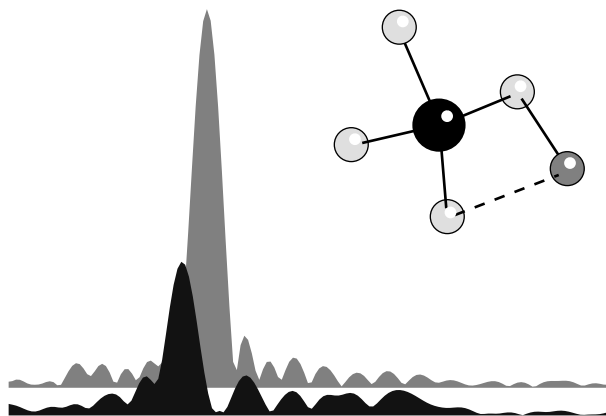

EXAFSPAK

A Suite of Computer Programs for Analysis of X-ray Absorption Spectra

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CONTENTS

	PAGE
PREFACE : HOW TO USE THIS MANUAL ..	4
A INTRODUCTION	5
A.1 SUMMARY OF PROGRAMS	5
A.2 SUMMARY OF FILES AND FILE TYPES ..	6
A.3 PLOTTING	7
A.3.1 PLOTTING DEVICES AND ROUTES	7
A.3.2 GRAPHICS TEXT CONTROL CHARACTERS	7
A.3.3 PLOTTING SYMBOLS	7
A.3.4 LINE TYPES AND PENS ..	8
A.3.5 USING GRAPHICS CURSORS	8
A.3.6 INCORPORATING GRAPHICS OUTPUT	8
INTO DOCUMENTS	
A.4 MENUS	9
A.4.1 SOME ELEMENTARY BUT USEFUL RULES	9
A.4.2 KEYSTROKE FILES	9
A.5 FLOW CHART OF DATA ANALYSIS	10
B MLIST, MVIEW, MCALIB, MDEAD and MAVE .	11
B.1 MLIST	11
B.2 MVIEW	12
B.3 MCALIB	13
B.4 MDEAD	14
B.5 MCONV	17
B.6 MAVE	17
C PROCESS	21
C.1 INTRODUCTION TO PROCESS	21
C.2 PROGRAM ORGANIZATION AND PLOTTING UTILITIES	22
C.3 STEP BY STEP DATA ANALYSIS	23
C.3.1 THE RAW DATA	23
C.3.2 THE PRE-EDGE FIT	24
C.3.3 THE SPLINE	25
C.3.4 THE EXAFS	27
C.3.5 THE FOURIER TRANSFORM	27
C.3.6 SAVING THE DATA	31
C.3.7 EDGE MANIPULATION ...	32
C.3.8 DEGLITCHING ..	34
C.3.9 RECALIBRATION	36
D OPT	36
D.1 OVERVIEW OF OPT	36
D.2 THE MAIN MENU	37
D.3 DATA INPUT AND THE PARAMETER-EDITOR	38
D.4 PLOTTING	40
D.5 FITTING THE DATA	41
D.6 OUTPUT	44
D.7 OPT TOOLS	44
D.7.1 SEARCH PROFILES	44
D.7.2 BEST INTEGER FITS	46
D.8 OPT <i>feff</i> SINGLE SCATTERING INTERFACE	47
D.9 OPT <i>feff</i> MULTIPLE SCATTERING INTERFACE ...	49
E MULDAT	50
F EDG_FIT	53
G THE PROCESS MANAGER UTILITY	55
H EXAFSPAK INSTALLATION	56
I BIBLIOGRAPHY	56
J DISCLAIMER	56

PREFACE : HOW TO USE THIS MANUAL

This manual describes the use of the EXAFSPAK programs for analysis of X-ray absorption spectra. Most of these programs were originally written by Graham George, under the Open VMS operating system, and were later ported to Linux, Tru64 UNIX and Microsoft Windows by Simon George. The purpose of this document is not to provide a complete description of all the capabilities of EXAFSPAK, but rather to provide sufficient information to allow the user to analyze data effectively. In many cases we have presented worked examples as the clearest way of describing a particular program. Rather than reading the entire manual the user may prefer to read the program summary and then proceed directly to running the programs. The programs PROCESS, OPT and MULDAT were initially designed to be self-sufficient and to be used without reference to a manual. We strongly encourage the user to experiment with the programs (especially PROCESS and OPT); they are, for the most part, quite robust, and the menu-driven architecture should make movement between sections quite simple.

Graham N. George, Simon J. George and Ingrid J. Pickering, April 2001.

A INTRODUCTION

A.1 SUMMARY OF PROGRAMS

The EXAFSPAK programs are launched at the command-line interface and will accept either a VMS or UNIX style of qualifier.

e.g. The command:

```
PROCESS /REC /DUMB NI
```

is equivalent to

```
process -rec -dumb ni
```

For historical reasons, OpenVMS-style commands are used as examples in this manual.

The EXAFSPAK EXAFS analysis package consists of eleven main programs, together with a number of utility programs. The capabilities and functions of the main programs are summarized in table I, below.

Table I
Mainstream Programs

Program	Function and/or capabilities
MLIST	Lists header comments and details of data data (XAS) files from the SSRL XAS data acquisition package.
MVIEW	MVIEW is used for examining the raw data (XAS) files.
MCALIB	MCALIB is used for obtaining re-calibration points from raw data (XAS) files. In most cases a first inflection energy of a metal foil spectrum is obtained. The result is written to an output file CALIBRATE.DAT or *.CAL file which is used by MAVE.
MDEAD	MDEAD is for use with solid state detectors which suffer from electronic deadtime problems. MDEAD reads a raw (XAS) data file containing a deadtime curve, determines electronic deadtimes and writes the output file DEADTIMES.DAT which is used by MAVE.
MAVE	MAVE computes an averaged data file from raw (XAS) data (correcting for electronic deadtimes using the information in DEADTIMES.DAT if needed). Selective weighting of individual data file array positions (sometimes called channels) is also available. MAVE also allows for energy calibration of data, and generates an .AVE (averaged) data file which is used by PROCESS and OPT.
PROCESS	PROCESS performs all the major EXAFS data reduction manipulations. Processed data is re-written to the .AVE file, and a number of formatted (ASCII) "data" files can be written. If Fourier filtering is required, PROCESS can generate unformatted .FIL files to be read by OPT.
OPT	OPT is the EXAFS curve fitting analysis program. It reads .AVE or .FIL files from PROCESS and can use a variety of different phase and amplitude functions.
MULDAT	MULDAT reads ASCII "data" files and produces stack plots <i>etc.</i> which can be used for publications. MULDAT is also useful for making measurements of peak heights, edge features, <i>etc.</i>
EDG_FIT	EDG_FIT performs pseudo-Voigt peak deconvolution of spectra (typically of edges), using a curve-fitting approach.
DATFIT	Fits spectra to a linear combination of other spectra.
FEFF_HLD	Sets up a parameter .HLD file for multiple scattering curve-fitting by OPT, using files generated by FEFF .

Utility Programs

Program	Function and/or capabilities
MCONV	Converts between the old SSRL <i>sdata</i> file format and the new SSRL XAS-collect file format (VAX only).
LISTAVE	Lists the header comments of .AVE files from PROCESS (see below).
MCMMASTER	Calculates absorption cross sections from the coefficients in the McMaster tables.
SAMPLE4	Computes ideal sample compositions for X-ray absorption transmittance measurements.
FLUOR	Corrects X-ray fluorescence data contained in an ASCII data file for distortions caused by self absorption (thickness) effects. The composition of the sample and the effective density must be known.

A.2 SUMMARY OF FILES AND FILE-TYPES

Table II

File	Data/Contents	Programs which create	Programs which use	Format
.AVE	Raw averaged data and results of processing, including EXAFS.	MAVE PROCESS OPT	PROCESS OPT	Binary
.FIL	Fourier filtered EXAFS data.	PROCESS	OPT	Binary
.EDG	Edge data and derivative.	PROCESS	PROCESS MULDAT	ASCII (<i>DATA</i>)
.FOU	Output file of Fourier transform.	PROCESS OPT	MULDAT	ASCII (<i>DATA</i>)
.FRM	Output of any chosen data from PROCESS.	PROCESS	MULDAT	ASCII (<i>DATA</i>)
.FRM	Hexadecimal dump of PROCESS .AVE file.	PROCESS	PROCESS	ASCII (<i>HEX</i>)
.FIT	EXAFS data and fit.	OPT	MULDAT	ASCII (<i>DATA</i>)
.SCH	Output of search profile from OPT.	OPT	MULDAT	ASCII (<i>DATA</i>)
.HLD	Fit parameters for use by OPT.	PROCESS OPT	PROCESS OPT	ASCII/Binary
.MUL	Data and plotting attributes of a plot (a saved plot).	MULDAT	MULDAT	Binary
.STP	Program setup information.	PROCESS OPT	PROCESS OPT	ASCII

The ASCII (*DATA*) format files are simply columns of numbers separated by spaces or tabs. These files can be read by MULDAT to generate figures and are also suitable for exporting to (for example) Apple Macintosh or PC machines for plotting.

A.3 PLOTTING

A.3.1 PLOTTING DEVICES AND ROUTES

All the EXAFSPAK programs use the same graphics: the *GPLOT* and *GRAFG* graphics libraries. The former controls "low-level" operations, such as drawing a line, while the latter deals with high level operations *e.g.* surface plots. In most programs the *GPLOT* graphics library requires both a *route* and a *device number*. The route directs output either to a file or to the terminal (TT:). The device numbers control which type of graphics output is produced and these are listed in the table below.

Table III — GPLOT device numbers

Device number	Output device
1	Tektronix 4010/4014 (10 bit)
2	Dec ReGIS
3	HPGL (eavesdrop mode)
4	Tektronix 4010/4014 (12 bit)
5	Tektronix 4010/4014 (10 bit, LN03R-Plus)
6	Tektronix 4010/4014 (10 bit, VT terminal)
7	Tektronix 4010/4014 (12 bit, LN03R-Plus)
8	Postscript
9	Encapsulated Postscript
10	X-Windows display
11	X-Windows display (#2)

- NOTES:**
- i.* Interactive graphics cursor input uses devices 1, 2 and 10 only.
 - ii.* LN03-plus printers use device 4, route to a file (*e.g.* PLOT.LN0), which can then be printed (use PRINT/PASSALL).
 - iii.* By far the best quality output is obtained with postscript, or encapsulated postscript.

A.3.2 GRAPHICS TEXT CONTROL CHARACTERS

Several control characters are used by the *GRAFG* label subroutine, which handles all labels etc. from programs such as *MULDAT*.

Table IV - graphics text control characters

Character	Effect
'	Italics - enclose text <i>e.g.</i> 'text'
^	Superscript, use \ to return to normal.
\	Subscript, use ^ to return to normal, <i>e.g.</i> H\2^SO\4 results in H ₂ SO ₄
!	Symbol:

!A !B !C !D !E !F !H !I !J !K !L !M !N !O !P !Q !R !S !T !U !V !W !X !Y !Z
 α β χ Δ ε γ λ μ ν Ω φ ρ Σ θ ξ ζ δ ω σ ψ π Å ° £ √

A.3.3 PLOTTING SYMBOLS

Table V - Plotting symbols

Plotting symbols (*e.g.* points on a *MULDAT* graph) are referred to by number:

•	■	▲	▼	●	◆	+	□	△	▽	⊙	◇
0	1	2	3	4	5	6	7	8	9	10	11

A.3.4 LINE TYPES AND PENS

The line type refers to the style of a line (dashed, solid *etc.*) and pen (usually) refers to the color or gray-scale of the graphic output. There are seven different line types available, and the number of pens depends upon the device (*e.g.* device=2 has 16 pens in all), both lines and pens are referred to by number :

<i>Line</i>	<i>Line type</i>
-----	6
-----	5
-----	4
-----	3
-----	2
.....	1
_____	0

A.3.5 USING GRAPHICS CURSORS

Input using graphics cursors is frequently required in many of the EXAFSPAK programs. The precise method for using these depends upon the type of terminal or workstation that the user is working with. Mouse support is provided in the form of graphic menus (a small area which can be selected with the mouse) which perform a particular function. The graphic menu functions can be duplicated by single key-presses (the user is usually prompted by the programs) .

A.3.6 INCORPORATING GRAPHICS OUTPUT INTO DOCUMENTS

Encapsulated postscript output routed to a file can often easily be incorporated into a document. For Microsoft Word and related products a third-party program is required to convert postscript or encapsulated postscript into bitmap style graphics.

The procedure for accomplishing this with DECwrite is outlined step by step below.

- i.* Select GPLOT device number 9, and route to a file (*e.g.* PLOT.EPS)
- ii.* Within **DECwrite** use the Options menu to select "**Full Menus**"
- iii.* Use "**File**" to select "**Links**" and choose "**Link to Picture ...**".
- iv.* Select the encapsulated postscript file that you created.
- v.* The plot can be positioned within **DECwrite** by depressing mouse button 1, and re-sized by depressing mouse button 2 (hold the shift key down to maintain the aspect ratio).
- vi.* The plot should be placed in a floating frame or an in-line frame (with "**Insert Styles ...**"), the latter being better for most purposes.

For Macintosh and PC the GNU program Ghostscript provides a convenient way of viewing, importing and manipulating postscript and encapsulated postscript files. On the Macintosh Graphicconverter together with Ghostscript can be used to generate a pict file.

A.4 MENUS

A.4.1 SOME ELEMENTARY BUT USEFUL RULES

The **EXAFSPAK** programs all use the same input-output library (*IOPAK*). This consists of routines that handle screen input and output, which are written in a mixture of *Fortran* and *Macro assembler*. There are some elementary but useful rules which are helpful to remember in running **EXAFSPAK** programs.

- i.* If you are asked to "**Press**" a key then only a single keystroke is required.
e.g. Press 1 to plot raw data :
- ii.* If you are asked to "**Enter**" a response then the *return* or *enter* key should be pressed after typing the response. Default or previously entered values are given in brackets. If these are acceptable then simply press return. New values can be entered separated either by commas or spaces, if a value is omitted then the default values are taken.
e.g. Enter R(low), R(high) & R(inc) [0.0, 7.00000, .020000] : , , 0.01
would result in only the value for R(inc) being changed to 0.01 .
- iii.* **Control Z** generally takes you back a level. If you are at the top level, then **control Z** will exit the program.
- iv.* **Control C** and **control Y** are sometimes trapped (*e.g.* in **OPT**), so do not rely on these to exit **EXAFSPAK** programs.

A.4.2 KEYSTROKE FILES

The *IOPAK* library can generate and use keystroke files (called **.LOG** files by default). These are best illustrated by an example. The program **PROCESS** can be run with the qualifiers **/LOGFILE**, **/RECOVER**, **/DUMB**, and **/AUTOMATIC**. All of these work by using keystroke files.

e.g. The command:

```
$ PROCESS/LOG NI
```

will start the program *PROCESS* and load the file **NI.AVE**. All keys press are written to the file **PROCESS.LOG**. If an identical session with process is desired but using a different data file, for example the file **NI2.AVE**, then the session can be replayed by using the command:

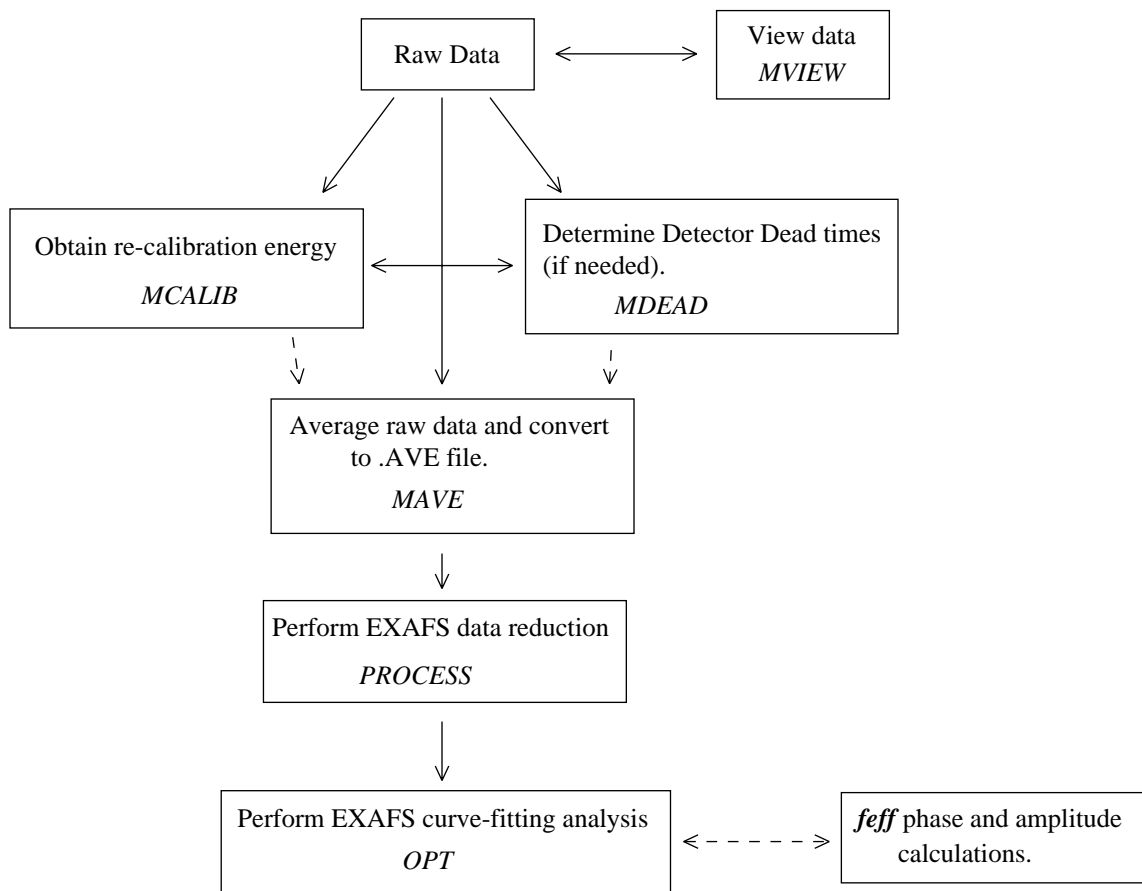
```
$ PROCESS/REC NI2
```

Alternatively, the user can specify the name of the keystroke file by **/LOG=MYFILE.KEYSTROKE** and **/REC=MYFILE.KEYSTROKE**

Keystroke files are very useful for running identical *PROCESS* sessions on a number of different files. The Open VMS command file **MULPROC.COM** reads a file containing a list of **.AVE** filenames and runs an identical **PROCESS** on each.

The **/DUMB** qualifier causes all terminal output apart from graphics to be suppressed while **/RECOVER** is operating.

A.5 FLOW CHART OF DATA ANALYSIS



Note : the package *feff* is not part of EXAFSPAK and must be obtained separately.

B. MLIST, MVIEW, MCALIB, MDEAD and MAVE

The SSRL XAS data acquisition software outputs data in SSRL binary or SSRL ASCII-format files. The programs MVIEW, MAVE, MDEAD and MCALIB read data directly from XAS files, to allow plotting, averaging, calculation of detector dead times and calibration, respectively.

B.1 MLIST

The program MLIST allows the user to view comments and details of raw data files.

Command:

```
MLIST INPUT_FILE_SPEC
```

Qualifiers:

Specification

<code>/HELP</code>	Lists command-line options
<code>/XWINDOWS=on/off</code>	Specifies whether X-Windows interface is to be used.
<code>/VERSION</code>	Gives compilation and GLIB dates.
<code>/ARRAY</code>	Lists data file array positions and labels
<code>/FIND=string</code>	Searched for files with "string" in comment line.
<code>/OUTPUT=filename</code>	Writes output to a named file.

Examples:

```
$ mlist SEMET-C-R_010.002 /array
```

```
SEMET-C-R_010.002 Selenomethionine crystal e along c, repeat of second orientation
```

```
-----  
Label                Index      Array  
-----  
Real time clock      1  
Requested Energy     2  
Achieved Energy      3  
I                    0 - 2    4 - 6  
IF                   7  
-----
```

This example illustrates the use of the `/array` qualifier.

```
$ mlist SE*.0* /find="powder"
```

```
SEMET-POWD_027.001 Selenomethionine powder sample, crystal moved out of beam
```

```
SEMET-POWD_027.002 Selenomethionine powder sample, crystal moved out of beam
```

This example illustrates the use of the `/find` qualifier.

B.2 MVIEW

The program MVIEW allows the user to plot data from a raw XAS file, with an optional ASCII dump of the plotted data. The ordinate is calculated according to the information given by the `/NUMERATOR` and `/DENOMINATOR` qualifiers. If the value specified with `/DENOMINATOR` is zero then no ratio is calculated, and the raw channels specified using `/NUMERATOR` are plotted.

Command:

`MVIEW INPUT_FILE`

<i>Qualifiers:</i>	<i>Specification</i>	<i>Default</i>
<code>/HELP</code>	Lists command-line options	
<code>/XWINDOWS=on/off</code>	Specifies whether X-Windows interface is to be used.	
<code>/VERSION</code>	Gives compilation and GLIB dates.	
<code>/ABSCISSA=n</code>	Channel for abscissa (x-axis)	3
	<code>/ABSCISSA=INDEX</code> plots point number.	
<code>/NUMERATOR=range</code>	Channel(s) for numerator	7-19
<code>/DENOMINATOR=n</code>	Channel(s) for denominator	4
<code>/SUMDATA</code>	Causes array positions to be summed.	
<code>/DEVICE=n</code>	GPLOT device	2
<code>/ROUTE=route</code>	GPLOT route	TT:
<code>/COLOURS=n</code>	Max. number of colours used in the plot	16
<code>/HIGHLIGHT</code>	Highlights one trace, space bar increments.	
<code>/CURSORS</code>	Graphics input cursors are called after plotting.	
<code>/LINE</code>	Lines are drawn in the plot (default)	
<code>/NOLINE</code>	No lines are drawn in the plot (use with <code>/POINTS</code>)	
<code>/POINTS=n</code>	Graphics symbol <i>n</i> is plotted at each data point.	0
<code>/TAKELOG</code>	Logs to be taken.	
<code>/NOTAKELOG</code>	No logs are taken (default).	
<code>/WRITE=[file_spec]</code>	Dumps plotted data to an ASCII (<i>DATA</i>) file.	
<code>/XMIN=value, /XMAX=value</code>	Specifies range for abscissa	range of data
<code>/YMIN=value, /YMAX=value</code>	Specifies range for ordinate	range of data
<code>/LOGFILE=[file_spec]</code>	Keystroke file for session.	
<code>/NOLOGFILE</code>	No Keystroke file (default)	
<code>/RECOVER=[file_spec]</code>	Recover from keystroke file	
<code>/DUMB</code>	Suppress terminal output	

Examples:

```
$ MVIEW MSOR_042.002/NUM=7-9;11;13-14;16-19
```

This example illustrates the use of the `/NUMERATOR` qualifier. Data channels 7,8,9,11,13,14,16,17,18,19 are used for the numerator in the plot. The denominator is channel 4 by default.

```
$ MVIEW/NUM=4/DEN=5/TAKELOG/WRITE=TRANSMITTANCE.DATA ZN_ZNFE2O4_018.003
```

This example plots the natural log of the ratio of channel 5 divided by channel 4 and writes the data into the ASCII file `TRANSMITTANCE.DATA`.

B.3 MCALIB

The program MCALIB allows the user to re-calibrate data by reading a standard from a raw XAS file. The results are displayed on the terminal screen and written to the ASCII file CALIBRATE.DAT. The program searches for peaks in the derivative and uses a quartic polynomial fitted to the data, combined with a Newton Raphson search algorithm to accurately find peak positions.

Command:

MCALIB INPUT_FILE

<i>Qualifiers:</i>	<i>Specification</i>	<i>Default</i>
/HELP	Lists command-line options	
/XWINDOWS=on/off	Specifies whether X-Windows interface is to be used.	
/VERSION	Gives compilation and GLIB dates.	
/ELEMENT=element_symbol	Element for calibration e.g. Cu, W, Pt.	Fe
/EDGE=edge_type	Edge for calibration e.g. K, L1, L3	K
/ABSCISSA=n	Channel for eV.	3
/NUMERATOR=n	Channel for numerator	5
/DENOMINATOR=n	Channel for denominator	6
/DEVICE=n	GPLOT device	2
/ROUTE=route	GPLOT route	TT:
/SMOOTH=value	Smoothing for derivative (0.0 = automatically set)	0.0
/PEAK=value	Fraction of biggest peak, below which peaks are ignored.	0.0
/DERIVATIVE=n	Derivative to be calculated.	1
/RANGE=value	eVhanne range for plot.	90.0
/TAKELOG	Logs to be taken (default).	
/NOTAKELOG	No logs are taken	
/POSITIVE	Positive peaks are searched for (default)	
/NEGATIVE	Negative peaks are searched for (e.g. if /DERIV=2)	
/NEWFILE	Clears old calibration information in output file.	
/OUT=filename	Writes calibration information to file.	CALIBRATE.DAT
/LOGFILE=filename	Keystroke file for session.	
/NOLOGFILE	No Keystroke file (default).	
/RECOVER=filename	Recover from keystroke file	
/DUMB	Suppress terminal output.	

Examples:

```
$ MCALIB/ELEM=NI/OUT=NITPP.CAL NITPP_044.001
```

This example calculates the calibration from the data in the file NITPP_044.001 accepting all the default values for the qualifiers, except for the element. In this case the program would calculate an ordinate of $\log(C_n/C_d)$ where C_n and C_d are the numerator and denominator array positions, respectively. In this particular case the default values (5 and 6, for C_n and C_d , respectively) correspond to outputs from ion chambers on either side of a nickel foil standard. The program calculates the first derivative, finds the peaks, which correspond to the first inflection points, and plots the result. Initially the program is focused upon the largest peak in the first inflection, the left and right cursors on the keyboard shift the focus to the peak on the left or right of the current focus. After selecting the appropriate peak the program can then be terminated by pressing any other key other than the cursor keys. The display would appear as shown in Figure B.2-1.

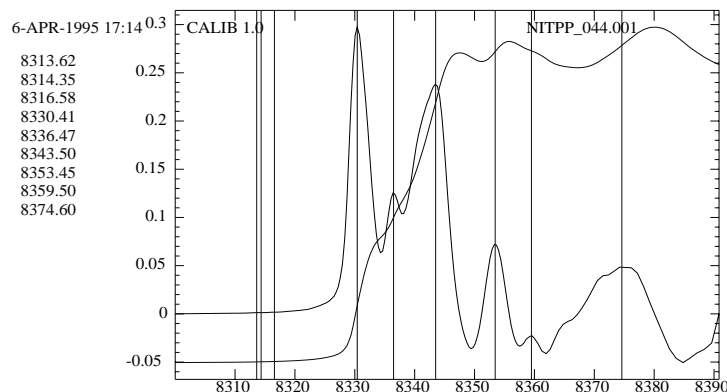


Figure B.2-1 An example of a calibration plot of a nickel foil.

MCALIB outputs the file specified by the /OUT qualifier which will contain a list of all the calibrations calculated in a particular session. Before making an entry in the output file, MCALIB checks that the edge information in the header of the file is consistent with the current calibration. If it is, then the calibration energy and the file name are appended to the end of the file, if not then a new output file is created. MCALIB output files can be used by MAVE to obtain values for data calibration. **Note : It is important to specify /NEWFILE when calibrating a new data set**, otherwise the new values may be appended to old ones. A typical MCALIB output file is listed below:

```
Fe K Edge, Table Value : 7111.29980eV Za : 26.0 I-edge : 1
IQP dehydrogenase, 95% active, reduced pH 10, Fe K-edge, 1mm cell, 1mm slits
```

Calibration	filename
7111.090	IQP-10-RED-FE_026.001
7111.072	IQP-10-RED-FE_027.001
7111.060	IQP-10-RED-FE_027.002
7111.074	IQP-10-RED-FE_027.003
7111.080	IQP-10-RED-FE_027.004
7111.086	IQP-10-RED-FE_027.005
7111.079	IQP-10-RED-FE_027.006
7111.086	IQP-10-RED-FE_027.007
7111.092	IQP-10-RED-FE_027.008
7111.060	IQP-10-RED-FE_027.002

Other valid Examples:

```
$ MCALIB/ELEM=W/EDGE=L1/OUT=WL1PAR.CAL/ABSCISSA=3/OUT=WCAL1.CAL WPAR_493_004.002
```

Tungsten L1-edge, eV in array position 3.

```
$ MCALIB/ELEM=S/EDGE=K/NUMERATOR=5/DENOMINATOR=4/NOTAKELOGS/DERIV=0 THIOS_012.001
```

Sulfur K-edge, eV in array position 3, calibrate on peaks in fluorescence data stored in array position 5, with I_0 in channel 4.

```
$ MCALIB /ELEM=Mo/ABSCISSA=4/DEV=2 MOSE-PROTEIN_034.003
```

Mo K-edge, eV in channel 4, calibrate on first inflection point, graphics displayed with plotting device number 2 (Regis).

B.4 MDEAD

The program MDEAD determines detector dead times from experimentally measured dead time curves and is designed for use with multi-element solid-state array detectors such as a Canberra 13 element Ge array. Experimentally these measurements can be made by scanning a slit blade through the incident X-ray beam while monitoring the output of all the detectors. All photon counting detectors suffer from electronic dead time to some degree. In the case of thallium doped sodium iodide, or plastic scintillators, this is usually negligible. In the case of solid-state detectors such as ultrapure germanium, or silicon (lithium) detectors, it can be quite significant. The electronic dead time is primarily associated with the shaping amplifier, and the method depends upon the collection of a total incoming count rate (ICR) signal from the shaping amplifier. This signal does not suffer from the same dead time effects as the shaped pulses, which are normally fed to a single channel analyzer (SCA). The corrections applied by EXAFSPAK are for that type of deadtime known as extending or paralyzing dead time, which is described by the equation $r = \kappa \rho e^{-\rho \tau}$ where τ is the dead-time, r the SCA, ρ the ICR, and κ is a constant of proportionality. Figure B.3-1 shows a dead time curve for the output of an SCA, and the close to linear relationship with I_0 for the ICR signal. In the ICR and the dead-time τ are known then the dead-time corrected SCA

counts r_c (i.e. the counts if there were no dead-time) are given by $r_c = \kappa\rho$, which can be calculated from the measured counts r by $r_c = r e^{\rho\tau}$.

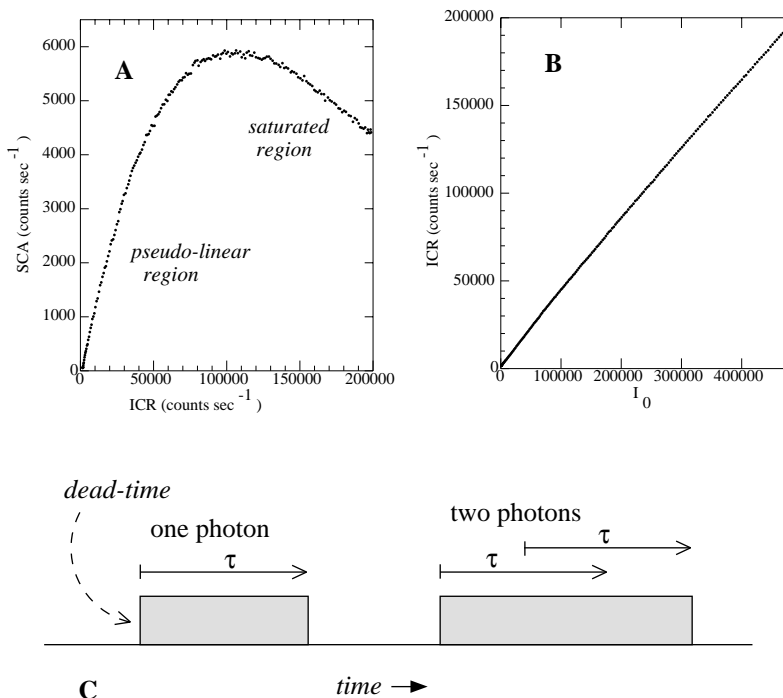


Figure B.3-1 A. Typical dead time curve for a single element of a Canberra 13 element Germanium detector. The photon energy was 10KeV, and the Gaussian shaping amplifier was operated at a shaping time of 0.5μsec. B. Linearity for the incoming count rate (ICR) signal from the shaping amplifier with the incident beam intensity (measured using an ion chamber). C. Schematic of origins of paralyzing electronic dead time, a single photon causes a dead-time τ, if a second photon arrives during the dead-time from a previous photon then the dead-time is extended by τ from the time of arrival of the second photon.

The purpose of the program MDEAD is to determine the values of κ , ρ , and τ , so that dead time corrections can be applied by the program MAVE. The command line `$ MDEAD INPUT_FILE`, where `INPUT_FILE` is an XAS raw data file, will launch the program MDEAD and the user is presented with the main menu, e.g.

```
$ MDEAD SB73_193_0012
```

```

Deadtime Calculations
-----
Press 1 to read file
  2 to clip data
  3 to plot data
  4 to fit data
  5 to plot fits
  6 for process manager
  7 for calculator
  8 to exit
:1

```

The data must first be read (menu option 1) and the single channel analyzer (SCA) channels must be paired with the appropriate amplifier incoming count rate (ICR) channels. This is illustrated in the following example dialog (note that <CR> means that return is pressed, accepting the default value(s)).

```

Reading file ... Enter array positions for count-time and I0 [1,4] :<CR>
201 Points      201
Enter first and last SCA array positions [7, 19] :<CR>
Enter ICR array position for position 8 [20] :<CR>
Enter ICR array position for position 9 [21] :<CR>
      :
Enter ICR array position for position 20 [32] :<CR>
All OK? [y/n] [Y] :<CR>

```

The user is then returned to the main menu, the dead time curves can now be clipped, plotted (using option 3), or fitted with the dead time equation $r = \kappa \rho e^{-\rho \tau}$ where r is the SCA, and ρ the corresponding ICR. If the data are fitted (menu option 4) the program asks :

```
Do you want to float Ro? [y/n] [N] :Y<CR>
```

This controls whether the offsets for the ICRs are floated in the fit, in our example dialog we select this, and the data are then fitted. The results are written to the file DEADTIMES.DAT , which is later read by MAVE for use in the dead-time correction process. A typical DEADTIMES.DAT is listed below :

SCA channel	SCA dead-time τ (μ sec)	ICR offset	Initial slope κ	ICR channel
8	7.2703	-1735.91	0.1766	21
9	7.2280	-1521.43	0.2449	22
10	7.0841	-1299.25	0.2689	23
11	7.1552	-1205.63	0.2327	24
12	7.4304	-1746.35	0.2207	25
13	7.1924	-1627.21	0.1923	26
14	7.0830	-1652.25	0.2024	27
15	8.5905	-1439.19	0.1827	28
16	8.7339	-1575.51	0.2559	29
17	7.2036	-1075.04	0.2423	30
18	7.3731	-1345.35	0.2218	31
19	7.2354	-1418.48	0.4387	32
20	7.4302	-1290.96	0.3716	33

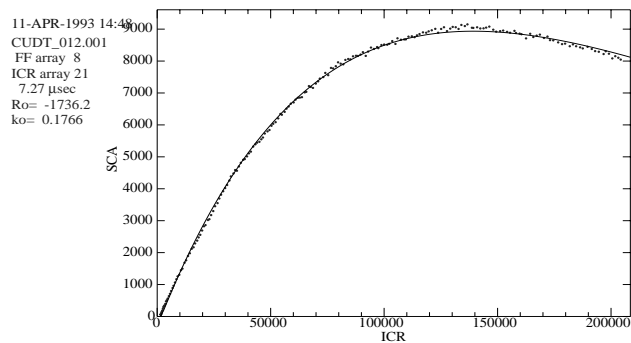


Figure B.3-2 Detector dead-time fitting using the program MDEAD. The solid line represents the best fit.

Selecting floating ICR offsets gives marginally better fits to the dead-time curves, however the actual values for the dead-times do not depend very much upon whether ICR offsets are floated.

B.5 MCONV

MCONV is used for converting obsolete SSRL Midas raw data *sdata* format binary files to the new XAS raw dat format. Files with the old *sdata* format come in two basic types, root files (e.g. CUGD_0194.SDATA;1) and continuation files or c-files (e.g. CUGD_0194.SDATA_00000001;1) both must be present in order for the *sdata* files to be accessed. The *sdata* run-time library must also be installed on the system, and this is available for VAX OpenVMS systems only. Users not wishing to install *sdata* on their systems should consider converting *sdata* files at SSRL where legacy OpenVMS VAX computers are maintained for this purpose.

MCONV copies the ordering of array positions in the *sdata* file. It should be noted that this is usually slightly different than for most XAS files :

Array positions for a typical Midas *sdata* file : 1: crystal, 2: mono (requested), 3: mono (achieved), 4: real-time-clock, 5: I0, 6: I1, 7: I2, 8: FF1 ... , 21: ICR1 ...

Array positions for a typical XAS file : 1: real-time-clock, 2: mono (requested), 3: mono (achieved), 4: I0, 5: I1, 6: I2, 7: FF1 ... , 20: ICR1 ...

Command:

MCONV SDATA_ROOT_FILE

Example:

Here we use MCONV to convert the *sdata* files CUGD_0194, which (in our example) has three c-files, and MCONV produces three XAS output files :

```
$ mconv CUGD_0194
  3 MIDAS c-files to read
Reading MIDAS c-file number 1
writing XAS file CUGD_0194.001
Reading MIDAS c-file number 2
writing XAS file CUGD_0194.002
Reading MIDAS c-file number 3
writing XAS file CUGD_0194.003
```

B.6 MAVE

MAVE is used for averaging raw XAS data files and outputs an .AVE file. In addition to catering for simple transmittance spectra, the program is designed to convert data from multielement solid state detector arrays and therefore can perform detector dead time calibration, statistical weighting of data from array elements *etc.*

Command:

MAVE INPUT_FILE_SPEC

<i>Qualifiers:</i>	<i>Specification</i>	<i>Default</i>
/HELP	Lists command-line options	
/XWINDOWS=on/off	Specifies whether X-Windows interface is to be used.	
/VERSION	Gives compilation and GLIB dates.	
/MCALIB=filename	MCALIB filename to read	no file read if filename omitted then CALIBRATE.DAT.
/OUTPUT=filename	.AVE filename to create	MAVE.AVE
/EXAPLT	Output to Farrell Lytle EXAPLT file.	
/EXXON	Output to an Exxon EXAPLT "ENERGY" file.	
/LOGFILE=[file_spec]	Keystroke file for session.	
/NOLOGFILE	No Keystroke file (default).	
/RECOVER=[file_spec]	Recover from keystroke file	
/DUMB	Suppress terminal output.	

Examples :

```
$ MAVE/OUT=NITPP.AVE NITPP_044.* ,NITPP_045.002
```

Would generate an output file NITPP.AVE, and would average all the files indicated by the input file specification.

If the no input file specification is given then MAVE uses the filenames in CALIBRATE.DAT (if present) previously generated by MCALIB.

```
$ MAVE/OUT=NITPP.AVE
```

To illustrate the use of MAVE, two sample dialogs are presented, the first is a simple transmittance sample, and the second is a data set from a 13 element Canberra Ge fluorescence detector array.

Example 1:

The first example is a low molecular weight nickel complex. In the following dialog <CR> indicates that the return key has been pressed. We assume that the program MCALIB has been run first and has generated a file named NITPP.CAL. The data files contain the output of the I0 and I1 ion chamber in array positions 4 and 5, respectively, and we wish to calculate the absorbance which is given by $\log(C_4/C_5)$. The data files will be recalibrated individually (the "shift individual spectra" question) and then interpolated to the abscissa of the first file for the average. This option requires that filenames be read from a MCALIB output file. The strategy to be used in averaging the data is selected by a series of questions :

```
$ MAVE/OUT=NITPP/MCALIB=NITPP.CAL
```

```
3 Files found :
1 NITPP_044.001
2 NITPP_044.002
3 NITPP_044.003
```

```
Do you want to remove files from this list? [y/n] [N] :<CR>
```

```
Do you want to change file weights? [y/n] [N] :<CR>
```

```
Enter array position for eV [3] :<CR>
```

```
Enter array position for rtc [1] :<CR>
```

```
Enter array position range for numerator [7, 19] :4,4<CR>
```

```
Enter array position range for denominator [4, 4] :5,5<CR>
```

```
Do you want to take logs? [y/n] [N] :y<CR>
```

```
Do you want to change array position weights? [y/n] [N] :n<CR>
```

```
Statistical weights :
```

```
Enter 1 to calculate, 2 to use weights from file, 3 for unit weights [2] :3<CR>
```

```
Do you want to exclude specific array positions? [y/n] [N] :<CR>
```

```
Recalibration ...
```

```
Do you want to shift individual spectra? [y/n] [N] :y<CR>
```

```
Enter apparent eV0, true eV0 [8330.39, 8331.60] :<CR>
```

```
Enter d-space, steps per degree [1.92013, 8000.00] :<CR>
```

```
Enter Za, E0 [28.0000, 8350.00] :<CR>
```

```
$
```

The file NITPP.AVE has now been created and can be analyzed using PROCESS and OPT (see below).

Example 2:

The second example is a dilute solution of a metalloprotein, measured with a Canberra 13 element Ge detector array. As before, the program MCALIB has already been run to calibrate all the scans in the data, and again we set up the strategy for the average, this time opting to use statistical weighting of the data. Initial questions concern the which array positions to use *etc*. In this example we have already determined (using MVIEW) that array positions 10 and 15 are non-functional, so that we wish to exclude these from the average, and that array position 12 is malfunctioning in several of the files.

```
$ mave/out=cu4_amt1
```

```
15 Files found :
1 CU4_AMT1_008.001
2 CU4_AMT1_008.002
3 CU4_AMT1_008.003
```

```
4 CU4_AMT1_008.004
5 CU4_AMT1_008.005
6 CU4_AMT1_008.006
7 CU4_AMT1_008.007
8 CU4_AMT1_008.008
9 CU4_AMT1_009.001
10 CU4_AMT1_010.001
11 CU4_AMT1_010.002
12 CU4_AMT1_010.003
13 CU4_AMT1_010.004
14 CU4_AMT1_010.005
15 CU4_AMT1_010.006
```

```
Do you want to remove files from this list? [y/n] [N] :<CR>
Do you want to change file weights? [y/n] [N] :<CR>
Enter array position for eV [3] :<CR>
Enter array position for rtc [1] :<CR>
Enter array position range for numerator [7, 19] :<CR>
Enter array position range for denominator [4, 4] :<CR>
Do you want to take logs? [y/n] [N] :<CR>
Do you want to change array position weights? [y/n] [N] :y<CR>
```

Answering "yes" to the last question above allows us to exclude the non-functional array positions (10 and 15) by setting the weights to zero for these array positions.

```
Position 7 weight [1.00000] :<CR>
Position 8 weight [1.00000] :<CR>
Position 9 weight [1.00000] :<CR>
Position 10 weight [1.00000] :0<CR>
Position 11 weight [1.00000] :<CR>
Position 12 weight [1.00000] :<CR>
Position 13 weight [1.00000] :<CR>
Position 14 weight [1.00000] :<CR>
Position 15 weight [1.00000] :0<CR>
Position 16 weight [1.00000] :<CR>
Position 17 weight [1.00000] :<CR>
Position 18 weight [1.00000] :<CR>
Position 19 weight [1.00000] :<CR>
Statistical weights :
Enter 1 to calculate, 2 to use weights from file, 3 for unit weights [2] :1<CR>
```

In the last option we have chosen to calculate statistical weighting of the data. This is done by obtaining an estimate of the signal to noise ratio. The signal is defined as the jump (edge jump) between two energies, one above and one below the absorption edge, and the noise is estimated by photon statistics as being proportional to the square root of the fluorescence counts (normalized to I_0). In general it is considered preferable to use weights calculated during data collection by XAS, and MAVe should only be used to calculate weights if these were not computed, or if they are considered unreliable for some reason. The basic procedure for calculating statistical weights is discussed in more detail at the end of this section.

```
Calculate statistical weights :
Enter ev-low, ev-high [8940.00, 9030.00] :<CR>
```

The next question allows us to exclude specific array positions in individual sweeps. In our example previous examination with MVIEW has indicated that array position 12 is malfunctioning in several scans. We now proceed to eliminate this array position from files 2, 3 and 4, and then to exit from this section by answering "0" to the **Enter file-number [0] :** question.

```
Do you want to exclude specific array positions? [y/n] [N] :y<CR>
Enter file-number [0] :2<CR>
1 CU4_AMT1_008.002
Enter array position to exclude [0] :12<CR>
Enter file-number [0] :3<CR>
2 CU4_AMT1_008.003
Enter array position to exclude [0] :12<CR>
```

```

Enter file-number [0] :4<CR>
  3 CU4_AMT1_008.004
Enter array position to exclude [0] :12<CR>
Enter file-number [0] :<CR>

```

The program now proceeds to inquire about recalibration. For spectra which have significant calibration energies (*i.e.* data that do not allign well) one might choose to shift individual spectra. If this choice is made then MAVE searches the list of files from MCALIB (read in from the CALIBRATE.DAT file) to match the current filename and then interpolates data (with a piecewise cubic spline) so that all files share a common calibrated energy scale (that corresponding to the first file. If the default is selected (as we do here) then the average of the calibration energies in CALIBRATE.DAT is used and no interpolation is performed. Final questions allow the user to confirm monochromator information derived from the input file.

Recalibration ...

```

Do you want to shift individual spectra? [y/n] [N] :<CR>
Enter apparent eV0, true eV0 [8982.03, 8980.30] :<CR>
Enter d-space, steps per degree [1.92013, 8000.00] :<CR>
Enter Za, E0 [29.0000, 9000.00] :<CR>

```

The program then proceeds through all files in the average, and creates the file CU4_AMT1.AVE which can be analyzed using PROCESS and OPT (see below).

We will now review the weighting scheme used by MAVE for statistical weighting of array positions in multi-element array detectors. Each array position will have a different signal to noise ratio (S/N), depending upon the electronics and location of the detector with respect to the sample. The signal S_i from array position i is assumed to be proportional to the edge jump (see figure B.4.1) $S_i \propto (A_i - B_i) = \Delta_i$, and the noise N_i is estimated from photon statistics to be proportion to the square root of the normalized fluorescence count rate $N_i \propto \sqrt{A_i}$ by application of a filter as previously described. Note that the points E_A and E_B are specified by the user at the input line :

```

Calculate statistical weights :
Enter ev-low, ev-high [8940.00, 9030.00] :<CR>

```

Defaults for E_A and E_B are calculated from the edge information in CALIBRATE.DAT.

The proper statistical weighting factor W_i , is proportional to $(S_i/N_i)^2$ normalized to the edge jump so that array positions with equal signal to noise ratios contribute equally so that $W_i = (S_i/N_i)^2/S_i$. The weighted average $\langle F \rangle$ of the data from all array positions F_i is then given by $\langle F \rangle = \sum W_i F_i / \sum W_i$

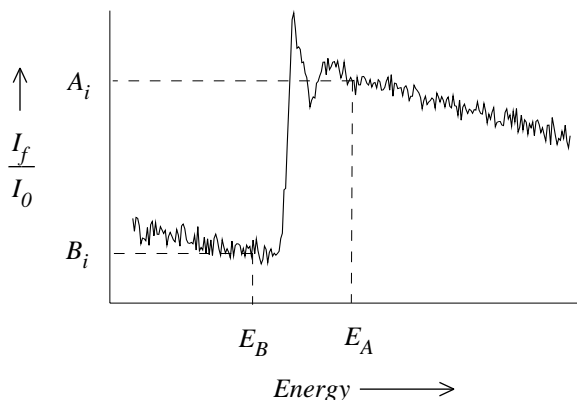


Figure B.4-1. Statistical weighting of data from array detectors

For more details of the statistical weighting of data from multi-element array detectors see Scott *et al. Proc. Natl. Acad. Science USA*, **1981**, 78, 644-667.

C. PROCESS

C.1 INTRODUCTION TO PROCESS

The program PROCESS is the main data reduction program for EXAFS and edge spectra. It is defined as a VMS command and can run with several qualifiers. The command line format is :

```
$ PROCESS INPUT_FILE
```

Where **INPUT_FILE** is an .AVE file generated by MAVE. This file contains averaged EXAFS data, and stores the data and details of any processing.

Qualifiers :

/HELP	Lists command-line options
/XWINDOWS=on/off	Specifies whether X-Windows interface is to be used.
/VERSION	Gives compilation and GLIB dates.
/AUTOMATIC	Runs automatically by execution of a keystroke file called PROCESS . AUTO
/LOGFILE=filename	
/RECOVER=filename	
/DUMB	

On starting PROCESS without the **/DUMB** qualifier, the main menu will appear. In what follows we will work through an example data set in the file MD1524.AVE, containing molybdenum *K*-edge EXAFS from a sample of molybdenum disulfide from the Climax Molybdenum Co. This data set is available as an example file with the programs.

e.g. The command line :

```
$ PROCESS MD1524
```

Will produce the PROCESS main menu :

MD1524.AVE

MD1524

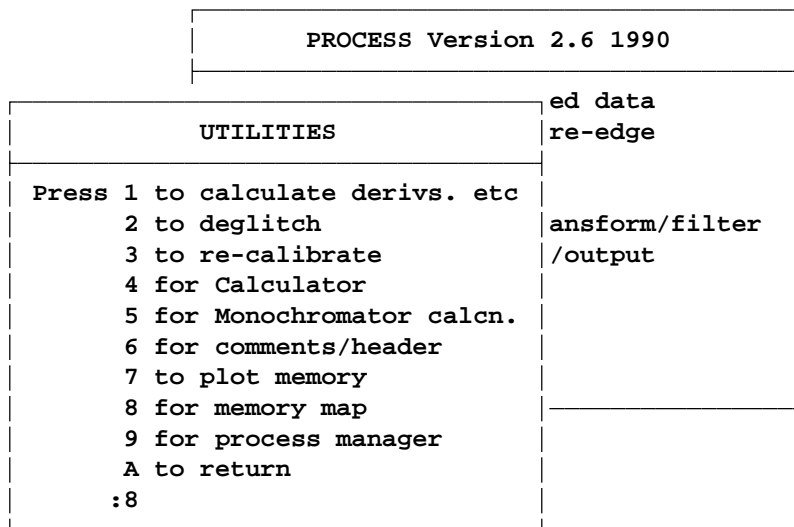
```
PROCESS Version 2.6 1990
Press 1 for raw averaged data
     2 for baseline/pre-edge
     3 for spline
     4 for EXAFS
     5 for Fourier transform/filter
     6 for file input/output
     7 for utilities
     8 for setup
     9 to Quit
:
```

G.N.George Oct 1990

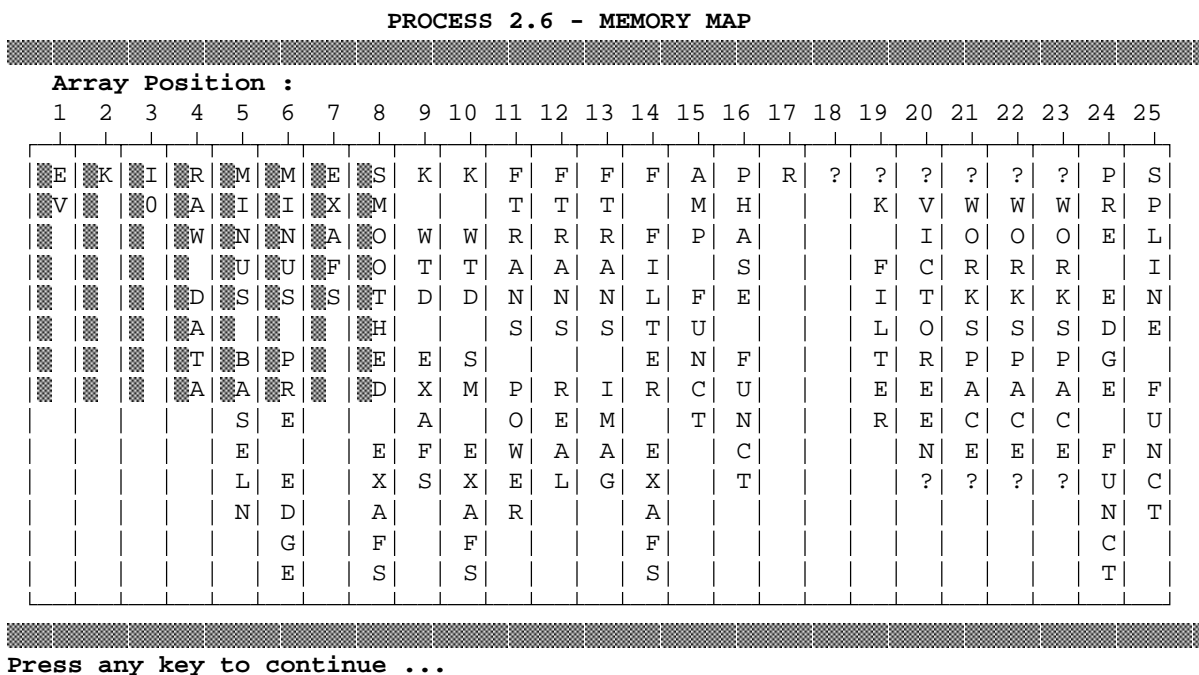
The screen is divided into two main regions; the scroll region is normally the bottom two lines on the screen, separated by a solid bar. Questions which require some response from the user generally appear in this region. The rest of the screen is usually reserved for plotting and for menus and other displays.

C.2 PROGRAM ORGANIZATION AND PLOTTING UTILITIES

Before we pursue the analysis of the molybdenum disulfide EXAFS data, it is important to understand the basic way in which PROCESS works. The program is based around a large two dimensional array, the first eight columns of which are saved in the .AVE file, together with additional information in the file header. In general, the different columns represent different stages in the data analysis. Insight can be gained by examining the memory map in the utilities menu:



The memory map is displayed :



The contents of each array element are described along side each column, and the histograms depict the columns that contain data. Initially, only the first eight columns are filled, as shown in our example above. PROCESS often refers to *array positions* which are the numbers given at the top of the memory map, e.g. array positions 1 and 6 would contain the energy (eV) and pre-edge subtracted X-ray absorption spectrum. Those array positions marked with a question mark (?) at the top are subject to change without notice, as are the spline and pre-edge array positions (although these are less frequently modified) by use as workspace. The program automatically keeps track of the array positions that have been used, and these will be shown by the histogram on displaying the memory map. After a session of data analysis the memory map might appear as follows :

PROCESS 2.6 - MEMORY MAP

Array Position :																									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	
E	K	I	R	M	M	E	S	K	K	F	F	F	F	A	P	R	?	?	?	?	?	?	P	S	
V		O	A	I	I	X	M			T	T	T		M	H			K	V	W	W	W	R	P	
			W	N	N	A	O	W	W	R	R	R	F	P	A				I	O	O	O	E	L	
				U	U	F	O	T	T	A	A	A	I		S			F	C	R	R	R		I	
				D	S	S	S	T	D	D	N	N	N	L	F	E			I	T	K	K	K	E	N
				A				H			S	S	S	T	U				L	O	S	S	S	D	E
				T	B	P		E	E	S				E	N	F			T	R	P	P	P	G	
				A	A	R		D	X	M	P	R	I	R	C	U			E	E	A	A	A	E	F
				S	E			A		O	E	M		T	N			R	E	C	C	C		U	
				E			E	F	E	W	A	A	E		C				N	E	E	E	F	N	
				L	E		X	S	X	E	L	G	X		T				?	?	?	?	U	C	
				N	D		A		A	R			A										N	T	
				G			F		F				F										C		
				E			S		S				S										T		

Press any key to continue ...

The contents of the various array positions can be plotted against one another using option 7 of the utilities menu. The plotting in PROCESS is done by a single routine, which allows manipulation of the data, if required, every time a graph is plotted. For example, if we select option 1 on the main menu :

Press 1 to plot raw data :1

A plot subsequently appears on the screen, with the sub-menu :

Press 1 to plot, 2 for hardcopy, 3 to edit, 4 for cursors, 5 for peaks :

The first option allows the current plot to be refreshed, the second generates a hardcopy to the designated hardcopy device and route (determined with setup on the main menu), the third allows the user to edit the data, the fourth calls the cursors, and the fifth engages a peak finding algorithm to look for peaks in the data (useful with edges and with Fourier transforms).

C.3 STEP BY STEP DATA ANALYSIS

The following will describe a typical dialog of a data analysis session. Each section can be entered from the main menu, or in order. For example, the spline section of the program can be entered from the main menu option 3. It is important to remember that *control Z* will take you back to the previous (in most cases the main) menu.

C.3.1 THE RAW DATA - main menu option 1

The first step in data analysis is usually to view the raw data, and this is achieved by using option 1 on the main menu :

Press 1 to plot raw data :1

At this point if the user presses a "1" then a plot of the data is produced, or if any other key is pressed (except for the cursor or any function keys) then the program proceeds to the next stage.

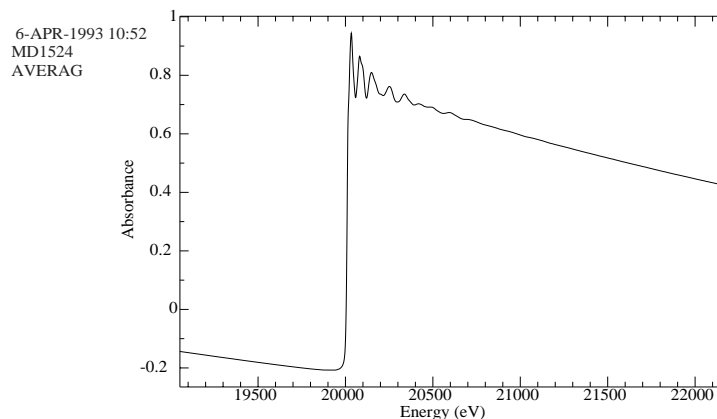


Figure C.3-1 Plot of the raw averaged data from process.

C.3.2 THE PRE-EDGE FIT - *main menu option 2*

Press 1 to subtract baseline file :

In most cases a baseline file is not required. A baseline file is an .AVE file which is heavily smoothed before subtracting from the data. This option would be used, for example, in the case of a fluorescence spectrum of a dilute aqueous sample measured with a fluorescent ion chamber detector. In this case a very significant background would be present in the data which could be mimicked by running a sample of the buffer in which the sample was dissolved, and subsequently subtracted as a baseline file. We now proceed with our example analysis, and the following dialog would appear in the scroll region at the bottom of the screen (note that **<CR>** signifies pressing a carriage return). The first operation is to subtract the pre-edge function. Here we fit a curve through the region of the data that lies before the initial rise of the absorption edge, the goal being removal of the background signal to isolate an X-ray absorption spectrum for the absorbing atom alone (*e.g.* a Mo only spectrum for a Mo EXAFS experiment).

```

Press 1 to subtract baseline file :<CR>
Press 1 to plot baseline subtraction :<CR>
Press 1 to subtract pre-edge :1
Press 1 for polynomial pre-edge fit, 2 for Gaussian, 3 for erf function :1
Enter eV(low), eV(high) [0.0, 19800.0] :<CR>
Enter order of polynomial for pre-edge [-1] :<CR>

```

The pre-edge subtraction selected is a polynomial. The Gaussian type should be used for solid state detector arrays where there is significant scatter is admitted to the SCA window at the low energy end of the scan. This gives a Gaussian tail to the data, and the Gaussian pre-edge function can be used to remove this. The polynomial pre-edge subtraction works by fitting a polynomial of order -1 in our example through the range 0.0 (*ie.* the start of the data) to 19980eV, just below the Mo *K* edge (as will generally be the case with our PROCESS example, the defaults are accepted). The program then fits the selected region with the polynomial, extrapolates through the whole data set, and subtracts it :

```

46 Points used in pre-edge fit
Press 1 to plot pre-edge result :1

```

On pressing 1 the pre-edge subtracted data is plotted, and an alternative plot which shows the data before and after the pre-edge subtraction and the polynomial (or Gaussian) itself is given by the next option. Note that the pre-edge region has been reduced to a flat line, and the post-edge region to a slow decay.

```

Press 1 for total pre-edge plot :1

```

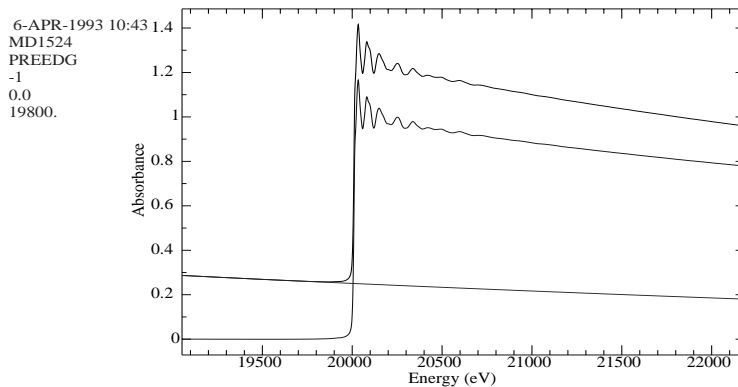


Figure C.3-2 Plot of the pre-edge subtraction. The raw data, the pre-edge polynomial and the pre-edge subtracted data are superimposed.

The Gaussian and erf pre-edge functions are particularly useful when processing spectra collected on dilute samples with a solid state detector. In this case the pre-edge has a rising Gaussian-like component which arises from X-ray scatter "leaking" into the SCA window at low energies. Although the erf function is a more accurate model of the background function, the Gaussian background often provides the more effective method:

```

Press 1 for polynomial pre-edge fit, 2 for Gaussian, 3 for erf function :3
Enter eV(low), eV(high) [0.0, 7075.0] :7075<CR>
Enter energy eV for middle of SCA window [6403.00] :<CR>
Enter window width, detector resolu. (eV) [750.000, 250.000] :720,225<CR>
Enter scaling factors a, b (y=a*y+b) [39.4161, 1.49405] :<CR>
Press 1 to plot pre-edge result :<CR>
Press 1 for total pre-edge plot :1

```

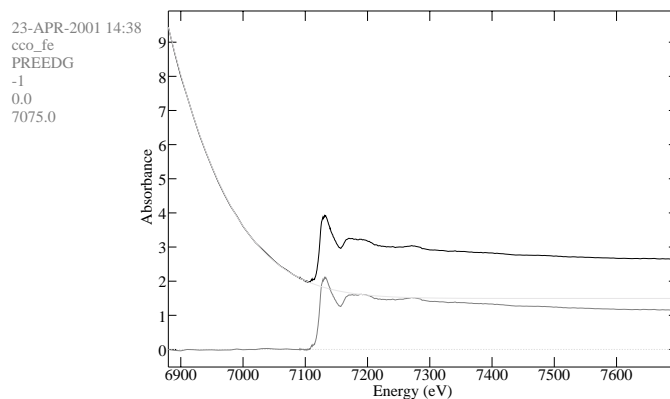


Figure C.3-2a Plot of the Gaussian pre-edge subtraction. Note that the data set is different than that used for the rest of this section.

C.3.3 THE SPLINE - main menu option 3

The next stage in the data analysis is the subtraction of the spline. A spline is a stiff but flexible curve that is comprised of several polynomials mathematically knotted together which is fit to the EXAFS region of the raw data. PROCESS defaults are often sufficiently accurate that the user can simply accept them.

```

Press 1 to subtract Spline :1
Do you wish to reset to defaults? [y/n] [Y] :<CR>
Enter Spline eV(low) & eV(high) [20025.0, 22183.1] :<CR>

```

The "reset to defaults" option should be selected when there are no previous splines contained in the header of the file (*i.e.* no previous session of PROCESS has been run), or when the previous spline is inadequate in some way. We accept the reset option (currently the default) and choose to spline over the entire range of the data (also the default - note that in subsequent sessions the defaults will be the last values entered).

```

Enter order of Spline & No. of ranges [4, 3] : ,4<CR>
Enter k-weighting for spline [4] :<CR>
Enter 1 to use Victoreen [1] :<CR>
Enter 1 for k-spaced spline points [0] :<CR>

```

The order of the spline refers to the order of the component polynomials, and the number of ranges refers to the number of individual polynomials. Because the data is over a particularly wide range with our molybdenum disulfide example we select 4 spline ranges (above), rather than the default of three. The other defaults are to use a k^4 weighting for the spline fit, which ensures an accurate fit at the crucial high energy end, and to use the Victoreen polynomial to normalize the data. The Victoreen polynomial is an expression for the absorption cross-section above a particular edge. The absorption coefficient, μ_{vic} , is given by $\mu_{vic} = C_{vic}\lambda^3 + D_{vic}\lambda^4$ where λ , the X-ray wavelength in Ångströms is $\lambda = (hc/E) = 12398.4/E$ (eV), and C_{vic} and D_{vic} are the tabulated Victoreen coefficients for a particular edge and element (in our case the Mo K-edge). Values for C_{vic} and D_{vic} are contained within PROCESS for most elements in the periodic table. When the Victoreen is used, the oscillatory part of the X-ray absorption, the EXAFS $\chi(k)$, is calculated by $\chi(k) = (\mu_{exp} - \mu_{spline})/\mu_{vic}$ where μ_{exp} is the experimental absorption (pre-edge result) and μ_{spline} is the spline fit. The use of the Victoreen polynomial ensures that any background problems with the data, or inadequacies with the pre-edge subtraction (the former are especially common for fluorescence data) do not distort the amplitude of the EXAFS. When the Victoreen is not used the EXAFS is given by $\chi(k) = (\mu_{exp} - \mu_{spline})/\mu_{spline}$. The dialog continues with entry of the spline points, and confirmation of the edge type and Victoreen coefficients:

```

Enter 3 Spline Points
Spline Point 1 [20564.5] :<CR>
Spline Point 2 [21104.1] :<CR>
Spline Point 3 [21634.6] :<CR>
Enter symbol for element [MO] :<CR>
Enter edge (K, L1,..) [K] :<CR>
Enter Victoreen Coefficients Cvic,Dvic [555.000, 336.000] :<CR>
Enter Edge jump u0 for ratio (0 = auto) [0.0] :<CR>
Enter eV to calc. u0 [20045.0] :<CR>

```

If a new spline is being calculated the "Edge jump u0 for ratio" should always be set to zero. The parameter specified by "Enter eV to calc. u0" requires some explanation. This value is the normalization point for the data, and the edge jump, or μ_0 value is the value of μ_{spline} at the normalization point energy; it should be just above the edge, but in cases where background is a problem care must be taken in choosing this point. In general it is not necessary to alter the spline points selected by PROCESS. If, however, a poor spline is obtained (as judged by improbably low- R (*i.e.* $\sim 1\text{Å}$) peaks in the Fourier transform, see below) then the user may either increase the polynomial order, the number of ranges, or change the position of the spline points. If either of the former two options are selected, then particular care must be taken to avoid removing actual EXAFS oscillations, especially at the high k -end of the spectrum. This latter comment is also relevant when fitting data of restricted k -range (*e.g.* out to a maximum of 9Å^{-1}), in this case the order and/or the number of ranges should be reduced.

```

Final falloff was 0.78 <CR>
Press 1 to plot spline removal :<CR>
Press 1 to plot spline removal + Victoreen :1

```

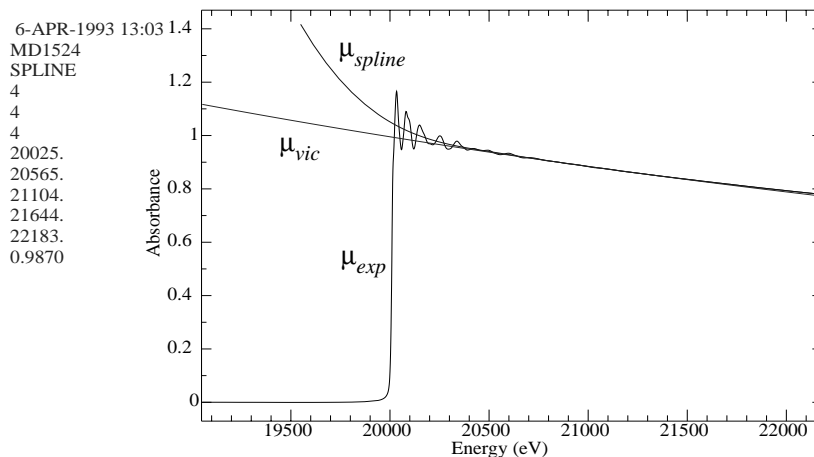


Figure C.3-3 Spline removal, using Victoreen polynomial to ratio the EXAFS

The "Final falloff" is the ratio μ_{vic}/μ_0 at the high energy end of the data , and should be less than 1.0 in all cases.

C.3.4 THE EXAFS - main menu option 4

The EXAFS can now be viewed in k -space, and an additional option to simultaneously view I_0 is often useful to identify crystal glitches in the data. k , the photo-electron wave number is a measure of the kinetic energy of the photo-electron, with wavelength λ_e , and is given by :

$$k = \frac{2\pi}{\lambda_e} = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} .$$

Press 1 to plot EXAFS :1
 Press 1 to plot EXAFS + I0 :1

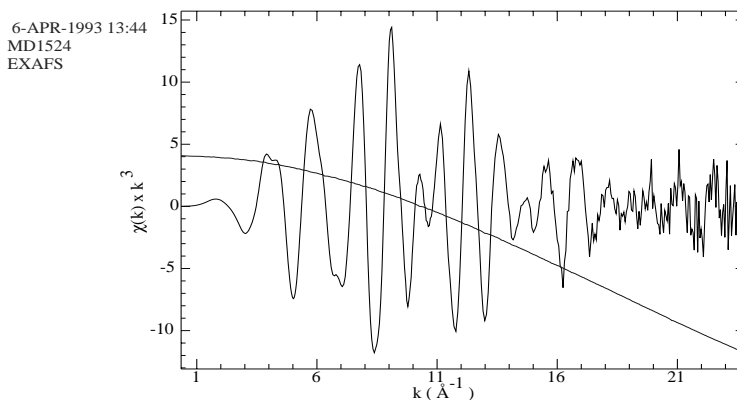


Figure C.3-4 EXAFS data plus I_0 plot

The EXAFS data can also be Gaussian smoothed, which is useful if fast Fourier transforms are to be used later on in the data analysis session. All fast Fourier transform algorithms require equal spacing in k , and the data must generally be interpolated to accommodate this. This is generally the case even when data collection specifies equal k -spacing, as energy calibration, which is generally performed subsequent to the collection, will change the k -spacing slightly. The smoothing makes the interpolation slightly better behaved in the case of noisy data.

Press 1 to Smooth EXAFS :1
 Enter 1 to k-Smooth, 2 to eV-Smooth [1] :<CR>
 Enter Min, Max & width for Smooth [.100000, 23.7999, .100000] :<CR>
 Press 1 to plot Smoothed + Unsmoothed EXAFS :1
 Press 1 to plot Smoothed EXAFS alone :<CR>

The next section deals with Fourier transforms and filtering of the data.

C.3.5 THE FOURIER TRANSFORM - main menu option 5

The EXAFS Fourier transform is generally given by :

$$\rho(R) = \frac{1}{4\pi^{1/2}} \int_{k_{min}}^{k_{max}} \chi(k) k^3 e^{i2kR} dk$$

It is common practice to phase-correct Fourier transforms. This is done using an EXAFS phase function, typically a theoretical one, for the dominant absorber-backscatterer interaction in the EXAFS. The effect of phase-correcting the transform is to move the peaks to values close to the actual absorber-backscatterer distances (R), if the absence of any phase correction the peaks will be at positions

$R+\Delta$, where Δ is approximately half the average phase shift slope for a given interaction. The Fourier transform equation including phase-correction is :

$$\rho(R) = \frac{1}{4\pi^{1/2}} \int_{k_{min}}^{k_{max}} \chi(k) k^3 e^{i2kR + i\phi(k)} dk$$

Where $\phi(k)$ is the appropriate EXAFS phase function (central atom + backscatterer atom phase). In general only the power spectrum, $|\rho(R)|$, of the Fourier transform is displayed, and it is important to realize that all phase information is missing in these plots. The power spectrum is given by :

$$|\rho(R)| = \left\{ \Re[\rho(R)]^2 + \Im[\rho(R)]^2 \right\}^{1/2}$$

The Fourier transform section has it's own menu :

```

PROCESS Version 2.6 1990
-----
Press 1 for raw averaged data
    2 for baseline/pre-edge
    3 for spline
    4 for EXAFS
    5 for Fourier transform
    6 for file input
    7 for utilities
    8 for setup
    9 to Quit
:5
-----
Fourier transform/filter
-----
Press 1 for Fourier transform
    2 for R-window (filter)
    3 for Back transform
    4 for phase & amplitude
    5 to return
:1
    
```

Option 1 on the Fourier transform menu allows calculation of the Fourier transform. The option of a Gaussian k -window is given. This has the effect of reducing the *ringing* or series-termination effects in the transform, but broadens transform peaks so that true structure can be lost. In our example, we use a window width of zero (see below), so that the window function merely specifies the range of the k -data to be transformed :

```

Press 1 to calculate Fourier transform :1
Enter 0 to use Unsmoothed or 1 to use Smoothed EXAFS [1] :<CR>
Enter Min, Max & width for k-window [.347823, 23.7999, 0.0] :<CR>
Enter power for k-Weighting [3] :<CR>
Press 1 to plot k-windowing :<CR>
    
```

The types of Fourier transform available are Fast Fourier transform (the default), a Simpson rule integration algorithm which evaluates the full Fourier transform, and a Maximum Entropy Transform. We recommend that the last option generally be left alone, as this type of transform is prone to artifacts if incorrectly used. The R-range for the transform, and increment in Å, can also be specified. Fourier phase correction is available with a choice of phase functions (corresponding to NPT in OPT) . In the dialog example we accept the default value of 1, which specifies the McKale tables:

```

Enter 1 for Fast FT, 2 for Simpson rule FT, 3 for Max Entropy Transform [1] :<CR>
Enter R(low), R(high) & R(inc) [0.0, 7.00000, .020000] :<CR>
Press 1 for phase correction :1
Enter Z for Absorber and backscatterer [42.0000, 16.0000] :<CR>
Enter 1 for theory, 2 for parameterized, 3 for F.T. [1] :<CR>
Enter edge (K, L1,..) [K] :<CR>
Enter No. of points for data interpolation [100] :200<CR>
Forward FFT - Max R : 13.33 R(inc) : 0.0178 .... 200 to 1500 points
Press 1 to plot Transform :1
    
```

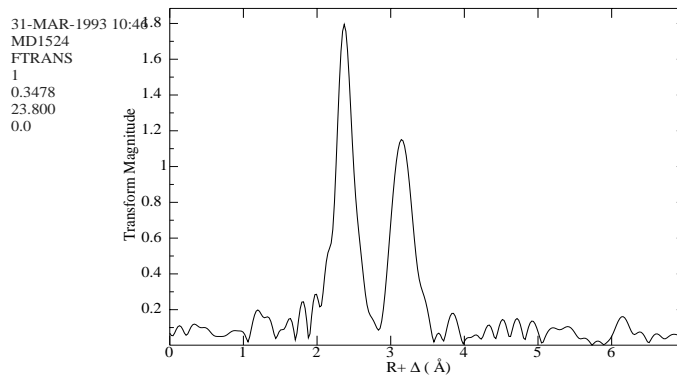


Figure C.3-5 The EXAFS Fourier transform

The number of points for data interpolation is specified as 200 in our example, rather than the default of 100, this is done because of the extended k -range of the data. Approximate values for the interatomic distances can be obtained by selecting option 5 (peaks) in the plot menu.

We will now proceed to Fourier filtering. The Fourier transform must first be re-calculated without phase-correction (return to the Fourier menu with *control-Z*). The reason for this is that the back-transform will be distorted at low k if phase-correction is used, although PROCESS does attempt to correct for this. This Fourier transform proceeds exactly as before, but without the phase-correction :

```

Enter 1 for Fast FT, 2 for Simpson rule FT, 3 for Max Entropy Transform [1] :<CR>
Enter R(low), R(high) & R(inc) [0.0, 7.00000, .020000] :<CR>
  Press 1 for phase correction :<CR>
Enter No. of points for data interpolation [200] :<CR>
  Forward FFT - Max R : 13.33 R(inc) : 0.0178 .... 200 to 1500 points
  Press 1 to plot Transform :
  Press 1 to plot Real & Imaginary components :<CR>
  Press 1 to generate transform file:<CR>
  Press 1 to read R-window :1
Do you wish to use cursor input :? [y/n] [Y] :<CR>
Enter width for R-window [.300000] :<CR>

```

There are a number of other options in the above dialog that are worth noting. The "transform file" is an ASCII file containing R , the power spectrum, and the real and imaginary parts of the transform, which can be plotted with MULDAT. The width for the R -window refers to the width of the Gaussian window which is to be used for filtering, we select the default of 0.3\AA (a good value for k -ranges $>10\text{\AA}^{-1}$). In our example we position the cursor at $R+\Delta=2.422\text{\AA}$ and 3.156\AA , on either side of the Mo-Mo peak, to filter out the Mo-Mo contribution in the EXAFS.

```

Do you wish to try again? [y/n] [N] :<CR>

```

The program will then plot the window, and ask for final confirmation that it is acceptable:

```

Is this windowing OK? [y/n] [Y] :<CR>
  Press 1 to back-transform :1
  Final phase adjusted by 42PI

```

The program will display the filtered data menu:

```

      Fourier-filtered data

Press 1 for filtered + unfiltered plot
  2 for filtered data alone
  3 for filtered data + Amplitude
  4 for Amplitude
  5 for total phase
  6 for phase + Amplitude
  7 to write .FIL file
  8 for linear phase search
  9 to return
  :
```

A number of different options are available for plotting. The first is a comparison of the filtered and unfiltered data, in our example this would appear as shown in Figure C.3-6. Option 7 writes the Fourier filtered data to a .FIL file, which can be read by OPT. The data are also decomposed into total effective phase and total effective amplitude, and a brief description of the method follows. For any EXAFS signal we can write :

$$\chi(k) = A(k) \sin \Phi(k)$$

Where the total effective phase $\Phi(k) = 2kR + \phi(k)$, and $A(k)$ is the total effective amplitude, we can now write :

$$\chi(k) = \frac{1}{2i} A(k) e^{i\Phi(k)} - \frac{1}{2i} A(k) e^{-i\Phi(k)}$$

If we now Fourier transform $\chi(k)$ into $\rho(k)$ (see above), the first term in the above equation corresponds to positive R values, while the second corresponds to negative R values. The latter are set by the program to zero, and the backtransform into k -space is then calculated. We then obtain a function $z(k)$, corresponding to only the first part of then equation, which can be used to obtain the EXAFS total phase and total amplitude functions :

$$\Phi(k) = \arctan \left\{ \frac{\Im [z(k)]}{\Re [z(k)]} \right\}$$

$$A(k) = \left\{ \Re [z(k)]^2 + \Im [z(k)]^2 \right\}^{\frac{1}{2}}$$

The total phase as calculated above will generally possess discontinuities every time the total phase function changes by more than 2π ; these are detected by PROCESS and automatically removed. The statement **Final phase adjusted by 42PI** indicates the number of such discontinuities (42 in our example) detected by PROCESS.

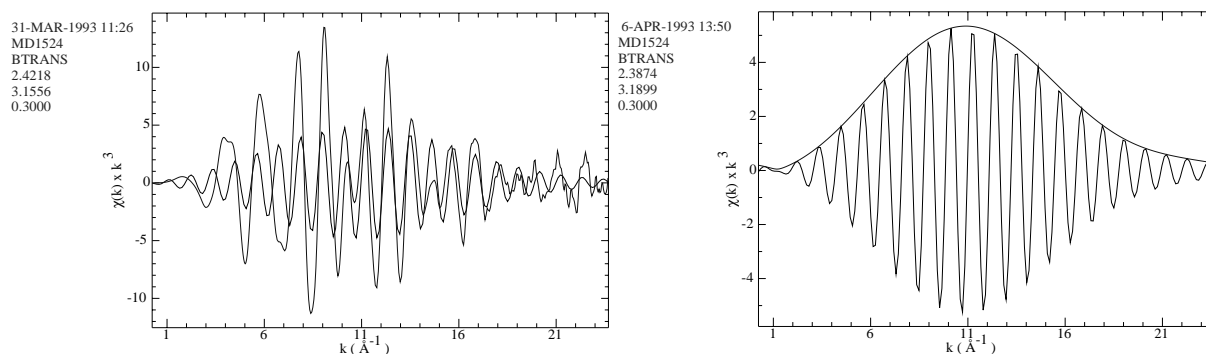


Figure C.3-6 The effect of Fourier filtering the outer shell on the EXAFS of MoS_2 . The left panel shows the Fourier filtered EXAFS plus the unfiltered data, and the right panel the filtered EXAFS plus the total amplitude function $A(k)$.

If structural information about the compound is known, *i.e.* it is to be used as a model compound, then the total phase and amplitude

functions can be used to calculate EXAFS phase and amplitudes for use in curve fitting analysis of unknown samples. We will go through the procedure for doing this for our example MoS_2 . On exiting the the filtered data menu PROCESS will return to the Fourier transform Menu (the filtered data menu can be re-gained by selecting option 3, backtransform, on the Fourier transform Menu). Select option 4 "phase and amplitude" and the program will prompt for various labels and input parameters, including a values for the coordination number, the bond length, and an estimate for the Debye-Waller factor (Sigma^{**2}). For well characterized tetrahedral molecules, the latter can be explicitly calculated from vibrational spectral data using the program TETRA, otherwise the user should enter a chemically reasonable value, or zero, or a value estimated by fitting the model data to theory phase and amplitudes, depending upon personal preference (but see section H, below).

```
Enter 6-Character   Compound Label [PHAAMP] :MoS2<CR>
Enter 6-Character   Absorber Label [123456] :Mo<CR>
Enter 6-Character   Amplitude Label [123456] :Mo-Mo<CR>
Enter 6-Character   Phase Shift Label [123456] :Mo-Mo<CR>
Enter Z for Absorber and backscatterer [42.0000, 0.0] : ,42<CR>
Enter Coordination number [4.00000] :6<CR>
Enter R & Sigma**2 [2.30000, 0.0055000] :3.17<CR>
  Press 1 to plot Amplitude, 2 for Phase, 3 for combination plot :3
```

On selecting the combination plot, the plot shown in figure C.3-7 is displayed.

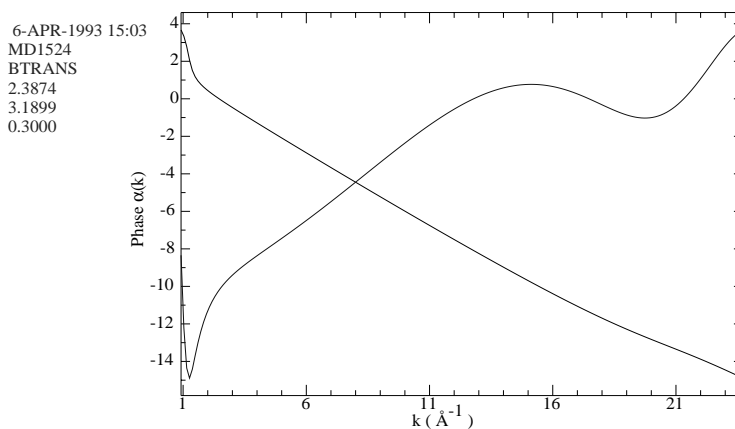


Figure C.3-7 EXAFS phase and amplitude functions obtained using PROCESS

The user is then prompted to change the structural input variables, or to write output files:

```
Press 1 to change N,R,Sigma etc., 2 to write files :2
Press 1 for .HLD file, 2 for DATA file :1
Enter Amplitude .HLD filename [EXAFS:AMPARY.HLD] :MO_MOA.HLD<CR>
Enter Phase shift .HLD filename [EXAFS:PHSARY.HLD] :MO_MOP.HLD<CR>
Do you wish to append to functions to any in the files? [y/n] [Y] :<CR>
```

The files MO_MOA.HLD and MO_MOP.HLD are created in a format which can be read by the curve-fitting program OPT.

C.3.6 SAVING THE DATA - main menu option 6

Before leaving the program PROCESS the data file must be saved (PROCESS will check that this has been done). This is done using the files menu from the main menu.

```

PROCESS Version 2.6 1990
Press 1 for raw averaged data
  2 for baseline/pre-edge
  3 for spline

FILES
form/filter
tput
Press 1 to write .AVE file
  2 to write formatted file
  3 to read new .AVE file
  4 to read formatted file
  5 to return
:1

```

Enter .AVE filename to write [MD1524.AVE] :<CR>

The program will overwrite the existing .AVE file, unless a new filename is specified. A variety of other output options are available from this menu. Option 2 allows the user to create a ASCII (*DATA*) file containing any combination of the array positions (see section C.2 above for a description of these).

C.3.7 EDGE MANIPULATION - main menu option 7-1 (utilities)

In this and the following sections describing PROCESS we will depart from our worked example of MoS₂, Mo *K*-edge data, turning instead to data collected at the sulfur *K*-edge and the Mo *L*_{III} and *L*_{II} edges for our example. PROCESS can manipulate edges using the calculate derivs. etc option of the utilities menu :

```

PROCESS Version 2.6 1990
UTILITIES
ed data
re-edge
Press 1 to calculate derivs. etc
  2 to deglitch
  3 to re-calibrate
  4 for Calculator
  5 for Monochromator calcn.
  6 for comments/header
  7 to plot memory
  8 for memory map
  9 for process manager
  A to return
:1
ansform/filter
/output

```

The Manipulate data menu offers a variety of derivatives smoothing and baseline subtraction options. In our example, we first select to reset - this loads the work array positions used with data array positions selected by the user. The defaults are positions 1 and 6, which correspond to eV and the pre-edge subtracted data, respectively.

Manipulate data	
Press 1 to reset 2 to clip data 3 to normalize data 4 to smooth data 5 for derivatives 6 to subtract baseline 7 to plot 8 to write .EDG file 9 to save A to read .EDG file B to return :1	ESS Version 2.6 1990 ed data re-edge erivs. etc ansform/filter /output e tor calcn. eader nager

A to return :1

Enter array positions (x,y) to manipulate [1, 6] :<CR>

Option 2 allows the data to be clipped, to exclude unwanted regions of the data. As our example contains more than one edge, we first plot it using option 7.

Manipulate data
Press 1 to reset 2 to clip data 3 to normalize data 4 to smooth data 5 for derivatives

Plot
Press 1 to plot data 2 to plot derivative 3 to plot data + deriv. 4 to return :1

The plot appears as shown in figure C.3.7-1

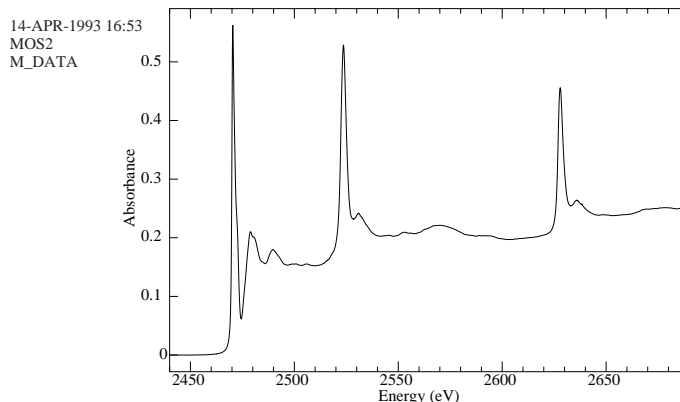


Figure C.3.7-1 Sulfur *K* (at about 2470 eV) and the Mo *L_{III}* *L_{II}* edges (2521eV and 2625eV, respectively) for MoS₂.

We wish to work with the sulfur *K*-edge, and from examining the plot we decide to clip our data from 2460 to 2500 eV. We return to the manipulate data menu and select option 2, then proceed to normalized the data (option 3) :

```
Enter eV-min and max to clip [2440.00, 2689.60] :2450,2500<CR>
Start and finish points [40, 261] :<CR>
```

```
Press 1 to normalize on max. intensity:<CR>
Enter y to normalize [.158323] :<CR>
```

The data will be normalized by dividing by the value of "y to normalize". The default is automatically set to the spline point, if one is present, or to the ordinate value for the last point in the clipped region. In our particular example, a low order spline (actually a straight line) was fitted to the region in between the sulfur *K*-edge and Molybdenum *L_{III}* edge, and the spline point is used. We will now calculate the unsmoothed second derivative of the edge spectrum by selecting option 5 on the manipulate data menu, and then choosing option 1 on the Derivatives menu :

```

Manipulate data
-----
Press
-----
Derivatives
-----
Press 1 for derivative
      2 for smoothed derivative
      3 to return
      :1
-----
9 to save
A to read .EDG file
B to return
:5

```

```
Enter derivative [2] :<CR>
```

The edge and its second derivative can then be displayed using the plot menu, and saved to an .EDG file using option 8 in the manipulate menu for later display (e.g. MULDAT) or further interpretation (e.g. EDG_FIT).

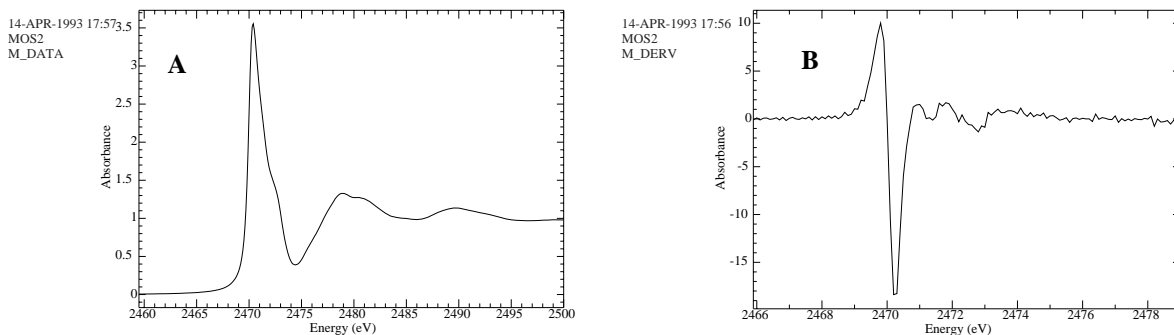


Figure C.3.7-2 The sulfur *K*-edge **A**, and second derivative **B** of MoS₂.

Option 9 in the manipulate menu is worth commenting upon. This allows the user to transfer the manipulated data back into the array positions from whence it originally came, allowing re-insertion of the manipulated data back into the mainstream EXAFS analysis. This might be useful, for example, if a piecewise cubic background had been subtracted from the data (option 2 of the "baseline" menu given by "subtract baseline" on the manipulate data menu).

C.3.8 DEGLITCHING - main menu option 7-2 (utilities - deglitch)

Data can be de-glitched in several different ways, perhaps the simplest being to edit the data just after the pre-edge subtraction stage using the editor which is available upon plotting. Points can simply be selected and moved or deleted, according to the user's preference. If points are deleted the deletion will trickle through the whole data array, so that that point is eliminated in all array positions.

The utilities menu has specialized tools for de-glitching. Upon selecting option 2 on the utilities menu the user is presented with two options :

```
Press 1 to deglitch, 2 to remove step :1
Press 1 to deglitch pre-edge data, 2 for EXAFS:1
Press 1 for cubic, 2 for least-squares polynomial :1
```

In our example we elect to deglitch the pre-edge data (in general this is better for large glitches as they can distort the spline), and use a cubic. A plot of the data will then be displayed (the user should use "zoom" to zoom in on the problem region) and the user should use the cursors to select four points, two on either side of the glitch to be removed, which describe a cubic (in our example) which will be interpolated through the middle two points to replace the glitch. The least squares polynomial works in a similar way, except that the two regions flanking the glitch are fitted to a polynomial (the order is user-defined) and this is extrapolated through the middle removing the glitch. Before this occurs the user is asked to confirm the de-glitching:

```
Replace glitch region - press 1 if OK :1
```

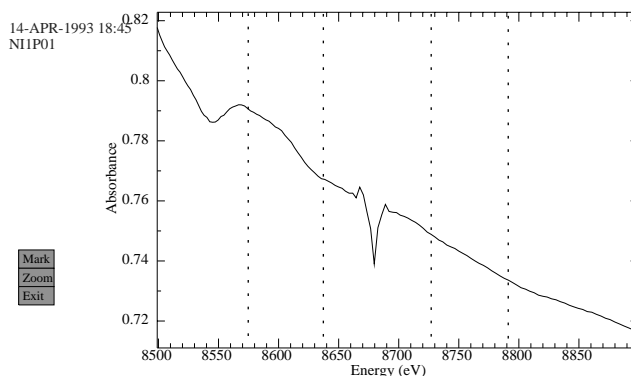


Figure C.3.8-1 Deglitching an XAS spectrum

The other main deglitching option "to remove step" is useful for removing discontinuities in the data, which might be due to a some unexpected experimental event (in which case the data really ought to be discarded) or due to edges of minor contaminants (contaminants at levels >0.1% cannot be treated this way), or multiple excitation edges (e.g. KL_L edges), which cannot removed any other way.

```
Press 1 to deglitch, 2 to remove step :2
Enter array positions for data [1, 6] :<CR>
Enter order of polynomial [4] :<CR>
Press 1 to use cursors to estimate step :<CR>
```

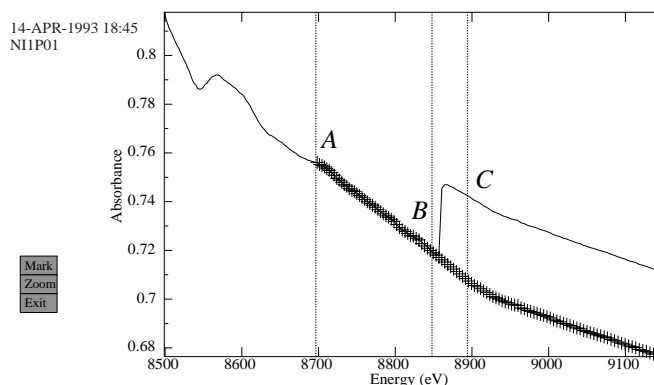


Figure C.3.8-2 Removing a step in XAS data.

In this option three energy points must be selected, two on one side (A and B in figure C.3.8-2) and one (C in the figure) on the other side of the step. The program fits the polynomial through the region described by the first two (A and B), extrapolates between B and C, determines the offset of the polynomial at C and shifts all the data on this side of the step by that offset. As before the user is asked to confirm the de-glitching before the data is altered:

```
Remove step - press 1 if OK :1
```

After the step has been subtracted, a final plot of the data with the step removed is displayed.

C.3.9 RECALIBRATION - *main menu option 7-3 (utilities - re-calibrate)*

The data can be recalibrated using option three of the utilities menu, our example is a Ni *K*-edge data set for which the calibration was not initially set.

```
Press 1 for new E0, 2 to change calibration :2
Enter true eV0 [8331.60] :<CR>
Enter apparent eV0 [0.0] :8332.21<CR>
Enter new e0 [8350.00] :<CR>
Enter 1 for eV shift, 2 for step shift [2] :<CR>
Enter steps/degree, d-space [2000.00, 1.92000] :<CR>
Motor step displacement [3.47266] :<CR>
```

The user is asked to confirm details of the monochromator (step/degree and d-space) as usual if *control-Z* is pressed at any point the recalibration is aborted and the user is returned to the menu.

D. OPT

D.1 OVERVIEW OF OPT

OPT is used for curve-fitting EXAFS data to obtain structural information. The capabilities of the latest version of OPT, Version 2.8, are described below, some of the features described may not be present in earlier versions of the software. The EXAFS equation, used by OPT in its most complete form is :

$$\chi(k) \approx S_0^2 \sum_{i=1}^n \frac{N_i S_i(k, R_i) F_i(k, R_i)}{k R_i^2} \exp\left(\frac{-2R_i}{\lambda(k, R_i)}\right) \exp\left(-2\sigma_i^2 k_i^2\right) \sin\left[2kR_i + \phi_i(k, R_i) + \phi_c(k)\right]$$

Variable	Meaning
k	Photo-electron wave number, a measure of the photoelectron wavelength, $k = 2\pi/\lambda_e$, and calculated from the X-ray energy above the threshold by $k = [0.262(E-E_0)]^{1/2}$.
S_0^2	Amplitude reduction factor due to shake up and shake off losses (otherwise known as the scale factor in OPT).
N_i	Coordination number for atom type i .
S_i	Total central atom loss factor. <i>feff</i> calculates a value for this, in other theories it is assumed to be unity.
F_i	Effective EXAFS scattering amplitude function.
R_i	Absorber-backscatterer distance for atom i .
λ_i	Photoelectron mean free path or inelastic scattering correction. This is calculated explicitly by <i>feff</i> but is not provided in the McKale tables. In the case of the McKale tables OPT uses an approximate curve called the <i>Universal curve</i> , calculated using a semi-empirical equation. No photoelectron mean free path correction is used with parameterized or PROCESS generated phases and amplitudes.
σ_i	Debye-Waller factor, the mean square deviation in R_i . OPT uses a simple Gaussian model, which will probably break down at high temperatures. At lower temperatures the approximation is generally very good.
ϕ_i	Backscatterer EXAFS phase function.
ϕ_c	Central atom EXAFS phase function. OPT adds ϕ_c and ϕ_i for each backscatterer. ϕ_c depends only on the edge and the type of atom that is absorbing, ϕ_r , on the other hand, depends on R_i and upon the type of backscatterer atom.

Various types of EXAFS phase and amplitude functions can be used by OPT, these are as follows:

1. McKale curved wave theory, using 1/ R interpolation to the initial value of R_i .

2. Parameterized phase and amplitudes.
3. Fourier filter extracted phase and amplitude functions (from PROCESS).
4. *feff* (version 5.05 or higher) curved wave single scattering theory.
5. *feff* (version 5.05 or higher) curved wave multiple scattering theory.
6. EXAFSPAK *feff* tables (available to *feff* license holders only).
7. ASCII file input - phase and amplitude data from some external source, columns of *k*, total phase, and amplitude are required.

OPT can read .AVE or .FIL files, although fitting of the raw (.AVE) data is recommended. The command line to run OPT is as follows:

```
$ OPT INPUT_FILE PARAMETER_FILE
```

Where **INPUT_FILE** contains the data to be fitted, and **PARAMETER_FILE** contains the structural information derived in the fit. The default file-type for the input file is .AVE. The parameter file has a mandatory .HLD file-type. If the parameter file does not exist, then OPT will warn the user and a new .HLD file will be created.

e.g.

```
$ OPT MD1524 MD1524
```

Will read data from the file MD1524.AVE and parameters from the file MD1524.HLD (MD1524.HLD will be created if it does not exist). In the following we will review the EXAFS curve-fitting analysis of the data file MD1524.AVE, which is a sample of MoS₂ obtained from the Climax Molybdenum company which was also our example for PROCESS. This file is available with the programs on request from the authors.

D.2 THE MAIN MENU

The main menu of OPT appears as follows :

```
OPT - Improved EXAFS Curve-fitting program - Version 2.8
```

```
OPT Version 2.8
```

```
Press 1 to read data etc.
  2 to change parameters
  3 to plot
  4 for curve-fitting
  5 for output
  6 for utilities
  7 to setup
  8 to quit
:
```

As with other EXAFSPAK programs, the menu items are ordered as they would normally be required. Option 1, to read the data, must have been executed before most of the other options can be run.

D.3 DATA INPUT AND THE PARAMETER-EDITOR

Selecting option 1 from the main menu with our example file results in the following dialog :

```
MD1524 489 Points in file, E0 = 20025.00
Enter k(min), k(max), Delta-k [1.00000, 14.0000, 0.0] :2,18
Cannot read parameter file
Enter # Components, power for k Weighting [1, 3] :2
Enter edge (K, L1,..) [K] :
Enter 1 for smoothed data, 2 for raw data [2] :
489 points in data file, 289 points w/in range
```

The k-range selected is 2 - 18 Å⁻¹ and the value for Delta-k is zero. Non-zero values for Delta-k cause the program to interpolate the data to equally spaced *k* points with a separation of Delta-k. The lower limit to the data to be fitted depends upon the type of phase and amplitude theory to be used; the use of curved wave theory (McKale, *feff*) permits lower values. The upper limit is generally defined by the signal to noise of the data. Following this, as the parameter file MD1524.HLD does not exist, OPT signals that it cannot be read and creates it. The number of components that we wish to fit is two, and we select *k*³ weighting (the default), in order to emphasize the high-*k* region of the data where the theory is most accurate, and to negate the amplitude reductions. Most of the questions are self-explanatory. The program then returns to the main menu, option 2 should be selected, and when this is done, the parameter editor screen will appear :

MD1524 k= 2.1 to 18.0 2 Shells 4 Variables 0 Iterns 0 F-vals									
Za= 42.0 Edge=K F=0.6776E+04 CPU= 0 00:00:00.20 23-MAR-1993 10:57:18									
1	Scale=0.9	2	Data E0=0	3	Wave-1 Sig-D=0	4	0	5	0
Component 1	ZBA=8	ZBP=8	NAT=1	NPT=1				
6 N=1	7 *R=2		8 *Sig^2=0.0025	9	E0=0	10	E1=0		
Component 2	ZBA=8	ZBP=8	NAT=1	NPT=1				
11 N=1	12 *R=2		13 *Sig^2=0.0025	14	E0=0	15	E1=0		

PF1 = Exit, PF2 = Next page, PF3 = Fix/Float/Link, PF4 = More ...

Initially, as the parameter file did not exist, all parameters have default values which are shown above. The parameter editor allows values to be readily changed using a few simple editing rules :

- i* The high-lighted region, containing the cursor, is the active field. A field is simply a data-entry point, *e.g.* a bond length *R*.
- ii* The left and right cursor keys allow the cursor to be moved within a field and, at the ends of the field, move to an adjacent field. The up and down cursor keys move the cursor up and down on the page.
- iii.* **Control H** moves to the previous field, **tab** and **enter** move to the next field.
- iv.* **Control B** copies the value from the field in the previous component.

Each parameter has a parameter number, given to the left of the parameter, and can be flagged to be floated in the fit, either freely, or in correlation with other parameters. We will now summarize the different parameters available

(those parameters marked § are not recommended to be floated in fits, ¶ indicates that the parameters have a different function with multiple scattering fits using *feff*):

- 1 **Scale** Overall scale factor S_0^2 - this should be about 0.9 for McKale and *feff*.
- 2 **Data E0** Data E_0 ($k=0$ point) shift in eV §.
- 3 **Wave-1 Sig-D** Anharmonic Debye-Waller for Component #1 §.
- 4 Not used at time of writing §.
- 5 Not used at time of writing §.

- 6 Coordination Number
- 7 **R** Absorber-backscatterer distance in Ångströms
- 8 **Sig^2** Debye-Waller σ^2 value in Å².
- 9 Threshold E_0 ($k=0$ point) shift in eV for the component.
- 10 **E1** Not used at time of writing §.

- ZBA** Atomic number for backscatterer amplitude function ¶.
- ZBP** Atomic number for backscatterer phase (usually the same as ZBA) ¶.
- NAT** Amplitude function type (1-6).
- NPT** Phase shift function type (1-6).

The amplitude and phase shift function types are **1**: McKale curved wave theory tables, **2**: parameterized, **3**: generated by PROCESS with complex Fourier backtransforms of experimental data, **4**: *feff-5* single scattering curved-wave theory, **5**: *feff-5* multiple scattering curved-wave theory, **6**: *feff-5* tables (for elements for hydrogen to americium) and **7**: an ASCII file PHAMP.DAT, containing columns of data with k , phase, and amplitude.

Fix/Float/Link flag Found to the right of the parameter number - this controls whether a variable (N , R , σ^2 etc.) is fixed, freely floated, or linked in the fit. The flag can be toggled using the PF3 key. A fixed parameter is denoted by no character (*ie.* a space), a freely floating parameter is denoted by an asterisk (*ie.* *), and linked parameters by /, + or -. Linked parameters are correlated with the variable in the previous component (*ie.* component $n-1$ for component n), so as to maintain either a constant ratio (/), a constant sum (+) or a constant difference (-) of the flagged parameters. The latter is useful, for example, in the case of coordination numbers, where it is often the case that the total coordination number is known.

- PF1 key** The PF1 key exits the parameter editor, the new parameters being saved to the parameter .HLD file.
- PF2 key** The PF2 key goes to the next page of parameters. OPT 2.7 can handle up to 40 components, which fit onto 5 pages.
- PF3 key** The PF3 key toggles the Fix/Float/Link flag, as described above.
- PF4 key** The PF4 key allows access to another set of commands, when it is pressed the line at the bottom of the screen becomes :

PF1 = Delete Component, PF2 = Swap, PF3 = Insert, PF4 = Change Za

In this new mode, PF1 will delete the current component, PF2 will swap it with the one above, PF3 will insert a new component, copying the current one. Finally, PF4 allows one to change the absorber atomic number Z_a , the edge type (K, LI, LII etc.) and the number of components. These can also be changed using option 1 of the main menu.

Please note: Many keyboards do not have PF keys, in some cases these are emulated by F1-4, or if even these are not available then the Shift-1 through Shift-4 can be used.

The parameter editor should be used to enter reasonable starting parameters. In the case of a complete unknown,

initial estimates of bond lengths can be obtained from the Fourier transform peak positions obtained with PROCESS. Following entry of reasonable starting parameters the parameter editor will appear as :

```
MD1524 k= 2.1 to 18.0  2 Shells  5 Variables  0 Iterns  0 F-vals
Za= 42.0 Edge=K  F=0.6776E+04  CPU=  0 00:00:00.20  23-MAR-1993 10:57:18
```

```
1 Scale=0.9  2 Data E0=0  3 Wave-1 Sig-D=0  4 0  5 0
```

```
Component 1  Mo-S  ZBA=16  ZBP=16  NAT=1  NPT=1
6 N=6  7 *R=2.38  8 *Sig^2=0.0025  9 *E0=-10  10 E1=0
Component 2  Mo-Mo  ZBA=8  ZBP=8  NAT=1  NPT=1
11 N=6  12 *R=3.16  13 *Sig^2=0.0025  14 /E0=-10  15 E1=0
```

The default, the McKale tables, has been selected for the phase and amplitude functions, and the E0 parameters have been linked so that they will maintain equal values in the fit. The PF1 key can now be pressed, to exit the parameter editor.

In most cases one would wish to plot the initial fit after entering reasonable parameters. This is covered in the next section.

D.4 PLOTTING

The plot menu is obtained by selecting option 3 on the main menu :

```

PLOT
-----
Press 1 to plot EXAFS
      2 for phase shift
      3 for amplitude
      4 for deriv phase
      5 for deriv amp.
      6 for lambda
      7 to return
      :1

OPT Version 2.8
-----
1 to read data etc.
2 to change parameters
3 to plot
4 for curve-fitting
5 for output
6 for utilities
7 to setup
8 to quit
      :3

```

A variety of plots are available, including the various pieces of the EXAFS equation - the total phase shift, the total amplitude, phase and amplitude derivatives (used by the Marquardt algorithm - see below), the photoelectron mean free path (lambda). In the current example we proceed directly to the PLOT EXAFS menu :

```

PLOT
-----
PLOT EXAFS
-----
Press 1 for data + fit
      2 for data
      3 for fit
      4 for residual
      5 for data + fit + residual
      6 for fit deconvolution
      7 for deconv. + fit
      8 for deconv. + data + fit
      9 to return
      :1

ion 2.8
-----
d data etc.
nge parameters
t
rve-fitting
tput
ilities
up
t

```

Again, a variety of plots are available. Of particular use are the options for plotting fit deconvolutions, which show the contribution of the various components, and the option for plotting the residual (4) which may indicate whether extra components are present. In the example we select option 1, to plot the EXAFS data and the initial fit on the same axes. The plot of the initial fit should appear as show in Figure D.4-1 below. The Fourier transform in our example is phase corrected using the phase function of the first shell. This can be changed by using the setup option of the main menu.

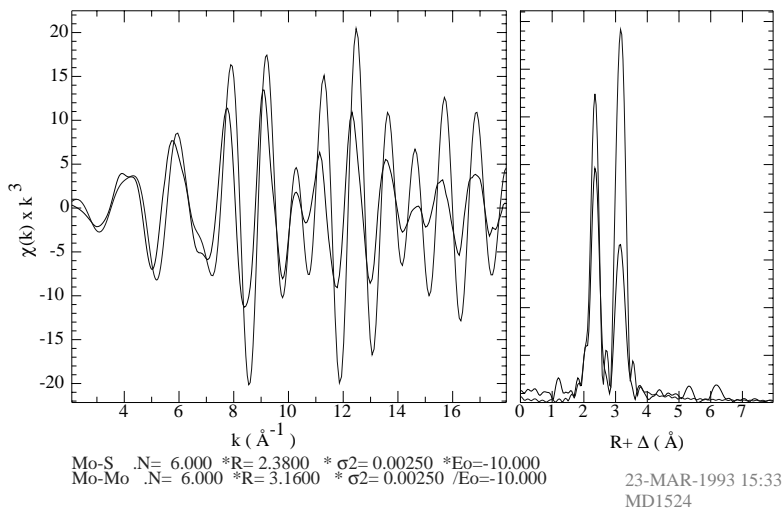


Figure D.4-1 Initial fit of MoS₂ EXAFS

D.5 FITTING THE DATA

From the plot above it can be clearly seen that the parameters which we guessed at require some optimization. In order to do this we return to the main menu, and select option 4, curve fitting:

```

OPT Version 2.8
Press 1 to read data etc.

CURVE-FITTING

Press 1 to start Eccles algorithm
  2 to start Marquardt algorithm
  3 for best-integer fits
  4 to change fit mode parameters
  5 to generate search profile
  6 for linear analysis
  7 to return
:2

```

By far the best option to choose at this point is number 2, the Marquardt algorithm. This is a very efficient method of minimization and all options are supported by it. Option number 1, the Eccles algorithm should not be used if correlated variables are fitted. The fitter will then launch with the same screen as the parameter editor, and will be updated every ten iterations (by default). When a minimum has been found the following screen will be presented :

Fit finished, hit any key for final analysis

MD1524 k= 2.1 to 18.0 2 Shells 5 Variables 48 Iterns 99 F-evals
Za= 42.0 Edge=K F=0.2666E+03 CPU= 0 00:00:11.56 23-MAR-1993 10:59:47

1 Scale=0.9 2 Data E0=0 3 Wave-1 Sig-D=0 4 0 5 0

Component 1	Mo-S	ZBA=16	ZBP=16	NAT=1	NPT=1
6 N=6	7 *R=2.40229	8 *Sig^2=0.00359	9 *E0=-13.694	10 E1=0	
Component 2	Mo-Mo	ZBA=8	ZBP=8	NAT=1	NPT=1
11 N=6	12 *R=3.17163	13 *Sig^2=0.00551	14 /E0=-13.694	15 E1=0	

The values in this screen are the final minimized parameters obtained by the fit. On pressing a key, a detailed final analysis of the fit is presented :

OPT 2.8

MD1524 Kmin= 2.08 Kmax=17.96 Deltak=0.000 280 Pts 2 Comp'ts 5 Variables
48 Iter'ns 99. F eval's Elfin=.10E-05 Dmp=.10E+03 F=0.266E+03 Za=42.0

1 Scale Factor = 0.900
2 Data Delta E0 = 0.00 eV
3 Wave 1 Sigma-D = 0.00 Angstroms
4 0.00
5 0.00

Component # 1 Mo-S Zba=16.00 Zbp=16.00 Nat=1 Npt=1 Integral= 53.148% [1]
6 Atom # = 6.000000
* 7 Distance = 2.402298 (0.001396) Angstroms
* 8 Sigma**2 = 0.003599 (0.000076) a**2
* 9 Delta E0 = -13.694571 (0.376997) eV
10 Delta E1 = 0.000000 eV

Component # 2 Mo-Mo Zba=42.00 Zbp=42.00 Nat=1 Npt=1 Integral= 46.852% [2]
11 Atom # = 6.000000
* 12 Distance = 3.171636 (0.001585) Angstroms
* 13 Sigma**2 = 0.005512 (0.000084) a**2
/ 14 Delta E0 = -13.694571 eV
15 Delta E1 = 0.000000 eV

Press any key to continue...

- Correlation Matrix -

Comp't	1	1	1	2	2
	R	Sig^2	Eo	R	Sig^2
Par.#	7	8	9	12	13
7	1.000	-0.301	0.898	0.806	-0.140
8		1.000	-0.278	-0.295	0.211
9			1.000	0.892	-0.248
12				1.000	-0.277
13					1.000

Press any key to continue...

Additional Statistical Information :

Normalised error (chi-squared) : 0.949769 F/(No.pts)
Reduced error (chi-squared) : 0.967037 F/(No.pts-No.Vars)
Weighted F-factor : 0.202451 (20.25%)
Expected Weighted F-factor : 0.205873
Expected resolution in distance, R : 0.989365E-01 Angstroms
Press any key to continue...

The various parameters and numbers given in the summary will now be described. The goodness of fit is described at the most elementary level by the F value (F=0.266E+03) in the third line of the summary, which is simply the sum of the squares of the differences between experimental and calculated curves. This is the value which is minimized by the fitting algorithms. The "Additional

Statistical Information" presented at the end of the summary gives various other manifestations of this number. The F-factor F in particular is somewhat analogous to the crystallographic R-factor :

$$F = \left[\frac{\sum k^6 (\chi_{\text{exptl}} - \chi_{\text{calcd}})^2}{\sum k^6 \chi_{\text{exptl}}^2} \right]^{1/2}$$

Also given in this section is the expected resolution in distance R , which is the expected smallest difference in interatomic distances resolvable for two similar contacts. This quantity, known as ΔR is simply given by the ratio $\Delta R = \pi / 2\delta k$ where δk is the k -range of the fitted data, in \AA^{-1} . In the summary, all the components are listed, together with estimates of the integrated contribution to the overall EXAFS amplitude, and a rank number in square brackets :

e.g.

Component # 2 Mo-Mo Zba=42.00 Zbp=42.00 Nat=1 Npt=1 Integral= 46.852% [2]

The Mo-Mo backscattering contributes about 47% of the total EXAFS, and is the second biggest component. These integrals and ranking are of particular use with multiple scattering calculations using *feff-5* as in this case it is often necessary to include many different components, each one corresponding to a different multiple scattering path. The ranks and % contributions can then be used to eliminate the less important ones.

The final refined parameters are listed, followed by estimated standard deviations in parentheses,

e.g.

*** 7 Distance = 2.402298 (0.001396) Angstroms .**

It is important to realize that the estimated standard deviations are only accurate when raw, unsmoothed, data are being fitted. Values for the 95% confidence limits can be obtained by simply scaling the estimated standard deviations. The upper diagonal half of the correlation matrix of parameters is also listed (the matrix is symmetrical). In the case of parameters which have been linked in the fit, the value in the correlation matrix is the total correlation of the linked parameters. This is the case with E0 in our example, where the values for components 1 and 2 are linked. Care should be exercised if any correlations are present that are greater than 0.9 as these values will be determined less precisely; this will also be reflected in the estimated standard deviations of the parameters. The fit summary can also be listed to a file (see the setup option of the main menu). Following the printout, OPT will then return to the main menu, and a plot of the fitted data can be viewed:

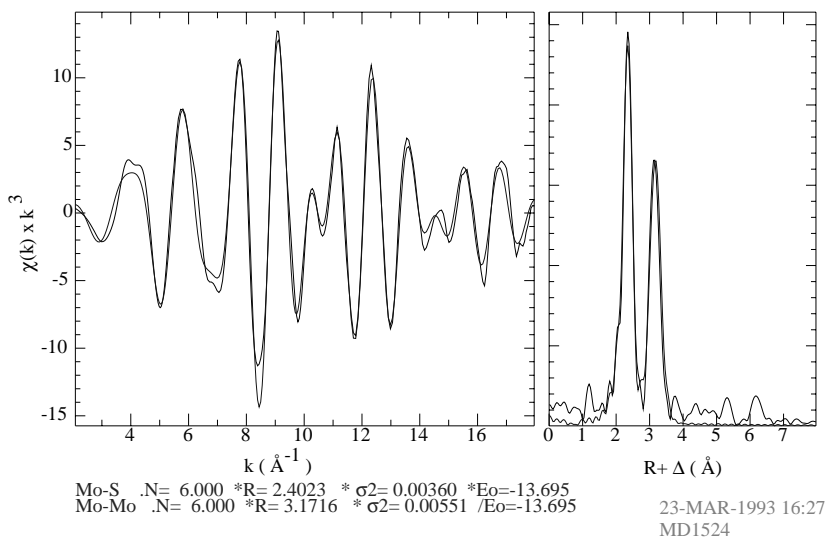


Figure D.5-1 Results of Marquardt algorithm curve fit.

D.6 OUTPUT

OPT always writes the parameter .HLD file containing the refined structural parameters (MD1524.HLD in our example), no user input is required for this. Other types of output are available from option 5 of the main menu :

```

      OPT Version 2.8
      Press 1 to read data etc.

OUTPUT

Press 1 to write fit + data to .FIT file
  2 to write fit to .AVE file
  3 to write residual to .AVE file
  4 to write Fourier transform file
  5 to write chi components
  6 to write Fourier components
  7 to return
:~
```

The most often used option is the first, which writes the data fitted, plus the current fit to a .FIT file, which is simply an ASCII(DATA) file which can be read by MULDAT later. It is important to note that the data are not *k*-weighted in the output file. Also particularly useful are options 4, which outputs the Fourier transform of the data and the fit, option 5 and option 6, which output the individual components in the fit (all are ASCII(DATA) format files).

D.7 OPT TOOLS

A variety of tools to assist in curve-fitting analysis of the data are part of OPT, these include search profiles, and best-integer fits.

D.7.1 SEARCH PROFILES

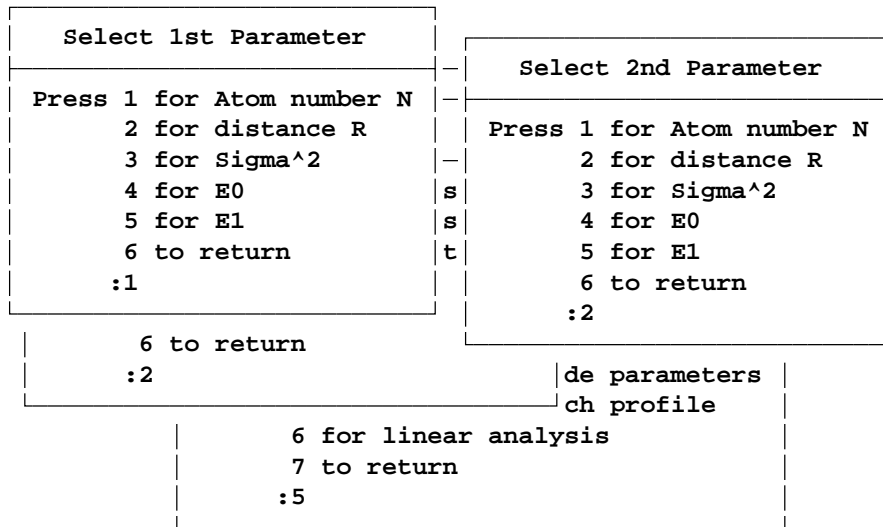
Search profiles are available using option 5 of the curve-fitting menu :

```

SEARCH
Press 1 for one parameter search
  2 for two parameter search
  3 for different functions
  4 to plot
  5 for output file
  6 to return
:2
etc.
algorithm
dt algorithm
fits
de parameters
ch profile
6 for linear analysis
7 to return
:5
```

Search profiles allow the fit error to be examined as a function of one or two of the variables in the fit. They are particularly useful in obtaining initial values for fits, or in checking to see if the minimum found by curve fitting is actually a convincing one. In our example we choose a two parameter search, and will vary the value of the coordination number against the interatomic distance for component (shell) number 2.

```
Enter shell number for first parameter [1] :2<CR>
Enter shell number for second parameter [1] :2<CR>
```



The ranges for the search parameters are prompted for, and the program will then proceed to calculate the the search profile :

```

1st param - Enter Min & Max for search [.100000, 6.10000] :.8,8.1<CR>
Enter No. of points [31] :<CR>
2nd param - Enter Min & Max for search [1.80000, 2.50000] :3.0,3.4<CR>
Enter No. of points [31] :<CR>
  
```

```

SEARCH
-----
Parameter Numbers :11      12
Shells :2         2
1      N          range 0.1    to 8.1
2      R          range 3      to 3.4
Search will calculate 961      simulations
CPU time for one simulation is 0 00:00:00.07
Projected CPU time for search is 0 00:01:07.28
  
```

```

Minimum found at 4.9      3.17333 Error = 246.401
  
```

```

Simulations 674
  
```

The search profile can be displayed using the plot option on the "search" menu, the "combination plot" will appear as shown in figure D.7.1-1, below.

Note that the CPU estimates have now become not particularly useful as the speed of computer processors has increased. The projection of the CPU time used was essential when this code was first developed (on a Digital Equipment Corp. VAX 11-750), but the CPU used for one simulation is generally less than the precision of reporting on modern computer systems.

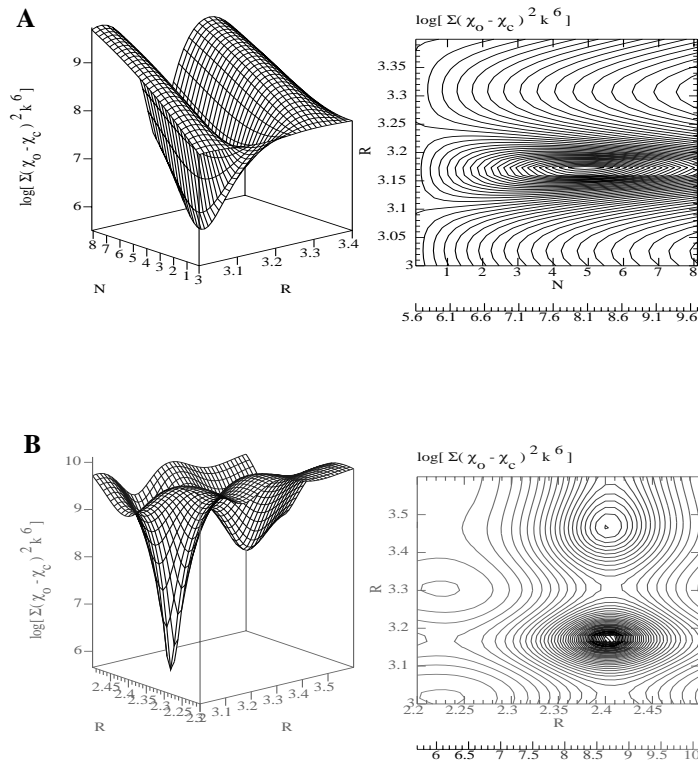


Figure D.7.1-1 Examples of search profiles **A** the worked example in the text, and, **B** an example showing a false minimum.

The "output file" option on the search menu will dump the contents of the search profile to an ASCII file, which can be plotted (*e.g.* using MULDAT) at a later date.

D.7.2 BEST INTEGER FITS

Best integer fits are a useful tool for determining coordination numbers, they allow a series of fixed coordination numbers to be tested, while other parameters are floated in the fit, to determine the best fit. :

```

OPT Version 2.8
Press 1 to read data etc.

CURVE-FITTING

BEST-INTEGER FITS

Press 1 to perform best N search
  2 to perform best 2-compt N search
  3 to perform best Z search
  4 to plot best integer profile
  5 to return
:1

```

The best-integer fits menu can be obtained by selecting option 3 of the curve-fitting menu. For our example we will perform a best N search for the first coordination shell of MoS₂. We have previously set the bond lengths and Debye-Waller factors to float in the fit, but have constrained E₀ to constant values.

```

Enter Component # for best integer fit [1] :<CR>
Enter min, max & increment for N [1.00000, 6.00000, 1.00000] :,8<CR>

```

The program will then launch the Marquardt curve-fitter for each of the specified coordination numbers. Upon completion a summary of the best integer fits is printed, which can also be shown graphically using option 4 on the best integer fit menu.

```

- Best integer fits -
Component # 1
  N = 1.000 Fit-error = 2085.28
  N = 2.000 Fit-error = 5728.42
  N = 3.000 Fit-error = 1638.13
  N = 4.000 Fit-error = 424.629
  N = 5.000 Fit-error = 285.097
> N = 6.000 Fit-error = 241.352 <
  N = 7.000 Fit-error = 262.863
  N = 8.000 Fit-error = 328.690
Press any key to continue ...

```

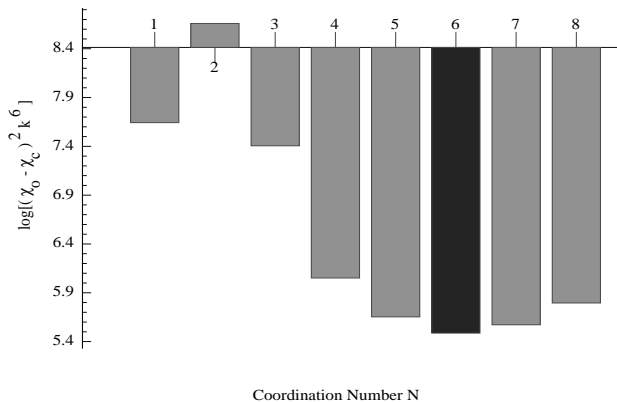
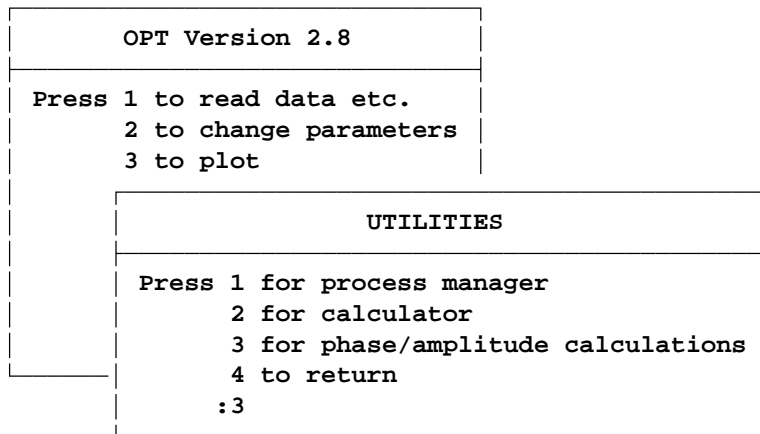


Figure D.7.2-1 Graphical display of best integer fit error vs. coordination number

D.8 OPT *feff* SINGLE SCATTERING INTERFACE

The program *feff* is not part of EXAFSPAK, and must be obtained separately as described in the credits displayed by OPT. OPT will run *feff* automatically, calculating the a set of phase and amplitudes which can then be used in curve fitting analysis of data. The *feff* interface is in the utilities menu obtained from option 6 of the main menu. In our example we will calculate the phase and amplitude functions for the Mo-S component, using the bond lengths we obtained in our earlier curve-fitting analysis.



Upon launching the *feff* interface the OPT displays a credits screen :

CREDITS

```

The program FEFF is not part of this EXAFS analysis package.
FEFF can be obtained from John Rehr of the Dept. of Physics at the
University of Washington, Seattle, WA 98195 (JJR@UWAPHAST.BITNET).
Credits :
J. Mustre de Leon, J.J.Rehr, R.C.Albers, S. Zabinsky

```

```

Enter shell [1] :<CR>
Enter absorber and backscatterer atomic numbers [42.0000, 16.0000] :<CR>
Enter interatomic distance [2.402298] :2.4<CR>
Program FEFF will now run -- this may take some time ...
Press any key to run FEFF ...<CR>

```

The output which follows is from *feff*, after the program has completed, the user is asked to confirm whether the phase and amplitudes should be added to the archive file (from where they will be accessible by OPT for curve fitting).

```

Feff 6.01a
MD1524 1 Mo-S OPT 2.8
Calculating potentials and phases...
  free atom potential and density for atom type 0
  free atom potential and density for atom type 1
  overlapped potential and density for unique potential 0
  overlapped potential and density for unique potential 1
  muffin tin radii and interstitial parameters
  phase shifts for unique potential 0
  phase shifts for unique potential 1
Preparing plane wave scattering amplitudes...
Searching for paths...
  Rmax 2.4023 keep and heap limits 0.000000 0.000000
Preparing neighbor table
  nfound nheap nheapx nsc r
  Paths found 1 (nheapx, nbx 1 2)
Eliminating path degeneracies...
  Plane wave chi amplitude filter 2.5%
  Unique paths 1, total paths 1
Calculating EXAFS parameters...
  Curved wave chi amplitude ratio 4.00%
  Discard feff.dat for paths with cw ratio < 2.67%
  path cw ratio deg nleg reff
  1 100.0000 1.000 2 2.4023
  1 paths kept, 1 examined.
Calculating chi...
  Use all paths with cw amplitude ratio 4.00%
  Use Debye-Waller factors from files.dat. S02 1.000
  feff0001.dat 100.0000
ff2chi done, 1/ 1 paths used.
Feff done. Have a nice day.
FORTRAN STOP
FEFF complete
Do you wish to add to the archive file? [y/n] [Y] :<CR>
Appending phases and amplitudes to FEFFPAR.HLD
Press any key to continue ...<CR>

```

The phase and amplitude functions calculated by *feff* can then be accessed by setting NAT=4 and NPT=4 in the parameter editor.

D.9 OPT *feff* MULTIPLE SCATTERING INTERFACE

Multiple scattering calculations using *feff* can, in many cases, yield a large number of individual scattering paths. Each of these paths is treated by OPT as a separate component in the fit, and the bond lengths and Debye-Waller factors must be linked in the fit according to the nature of the multiple scattering path concerned. Setting NAT=5 and NPT=5 causes OPT to use the *feff* multiple scattering interface. *feff* generates files containing the effective EXAFS phase, amplitude, mean-free path *etc.* for each multiple scattering path that the program considers significant. These files are named **FEFFnnnn.DAT**, where nnnn is the file number, *e.g.* the first path would be stored in **FEFF0001.DAT** and the second in **FEFF0002.DAT**. These files must be in the current default directory for OPT to access them correctly. When the OPT variables NAT and NPT have been set to 5, ZBA (and ZBP) no longer specifies the backscatterer atomic number, but instead specifies the file (scattering path) number.

The program FEFF_HLD should be used to prepare OPT .HLD files correctly set up to use *feff* output. FEFF_HLD reads the *feff* output files **PATHS.DAT**, **FILES.DAT** and **SIG2.DAT**, and automatically generates the file **PATHS.HLD** which is a OPT parameter file correctly set up for the multiple scattering curve-fitting (*n.b.* the card **PRINT 0 0 0 1** must be included in the **FEFF.INP** file when running *feff*). The use of *feff* with OPT should only be attempted by expert users. Very careful attention must be paid to the use of correlated variables in the curve-fitting or meaningless results can easily be obtained.. The flow chart shown in figure D.9-1 summarizes the sequence of programs which might be used to set up the program.

* For more information about *feff* see the following references :

Rehr, J.J.; Mustre de Leon, J.; Zabinsky, S.I.; Albers, R.C.; *J. Am. Chem. Soc.* **1991**, *113*, 5135-5140.

Mustre de Leon, J.; Rehr, J.J.; Zabinsky, S.I. *Phys. Rev. B* **1991**, *44*, 4146-4156.

Rehr, J.J.; Albers, R.C. *Phys. Rev. B* **1990**, *41*, 8139-8149.

Rehr, J.J.; Albers, R.C.; Zabinsky, S.I. *Phys. Rev. B* **1992**, *69*, 3397-3400.

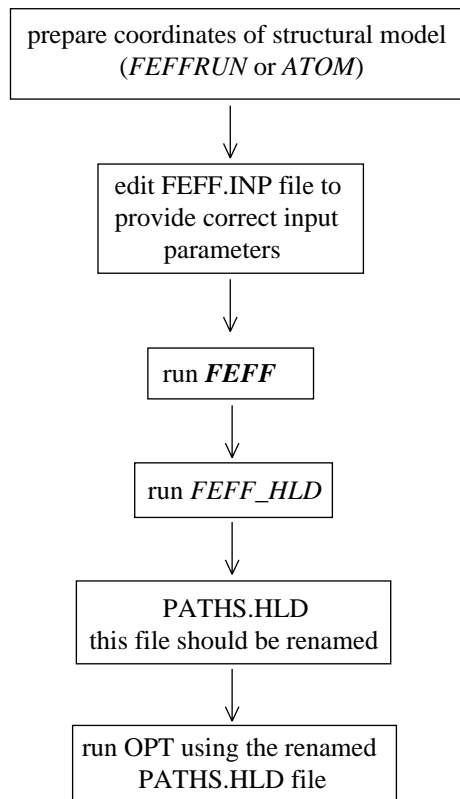


Figure D.9-1 Possible sequence of programs for the OPT *feff* interface.

E. MULDAT

MULDAT is the major means of producing good publication quality hard copy plots with EXAFSPAK programs, although it is certainly not limited to output from EXAFSPAK. MULDAT will read any ASCII file which contains columns of decimal numbers separated by spaces or tabs. Any header lines (lines with non-alphanumeric characters) are skipped. The program can store graphs in a device independent way in .MUL files, which can be re-loaded in another session by simply typing **MULDAT FILENAME.MUL** (.MUL files can be created using the utilities option of the main menu - see below).

Command :

MULDAT [file_spec]

Qualifiers:

/HELP	Lists command-line options
/XWINDOWS=on/off	Specifies whether X-Windows interface is to be used.
/VERSION	Gives compilation and GLIB dates.
/FILE=[file_spec]	Reads ASCII files described by file_spec, columns 1 and 2.
/SCALED	Automatically scales plot.
/LOGFILE=[file_spec]	
/RECOVER=[file_spec]	
/DUMB	

Simply typing MULDAT at the command line prompt will launch the program, and the user will be presented with the main menu:

```
MULDAT Version 1.4
Press 1 to input filenames
    2 to change offsets etc.
    3 to change plot scale
    4 to change axis setup
    5 to plot
    6 for utilities
    7 to annotate
    8 to draw line
    9 to draw arrow
    A for extras
    B to quit
:1
```

We will work through the creation of an example plot, the results of curve-fitting the EXAFS of $K_2Ni(CN)_4$ using the curved-wave multiple scattering program *feff* in combination with OPT. Several files are required, the .FIT file output from OPT (K2NICN4.FIT) and the EXAFS deconvolution file also from OPT (CHI.FRM). We will display a total of six traces on the plot, the experimental data, the results of curve-fitting, and the four main components in the EXAFS. The first two are stored in different columns of K2NICN4.FIT, and the last four in CHI.FRM. We first input the filenames :

```
Enter max. number of traces in plot [0] :6<CR>
Enter trace numbers to read [1,1] :,6<CR>
Trace 1 Enter filename [] :K2NICN4.FIT<CR>
Enter column No.s (x,y) to read [1, 2]:<CR>
Trace 2 Enter filename [] :K2NICN4.FIT<CR>
Enter column No.s (x,y) to read [1, 2]:,3<CR>
Trace 3 Enter filename [] :CHI.FRM<CR>
Enter column No.s (x,y) to read [1, 2]:<CR>
Trace 4 Enter filename [] :CHI.FRM<CR>
Enter column No.s (x,y) to read [1, 2]:,3<CR>
Trace 5 Enter filename [] :CHI.FRM<CR>
Enter column No.s (x,y) to read [1, 2]:,4<CR>
Trace 6 Enter filename [] :CHI.FRM<CR>
Enter column No.s (x,y) to read [1, 2]:,5<CR>
```

The program now reads the files ...

```
1 K2NICN4.FIT 249 points read in
2 K2NICN4.FIT 249 points read in
  :
6 CHI.FRM 249 points read in
All files read OK
```

Our next action will be to set up the offsets *etc.* including k^3 -weighting the data, as the output from OPT is unweighted.

```
Enter trace numbers to setup [1, 6] :<CR>
File 1. Do you wish to plot points? [y/n] [N] :<CR>
File 1. Do you wish to plot a line? [y/n] [Y] :<CR>
Enter line, pen no. and fill [0, 1, 0] :<CR>
File 1. Y = b + a*Y**c, Enter a,b,c [1.00000, 0.0, 0.0] :,10,3<CR>
File 1. X = b + a*Y**c, Enter a,b,c [1.00000, 0.0, 0.0] :<CR>
  :
```

We select various line types (see section A) for the traces in the plot, and vertically displace traces 1 and 2 by 10. The data can now be plotted (option 5) with auto-scaling, the plot will appear as shown in figure E.1

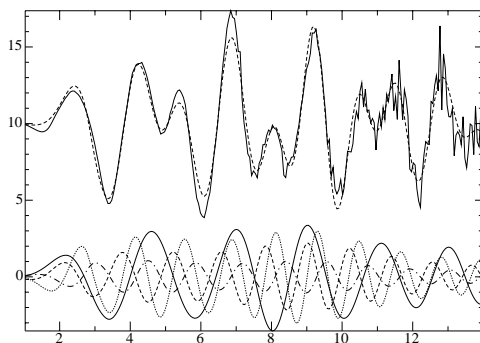


Figure E.1 Muldat example plot of $K_2Ni(CN)_4$ curve-fitting

Although we will not use it in our example, we draw attention to the cursor input facilities in MULDAT. If the C key is pressed with the plot on the screen, then the graphics cursors are called, and a small menu will appear with the options *Position*, *Mark*, *Zoom*, *Out* and *Exit*. The *Position* (and *Mark*) options allow the user to determine the position of cursor on the plot, together with the separation from a previously *Marked* position. This information can be written to the file MULDAT_OUT.LIS by selecting *Out* option (which itself can later be plotted with MULDAT). This option is very useful if, for example, measurements of a large number of peak positions are to be made. The scaling can be adjusted using the *Zoom* option in the usual way.

Returning to our example, we now decide to separate the last four traces, to do this we select option 2 again, and then plot once more using option 5. After some cycles of positioning and plotting we decide upon the plot shown in figure E.2 We re-scale the plot using option 3 of the menu, and add axis labels to the plot using option 4, and then re-plot the graph.

Selecting option 3 :

```
Enter plot x,y limits [1.02401, 13.9806, -1.04665, 37.3629] :1,14,-5,40<CR>
Enter page x,y limits [6000.00, 30000.0, 6000.00, 30000.0] :<CR>
```

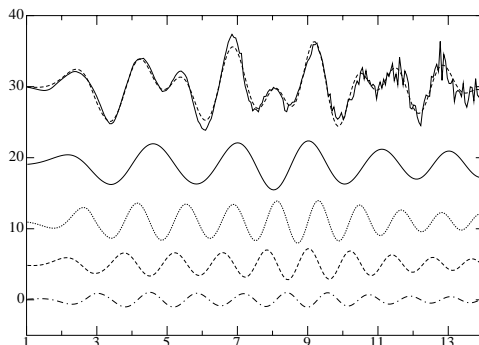


Figure E.2 Muldat example plot of $K_2Ni(CN)_4$ curve-fitting

We can now add labels to the x and y-axes using option 4 of the main menu, annotate using option 7, and draw additional straight lines on the plot using option 8 of the main menu (*n.b.* see sections A.3.2-4 for information upon graphics control characters *etc.*). Snap-grids can be turned on and off using option A of the main menu. These allow annotations and lines to be aligned with a grid in the central area of the plot. The completed plot might appear as shown in figure E.3

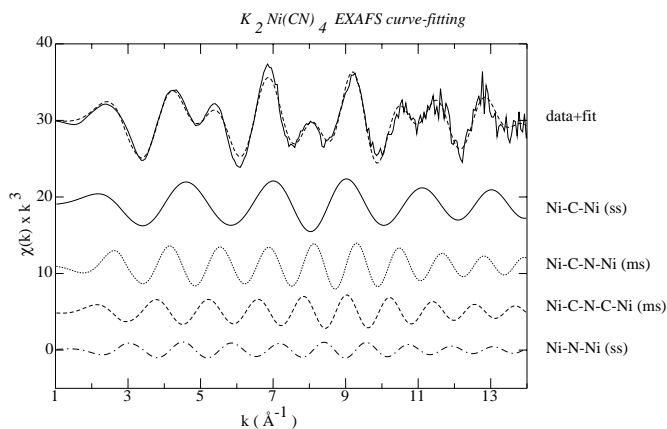


Figure E.3 Final muldat example plot of $K_2Ni(CN)_4$ curve-fitting.

F EDG_FIT

The program EDG_FIT allows peak deconvolution of X-ray absorption edge spectra, this is useful to obtain accurate peak positions and areas. The experimental data can be fitted to a sum of pseudo-Voigt peak shapes, plus a step function. The pseudo-Voigt is an approximation of the expected lineshape function, which will be a convolution of a Gaussian lineshape, defined by the monochromator resolution, with a Lorentzian lineshape from the core-hole broadening. The pseudo-Voigt peakshape is simply a sum of Gaussian and Lorentzian peakshapes :

$$I_V = mI_G + (1 - m)I_L$$

$$I_G = \exp \left\{ \frac{-\ln 2 (E - E_m)^2}{\left[\frac{(W + (E - E_m)\eta)}{\xi} \right]^2} \right\}$$

$$I_L = \frac{[W + (E - E_m)\eta]^2}{[W + (E - E_m)\eta]^2 + (E - E_m)^2}$$

Where I_G and I_L are the Gaussian and Lorentzian lineshape components, respectively, m is the mixing factor determining the proportion of each, W is the half-linewidth, E is the abscissa (X-ray energy for edge spectra), E_m is the position of the peak, η is the peak skew, and ξ is the ratio of Gaussian to Lorentzian linewidths (lw-ratio). The step function is simply the integral of this function with $\eta = 0$ and $\xi = 1$ (comprised of an erf and an arctangent function for the Gaussian and Lorentzian parts, respectively). A squaric polynomial is also included to approximate any background function of the spectrum. Neglecting the latter, the spectrum, $I(E)$, is fit to the function : $I(E) = a_0 I_0(E) + \sum_i a_i I_{Vi}(E)$ where a_i and I_{Vi} are the peak amplitudes and peak shape functions (defined above),

respectively, the summation is over all peaks included in the fit, and a_0 and $I_0(E)$ are the step function amplitude, and the step function, respectively. The program is started by simply typing EDG_FIT, and will then display the main menu:

```

EDG-FIT 1.1
-----
Press 1 to read data
     2 to change parameters
     3 to plot
     4 to fit data
     5 for output
     6 for process manager
     7 to quit
:

```

The data should first be read using option 1, in our example we will fit a sulfur K-edge .EDG data file generated by PROCESS :

```

Enter data file to fit [ ] : tp2ca_279.edg<CR>
Reading file tp2ca_279.edg
Clip data ...
Enter min,max for data [2449.69, 2509.61] :<CR>
Enter start and finish points [1, 342] :<CR>
Enter parameter filename [tp2ca_279.par] :<CR>

```

Here, we have restored parameters from a previous EDG_FIT session. The parameters can now be modified option 2 of the main menu, to which the program responds :

```

Enter # of peaks [6] :<CR>
Enter X-delta [16.0000]<CR>

```

The parameter X-delta is the number of half-widths either side of the peak position each peak will be calculated. This number should be at least 4.0, and larger numbers will yield more accurate (but slower to calculate) peak fits. The "offset", "slope" and "twist" refer to the coefficients of the background squaric polynomial function. The parameter editor is command line driven, and can be exited by

entering 0 or control-Z. In our example, we will change the intensity of the first peak, and then exit the parameter editor.

	1	2	3	4	5	6	7
	Amplitude	position	half-width	mixing	offset	slope	twist
1	*0.873	* 2474.070	*0.700	*0.581	0.152E-02	0.163E-02	0.336E-04
	Amplitude	position	half-width	mixing	skew	lw-ratio	
2	* 1.72	* 2470.230	*0.571	0.599	0.000E+00	0.697	0.000E+00
3	* 3.09	* 2471.640	*0.487	^0.599	0.000E+00	1.16	0.000E+00
4	* 1.29	* 2473.250	* 1.17	^0.599	0.000E+00	0.710	0.000E+00
5	*0.318	* 2475.390	* 1.34	^0.599	0.000E+00	0.507	0.000E+00
6	*0.638	* 2479.410	* 2.88	^0.599	0.286	1.81	0.000E+00
7	*0.105	* 2485.330	* 2.47	^0.599	0.300	1.81	0.000E+00

```
Enter I,J to change or 0 to exit [1, 1] :2,1<CR>
Enter Amplitude [1.71780] :1.9<CR>
0:fix, 1:float, 2:link [1] :<CR>
Enter I,J to change or 0 to exit [1, 1] :0<CR>
```

In EDG_FIT linked parameters simply hold the value of the corresponding parameter of the previous peak, and are denoted by the ^ character to the left of the linked parameter (freely floating parameters are denoted by an asterisk). At this stage one would normally plot the fit, using option 3 of the main menu. In our example, however, we will go straight to fitting the data using option 4, we choose the defaults of a maximum of 10000 total peak-shape function evaluations (the fitting routine will bail out after this number), and a error-printout every 20 evaluations :

```
Enter max. evaluations [10000] :<CR>
Enter Error print frequency [20] :<CR>
0.870221E-04
      7
      7
```

Unlike OPT, which uses custom-written fitting algorithms, EDG_FIT uses the double precision version of the public domain MIN-PAK fitting library (Argonne National Laboratory; B.S. Garbow, K.E. Hillstrom, J.J. More) which can handle the large numbers of variables (22 in our example) required in analysis of edge data. After the data have been fitted we view the fit using option 3 of the main menu :

```
Enter GPLOT device number for plot [2] :<CR>
Enter route for plot [TT:] :<CR>
Do you want a colour plot? [y/n] [Y] :<CR>
Enter symbol number for data points [0] :<CR>
Enter plot scale x,y [1.00000, .800000] :.,1<CR>
```

The fit is then displayed, together with the residual, as illustrated in figure F-1 below.

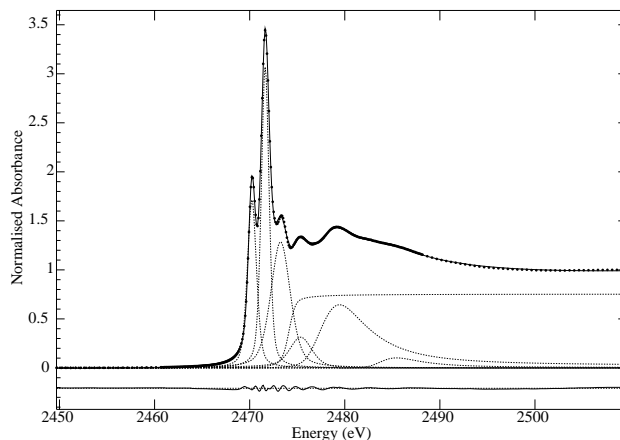


Figure F-1 EDG_FIT plot of peak deconvolution. The individual peaks are shown, together with the step function and the residual of the fit (lower curve).

The final values of the parameters can be viewed by re-entering the parameter editor (menu option 2) and an ASCII (*DATA*) output file of the fit can be created using option 5 of the main menu.

G THE PROCESS MANAGER UTILITY

The Process Manager is only present in the old Open VMS implementation of EXAFSPAK. It is not included in the new release of the Open VMS, Windows or the Unix versions. This utility was originally designed to give multi-session capability to terminal based environments, and is basically obsolete with modern windowing computer systems. The process manager allows the user to swap between EXAFSPAK programs in a simple manner, allowing, for example, concurrent sessions of OPT, MULDAT and PROCESS. The process manager can be found in the utilities menu of most applications. On selection within the program MULDAT, the following screen might appear.

```
DKA200:[GEORGE.MAIN.EXAFS.EXAFS]MULDAT.EXE;167
CPU time used   : 0 00:00:00.73
   2E6  MULDAT  Making the figure here
PROC_ID - TITLE - Comments:
   21A  PROC26  Working up the data here
   2E6  MULDAT  Making the figure here
```

Press PF1 for Options Menu, PF2 for next page, PF4 to Exit

In this example, two processes are active; PROCESS and MULDAT, and these are listed, with process id, title and comments. The processes in the list can be highlighted by moving the up and down cursor keys, and the highlighted process can be attached, deleted or its comments modified by pressing the PF1 key, which will pull down the options menu:

```
DKA200:[GEORGE.MAIN.EXAFS.EXAFS]MULDAT.EXE;167
CPU time used   : 0 00:00:00.73
   2E6  MULDAT
PROC_ID - TITLE - Comments:
   21A  PROC26  Working up the data here
   2E6  MULDAT  Making the figure here
```

Press PF1 for Optio

IOSPM - SUB-PROCESS MANAGER

```
Press 1 to attach to a process
   2 to spawn a new VMS subprocess
   3 for process information
   4 to change process comments
   5 to delete a process
   6 to return
:█
```

H EXAFSPAK INSTALLATION

The EXAFSPAK programs can be obtained on the World-Wide-Web :

<http://www-ssrl.slac.stanford.edu/exafspak.html>.

Follow this link to lead to the latest versions of Open VMS, UNIX and Windows 95/98/NT/2000 EXAFSPAK, together with current installation instructions

Comments, problems, or suspected bugs in the programs or setup procedure should be reported to the authors. Custom installations can be performed by the authors upon request.

We welcome comments from users of EXAFSPAK. Please feel free to contact the authors, either by electronic mail, or by mail, in order to communicate any comments (including suggestions of possible improvements), program bugs or suggestions for improvement. If users believe that they have discovered a program bug a careful note should be made of the following:

1. The program, and the exact command line that was used to run it.
2. The module and routine names (and line numbers, if given) given in the symbolic stack dump (if the program crashes) and any error messages reported by the program.

Note: Some obsolete EXAFSPAK programs (*i.e.* SVIEW, DEAD, CALIB and AVEX), and the EXAFSPAK converter MCONV require *sdata* run time libraries in order to read SSRL raw data files. These must be obtained by separate application to the SSRL computer group and installed upon the host machine before running the EXAFSPAK SETUP.COM. The *sdata* run-time library only operates on VAX hardware.

I. BIBLIOGRAPHY

There is presently no good texts which deals with *all* aspects of XAS data analysis. The following is a partial list of useful reference books which may be consulted.

X-ray Absorption. Principals, Applications, Techniques of EXAFS, SEXAFS, and XANES (Eds. Koningsberger, D.C.; Prins, R.) John Wiley and Sons Inc., **1988** ISBN 0-471-87547-3 *A compendium of eleven chapters written by thirteen international contributors. A good reference text which is fairly up to date on most aspects of EXAFS.*

Teo, B.K. *EXAFS: Basic Principals and Data Analysis*. Springer-Verlag **1986** ISBN 3-540-15833-2 *A good general text for elementary aspects of data analysis. Multiple scattering is treated, however recent theoretical advances have made this section a little out of date.*

J. DISCLAIMER

We believe the programs that are described in this manual, collectively known as EXAFSPAK, to be largely error-free. Nevertheless, in any large body of code it is difficult to guarantee that there are absolutely no errors. Similarly, it is also possible that in this manual we have inadvertently made errors. The EXAFSPAK programs and any accompanying documentation are used at entirely at the user's own risk. The authors are not responsible for any direct or consequential damages suffered by any parties from the use of EXAFSPAK programs or of any accompanying documentation.

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