SBFIT
Sideband fitting for MEMAS

Contents

1 Compiling

Two `Makesfiles` are provided. To compile executables, run:
`> make -f Makefile-sbfit-linux` or
`> make -f Makefile-sbfit-mac`

2 Data processing

NMR data processing must provide files with the spectrum, cumulative integral, and derivative spectrum, e.g. with nmrPipe:

```
#!/bin/tcsh

nmrPipe -in test.fid \
| nmrPipe -fn COADD -axis Y -cList 1.0 1.0 1.0 1.0 \
| nmrPipe  -fn EM -lb 70 -c 0.5                    \
| nmrPipe  -fn ZF -size 32768                      \
| nmrPipe  -fn FT -auto                            \
| nmrPipe  -fn PS -p0 53.6 -p1 0.00 -di -verb      \
| nmrPipe -fn EXT -x1 -70ppm -xn 80ppm -sw         \
| nmrPipe -fn BASE -nw 20 -nl 0% 5% 95% 100%       \
| nmrPipe -fn MULT -inv -c 1024                    \
| nmrPipe -fn MULT -inv -c 10000                   \
   -ov -out test.ft

nmrPipe -in test_lb100.ft                          \
| nmrPipe -fn INTEG                                \
| nmrPipe -fn MULT -inv -c 10000                   \
-ov -out test.int

nmrPipe -in test_lb100.ft                          \
| nmrPipe -fn DX                                   \
-ov -out test.dx

pipe2txt.tcl -index Hz test.ft > ft.dat
pipe2txt.tcl -index Hz test.int >  integ.dat
pipe2txt.tcl -index Hz test.dx >  deriv.dat
```

Note that for now the `-fn MULT -inv -c 10000` scaling of integrals is necessary, owing to a hard-coding of this factor into the analysis.

3 Lorentzian Fitting

The fitting utilities are comprised (currently) of three executables. It is expected that these executables will be run from shell scripts. Whether run from a script or not, shell vari-

ables `OUTPATH` and OUTBASE must be defined in the command-line shell from which the executables are run. And example shell script is given in section 5
Each executable takes different options, and accomplishes a different purpose. Any options which the executable does not expect will cause an error. All options listed are necessary. Each option has a binary digit associated with it, and the "check" sum of all such codes is given in the error message for any missing options. The error message also provides some information to help interpret and fix the error.
A subdirectory is created if it doesn't previously exist. A `.log` file is written into this output directory. Executables run subsequent to the first run which created the directory and log file will append their comments to the log file, and won't overwrite information from previously run executables. All other output files **will** overwrite previously generated files, if the `APPENDOUTFILE` option was previously used.

3.1 `init_spectralfit_data`

Use this executable for the initial read of the spectrum, integral, and derivative from the FID processing, and give initial values to the fitting parameters at the same time. One needs to visually inspect the processed FID to pick some approximate initial values. The required options (with their binary codes) are

[1]	`SPECTRUMFILE`	(2 cols: frequency intensity)
[2]	`INTEGRALFILE`	(2 cols: frequency integral)
[4]	`DERIVATIVEFILE`	(2 cols: frequency derivative)
[8]	`APPENDOUTFILE`	(append to output filenames)
[16]	`MINSB`	(most negative sideband index)
[32]	`MAXSB`	(most positive sideband index)
[64]	`MAS`	(mas speed)
[128]	`FWHM`	(initial full width half max of mas sidebands)
[256]	`FWHMISO`	(initial full width half max of isotropic)
[512]	`CENTRE`	(initial centre freq of mas centreband)
[1024]	`CENTREISO`	(initial freq of isotropic peak)
[2048]	`AMPISO`	(initial intensity of isotropic peak)
[4096]	`CENTREISO2`	(centre freq of 2nd isotropic peak)
[8192]	`FWHMISO2`	(full width half max of 2nd isotropic peak)
[16384]	`AMPISO2`	(intensity of 2nd isotropic peak)
[32768]	`ALPHA`	(not currently implemented)

3.2 `analyze_baseline`

This executable reads in a `.lfit` file generated by `init_spectral_data` and performs average, standard deviation, and autocorrelation statistics on a defined noise region (using symmetric regions about zero). Statistics are calculated separately for the spectrum, integral, and derivative spectra. Autocorrelations are written to a `.nac` (**n**oise **a**uto**c**orrelation) file. Where autocorrelation persists to a long lag, small noise regions are necessary to get a more accurate estimate of the standard deviation, which is necessary for sensible errors on sideband intensities when fitting in later steps. The required options are:

[1] `DATAFITFILE` (.lfit raw & fit spectrum, integral, derivative)
[2] `NMINFREQ` (inner frequency value for noise region) Data error is presumed
[4] `NMAXFREQ` (outer frequency value for noise region)
to be the rms of noise in the spectrum, and these statistics are calculated using all points between ±NMINFREQ and ±NMAXFREQ, where the spectrum of interest is presumed to be safely contained between +MINFREQ and −MINFREQ. You are free to use whatever noise levels you want when fitting in subsequent steps, but this will effect optimised parameter error estimates.

3.3 `fit_spectral_data`

This executable reads in a `.lfit` file generated by either `init_spectral_data`, or an earlier run of this same executable. In addition to an incremental `.lfit` file, a `.lrntz` file is output which gives the scaled lineshapes for all of the component lorentzians, with frequency in the first column, isotropic intensity in the second column, a second isotropic peak intensity is the third column, and MAS sideband intensities in columns four through the end, corresponding to the `MAXSB` through the `MINSB` sideband indices. A `.sbdat` file is also output, which can be concatenated with similar files from analyses at other spin rates for the sample and then used as input to the maximum entropy MAS analysis. The required options are

[1]	`DATAFITFILE`	(.lfit raw & fit spectrum, integral, derivative)
[2]	`APPENDOUTFILE`	(append to unoriented output filename)
[4]	`FITCONFIG`	(sum of 4 spectrum, 2 integral, 1 derivative)
[8]	`FITAMPS`	(fit MAS amplitudes 0 or 1)
[16]	`FITAMPISO`	(fit isotropic amplitude 0 or 1)
[32]	`FITFWHM`	(fit full width half max of mas sidebands 0 or 1)
[64]	`FITFWHMISO`	(fit full width half max of isotropic 0 or 1)
[128]	`FITCENTRE`	(fit centre freq of mas centreband 0 or 1)
[256]	`FITCENTREISO`	(fit freq of isotropic peak 0 or 1)
[512]	`MAXITER`	(maximum fitting iterations)
[1024]	`SIGMASPE`	(spectral data error)
[2048]	`SIGMAINT`	(integral data error)
[4096]	`SIGMADER`	(derivative data error)
[8192]	`FITCENTREISO2`	(fit freq of 2nd isotropic peak 0 or 1)
[16384]	`FITFWHMISO2`	(fit full width half max of 2nd isotropic 0 or 1)
[32768]	`FITAMPISO2`	(fit amplitude of 2nd isotropic peak 0 or 1)
[65536]	`FITALPHA`	(not currently implemented: set to 0)

3.4 `fit_gnuplot`

This executable reads in a `.lfit` file generated by either `init_spectral_data` or `fit_spectral_data`, and writes a gnuplot script file which plots from both the `.lfit` and `.lrntz` files. The output `.gp` and `.eps` files use the same `APPENDOUTFILE` suffix. The required options are

[1] `APPENDOUTFILE` (file set suffix)

4 Options Reference

ALPHA Not currently implemented, but it has to be there. AMPISO An initial guess for the intensity of isotropic peak. This is not the peak intensity, but the scaling factor for the whole Lorentzian lineshape. Using perhaps a more realistic guess for the fwhm_iso than what you actually specify in FWHMISO, multiply the peak intensity by ($\pi/2$ * fwhm) and use this for your initial guess. Set to zero if there appears to be no isotropic peak resolved from the MAS manifold centreband.

AMPISO2 An initial guess for the intensity of a second isotropic peak. Follow guidance for AMPISO. Set to 0 (zero) if there is only one isotropic peak.

APPENDOUTFILE Output files are given specific extensions, but this option is used to specify a customized string which is appended to the basename of the file. It is used to specify both input and output files when used for fit_gnuplot.

CENTRE Initial guess for the frequency of mas centreband.

CENTREISO Initial guess for frequency of the isotropic-phase peak.

CENTREISO2 Initial guess for frequency of a second isotropic-phase peak.

DERIVATIVEFILE A file containing two columns of data: frequency (identical values as for the SPECTRUMFILE), and spectral derivative values.

DATAFITFILE Raw & fit spectrum, integral, derivative, i.e. the .lfit file generated from the init_spectralfit_data or fit_spectral_data executables

FITALPHA Not currently implemented, but it has to be there. Set to 0 (zero) FITAMPS Set nonzero to fit/optimise MAS sideband amplitudes.

FITAMPISO Set nonzero to fit/optimise amplitude of isotropic-phase peak.

FITAMPISO2 Set nonzero to fit/optimise amplitude of a second isotropic-phase peak.

FITCENTRE Set nonzero to fit/optimise centre frequency of mas centreband.

FITCENTREISO Set nonzero to fit/optimise frequency of isotropic peak.

FITCENTREISO2 Set nonzero to fit/optimise frequency of a second isotropic peak.

FITCONFIG Specify whether to fit the spectrum and/or integral and/or derivative by summing binary codes: 4 for spectrum, 2 for integral, and 1 for derivative. For example, use 4 to fit spectrum only, 6 to fit spectrum and integral but not derivative, and 7 for all three.

FITFWHM Set nonzero to fit/optimise full-width-half-max of mas sidebands.

FITFWHMISO Set nonzero to fit/optimise full-width-half-max of isotropic-phase peak

FITFWHMISO2 Set nonzero to fit/optimise full-width-half-max of a second isotropic-phase peak

FWHM Initial guess for the full width half max of mas sidebands. It is better to err on the side of too narrow, and let the fit make the peaks wider.

FWHMISO Initial full width half max of an isotropic-phase peak. Again, it is better to err on the side of specifying a width which is more narrow than the peak probably is, but be sure

to still make it wide enough to be at least 4-times the digital resolution.

`FWHMISO2` Initial full width half max of a second isotropic-phase peak. Follow advice in FWHMISO above. Do not set to 0 (zero), to avoid a divide by zero in Lorentzian lineshape calculation. `INTEGRALFILE` A file containing two columns of data: frequency (identical values as for the `SPECTRUMFILE`), and cumulative integral values.

`MAS` (mas speed)

`MAXITER` Maximum fitting iterations.

`MAXSB` Most positive sideband index to be included in the fit

`MINSB` Most negative sideband index to be included in the fit

`NMINFREQ` inner frequency value for noise region for statistical analysis of baseline

`NMAXFREQ` outer frequency value for noise region for statistical analysis of baseline

`SIGMADER` RMS deviation of data in the derivative spectrum

`SIGMAINT` RMS deviation of data in the integral curve

`SIGMASPE` RMS deviation of data in the spectrum

`SPECTRUMFILE` A file containing two columns of data; frequency and spectral intensity. The spectrum should have the flattest baseline possible. The frequency values must be the same as for the integral file and the derivative file.

5 Example Shell Script

At the top of the script below, custom shell environment variables:
`BIN` the directory where the executables are found;
`OUTPATH` feeds the code with the leading path for output files;
`OUTBASE` is the directory name, and basename, to be used for all output;
`OWSAFETY` should be set to "nosafe" or "safe" depending on whether you want to avoid overwrite warning prompts.
This script is performed in three stages, controlled with customized variables `init`, `noise`, and `fit`, controlled from the top of the script for convenience.

1. You must first inspect the processed spectrum and decide how many sidebands to include, whether and how much to include of an isotropic peak, and determine approximate values for centre frequencies and linewidths. Running this script with the `init` stage enabled clears previous work, reads the user's parameter estimates, and automatically finds initial values to use for spinning sideband amplitudes. Calculations with these values are performed and available for inspection via gnuplot.

2. The initial output should be inspected, and inner and outer frequencies selected to use for noise-bracketing in the second `noise` stage of the shell script.

3. Once realistic standard deviations of noise are known, fitting can be performed with

any combination of parameters to be optimised, using the spectrum, integral, and/or derivative. Here we first fit the spectrum only, then again with all three, before plotting via gnuplot again.

Note also that several custom `echo` statements are used to provide as little or as much information on script progress. Provided the script is executable (fix with `> chmod u+x` if not) it is run from the command line with simply
`> ./scriptname`

```
#!/bin/bash -l

export BIN="../../Src"
export OUTPATH="`pwd`"
export OWSAFETY="nosafe"

export OUTBASE="dmpe7dmpg3control_T37_1200b_fit"
echo $OUTBASE

init=0
noise=0
fit=1

if (( $init ))
    then
echo "initializing ..."

rm -r $OUTBASE

$BIN/init_spectralfit_data\
    SPECTRUMFILE "tmp1-1200b.dat"\
    INTEGRALFILE "tmp2-1200b.dat"\
    DERIVATIVEFILE "tmp3-1200b.dat"\
    APPENDOUTFILE "-init"\
    MAS 1200\
    MINSB -7\
    MAXSB 8\
    FWHM 500\
    FWHMISO 100\
    CENTRE 571\
    CENTREISO 660\
    AMPISO 3000\
    FWHMISO2 100\
    CENTREISO2 620\
    AMPISO2 3000\
    ALPHA 1
```

```
$BIN/fit_gnuplot\
    APPENDOUTFILE "-init"
fi

if (( $noise ))
    then
echo "analyzing baseline ..."

$BIN/analyze_baseline\
    DATAFITFILE $OUTBASE/${OUTBASE}-init.lfit\
    NMINFREQ 15000\
    NMAXFREQ 15200
fi

if (( $fit ))
    then
echo "fitting ..."

echo "... spectrum only ..."
$BIN/fit_spectral_data\
    DATAFITFILE $OUTBASE/${OUTBASE}-init.lfit\
    APPENDOUTFILE "-4a"\
    FITCONFIG 4\
    FITAMPS 1\
    FITAMPISO 1\
    FITFWHM 1\
    FITFWHMISO 1\
    FITCENTRE 1\
    FITCENTREISO 1\
    MAXITER 500\
    SIGMASPE 0.04\
    SIGMAINT 0.0001\
    SIGMADER 0.008\
    FITAMPISO2 1\
    FITFWHMISO2 1\
    FITCENTREISO2 1\
    FITALPHA 0


echo " ... spectrum, integral and derivative ..."
$BIN/fit_spectral_data\
    DATAFITFILE $OUTBASE/${OUTBASE}-4a.lfit\
    APPENDOUTFILE "-7a"\
    FITCONFIG 7\
```

```
    FITAMPS 1\
    FITAMPISO 1\
    FITFWHM 1\
    FITFWHMISO 1\
    FITCENTRE 1\
    FITCENTREISO 1\
    MAXITER 500\
    SIGMASPE 0.04\
    SIGMAINT 0.0001\
    SIGMADER 0.008\
    FITAMPISO2 1\
    FITFWHMISO2 1\
    FITCENTREISO2 1\
    FITALPHA 0


$BIN/fit_gnuplot\
    APPENDOUTFILE "-7a"
fi
```

6 Analytical expressions used in fitting

Fitting Lorentzians to manifold of magic angle spinning peaks

6.1 Lorentzian lineshape

Lorentzian line with integral $(-\infty \to \infty)$ of A_n, sideband index n and mas rate ν_r, centreband frequency ν_0, and full linewidth at half maximum fwhm:

$$\ell_n(\nu) = \frac{A_n}{\pi} \cdot \frac{2 \cdot \text{fwhm}}{\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2} \tag{1}$$

$$= \frac{A_n}{\pi} \cdot L(\nu) \tag{2}$$

6.1.1 Partials

Partial derivatives of lorentzian line with respect to fwhm, centreband frequency, and amplitude.

$$\frac{\partial \ell_n(\nu)}{\partial A_n} = \frac{1}{\pi} \cdot \frac{2 \cdot \text{fwhm}}{\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2} \tag{3}$$

$$= \frac{1}{\pi} L(\nu) \tag{4}$$

$$\frac{\partial \ell_n(\nu)}{\partial \nu_0} = \frac{A_n}{\pi} \cdot (-8)(\nu_0 + n \cdot \nu_r - \nu) \cdot \frac{2 \cdot \text{fwhm}}{\left[\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2\right]^2} \tag{5}$$

$$= \frac{A_n}{\pi} \cdot \frac{-8 \cdot (\nu_0 + n \cdot \nu_r - \nu)}{\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2} \cdot L_n(\nu) \tag{6}$$

$$= -4 \cdot \frac{A_n}{\pi} \cdot (\nu_0 + n \cdot \nu_r - \nu) \cdot \frac{L_n(\nu)^2}{\text{fwhm}} \tag{7}$$

$$\frac{\partial \ell_n(\nu)}{\partial \text{fwhm}} = \frac{A_n}{\pi} \cdot \left\{ \frac{2}{\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2} + \frac{-4 \cdot \text{fwhm}^2}{\left[\text{fwhm}^2 + (\nu_0 + n \cdot \nu_r - \nu)^2\right]^2} \right\} \tag{8}$$

$$= \frac{A_n}{\pi} \cdot \left(\frac{L(\nu)}{\text{fwhm}} - L(\nu)^2 \right) \tag{9}$$

6.2 Cumulative Integral of Lorentzian

Cumulative integral from the left edge ν_+ of a spectrum to a given frequency ν:

$$\int_{\nu_+}^{\nu} \ell(\nu) = i(\nu) = \frac{A_n}{\pi} \cdot \left\{ \tan^{-1}\left(-2\frac{\nu_0 + n\cdot\nu_r - \nu_+}{\text{fwhm}} \right) - \tan^{-1}\left(-2\frac{\nu_0 + n\cdot\nu_r - \nu}{\text{fwhm}} \right) \right\} \quad (10)$$

$$= \frac{A_n}{\pi} \cdot \tan^{-1}\left\{ \frac{2\cdot\text{fwhm}\cdot(\nu_+ - \nu)}{\text{fwhm}^2 + 4\cdot(\nu_0 + n\cdot\nu_r - \nu_+)(\nu_0 + n\cdot\nu_r - \nu)} \right\} \quad (11)$$

$$= \frac{A_n}{\pi} \times \tan^{-1}\left\{ \frac{2\cdot\text{fwhm}\cdot(\nu_+ - \nu)}{\text{fwhm}^2 + 4\cdot\nu_0^2 + \nu_0\cdot 4\cdot(2\cdot n\cdot\nu_r - \nu_+ - \nu) + 4\cdot(n^2\nu_r^2 - n\cdot\nu_r(\nu+\nu_+) + \nu_r\cdot\nu)} \right\} \quad (12)$$

$$= \frac{A_n}{\pi} \cdot \tan^{-1}\left\{ \frac{\mathcal{U}}{\mathcal{V}} \right\} \quad (13)$$

6.2.1 Partials

In general, derviative of arctan is

$$\frac{\mathrm{d}[\arctan(u)]}{\mathrm{d}x} = \frac{1}{1+u^2}\cdot\frac{\mathrm{d}u}{\mathrm{d}x} \quad (14)$$

and

$$\frac{\mathrm{d}[\arctan(\frac{u}{v})]}{\mathrm{d}x} = \frac{1}{1+\frac{u^2}{v^2}}\left(v\frac{\mathrm{d}u}{\mathrm{d}x} - u\frac{\mathrm{d}v}{\mathrm{d}x} \right)\frac{1}{v^2} \quad (15)$$

$$= \frac{1}{u^2+v^2}\left(v\frac{\mathrm{d}u}{\mathrm{d}x} - u\frac{\mathrm{d}v}{\mathrm{d}x} \right) \quad (16)$$

$$\frac{\partial i(\nu)}{\partial A_n} = \frac{1}{\pi}\cdot\tan^{-1}\left\{ \frac{\mathcal{U}}{\mathcal{V}} \right\} \quad (17)$$

$$\frac{\partial i(\nu)}{\partial \nu_0} = -\frac{A_n}{\pi}\left(\frac{4}{\mathcal{U}^2+\mathcal{V}^2} \right)\cdot\mathcal{U}\cdot\left(2\cdot\nu_0 + 2\cdot n\cdot\nu_r - \nu_+ - \nu \right) \quad (18)$$

$$\frac{\partial i(\nu)}{\partial \text{fwhm}} = \frac{A_n}{\pi}\left(\frac{\mathcal{U}}{\mathcal{U}^2+\mathcal{V}^2} \right)\cdot\left[\frac{\mathcal{V}}{\text{fwhm}} - 2\cdot\text{fwhm} \right] \quad (19)$$

6.3 Derivative of Lorentzian

Derivative of Lorentzian line with respect to ν:

$$\frac{\mathrm{d}\ell(\nu)}{\mathrm{d}\nu} = d(\nu) = \frac{A_n}{\pi} \cdot \frac{8 \cdot \mathrm{fwhm} \cdot (\nu_0 + n \cdot \nu_r - \nu)}{\left[\mathrm{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2\right]^2} \tag{20}$$

$$= \frac{A_n}{\pi} \cdot \frac{\mathcal{U}}{\mathcal{V}^2} \tag{21}$$

6.3.1 Partials

In general

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{u}{v^2}\right) = \frac{1}{v^2}\frac{\mathrm{d}u}{\mathrm{d}x} - 2\frac{u}{v^3}\frac{\mathrm{d}v}{\mathrm{d}x} \tag{22}$$

$$\frac{\partial i(\nu)}{\partial A_n} = \frac{1}{\pi} \cdot \frac{\mathcal{U}}{\mathcal{V}^2} \tag{23}$$

$$\frac{\partial i(\nu)}{\partial \nu_0} = \frac{A_n}{\pi} \cdot \left(\frac{8 \cdot \mathrm{fwhm}}{\mathcal{V}^2} - 2\frac{\mathcal{U}}{V^3}\frac{\mathcal{U}}{\mathrm{fwhm}}\right) \tag{24}$$

$$= \frac{A_n}{\pi} \cdot \left(\frac{8 \cdot \mathrm{fwhm}}{\mathcal{V}^2} - \frac{2}{\mathrm{fwhm}}\frac{\mathcal{U}^2}{V^3}\right) \tag{25}$$

$$= \frac{A_n}{\pi} \cdot \left(\frac{2}{\mathcal{V}^2}\right)\left(4 \cdot \mathrm{fwhm} - \frac{1}{\mathrm{fwhm}}\frac{\mathcal{U}^2}{\mathcal{V}}\right) \tag{26}$$

$$\frac{\partial i(\nu)}{\partial \mathrm{fwhm}} = \frac{A_n}{\pi} \cdot \left(\frac{\mathcal{U}}{\mathrm{fwhm}}\frac{1}{\mathcal{V}^2} - \frac{4 \cdot \mathcal{U} \cdot \mathrm{fwhm}}{\mathcal{V}^3}\right) \tag{27}$$

$$= \frac{A_n}{\pi} \cdot \left(\frac{\mathcal{U}}{\mathcal{V}^2}\right) \cdot \left(\frac{1}{\mathrm{fwhm}} - \frac{4 \cdot \mathrm{fwhm}}{\mathcal{V}}\right) \tag{28}$$

6.4 Manifold of peaks

A manifold of spinning sidebands is a sum of the lineshapes described above for a set n of sequential integer values from some maximally negative to some maximally positive index. By definition, the first moment of density in the powder in the isotropic chemical shift, or centreband position when spinning. We force this condition when fitting by make all MAS peak sideband amplitudes independent except one. We choose the $n = -1$ peak to be dependent on the others, i.e.

$$A_{-1} = \sum_{n \neq -1} n \cdot A_n \tag{29}$$

The spectrum, integral, and derivative is an sum of all peaks, and the residuals and Jacobian therefore must include all components. We must therefore adapt the expressions above to include the summation over all peaks.

6.5 MAS manifold of Lorentzian peaks

MAS spectrum S_{ν_r} at mas rate ν_r is a sum over a number of lorentzians with individual integrals A_n, sideband index n, centreband frequency ν_0, and full linewidth at half maximum fwhm, using

$$L_n(\nu) = \frac{2 \cdot \text{fwhm}}{\text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2} \tag{30}$$

$$S_{\nu_r}(\nu) = \pi^{-1} \left(\sum_{n \neq -1} A_n L_n(\nu) \right) + \pi^{-1} L_{-1}(\nu) \cdot \left(\sum_{n \neq -1} n \cdot A_n \right) \tag{31}$$

$$= \frac{1}{\pi} \sum_{n \neq -1} A_n \cdot \Big(L_n(\nu) + n \cdot L_{-1}(\nu) \Big) \tag{32}$$

$$\tag{33}$$

6.5.1 Partials

Partial derivatives of lorentzian line with respect to fwhm, centreband frequency, and amplitude.

$$\frac{\partial S_{\nu_r}(\nu)}{\partial A_{n \neq -1}} = \frac{1}{\pi} \left(L_n(\nu) + n \cdot L_{-1}(\nu) \right) \tag{34}$$

$$\frac{\partial S_{\nu_r}(\nu)}{\partial \nu_0} = -\frac{4}{\pi \cdot \text{fwhm}} \sum_n A_n \left(\nu_0 + n \cdot \nu_r - \nu \right) \cdot L_n(\nu)^2 \tag{35}$$

$$\tag{36}$$

$$\frac{\partial S_{\nu_r}(\nu)}{\partial \text{fwhm}} = \frac{1}{\pi} \sum_n A_n \cdot \left(\frac{L_n(\nu)}{\text{fwhm}} - L_n(\nu)^2 \right) \tag{37}$$

6.6 Cumulative Integral of Lorentzian MAS manifold

Cumulative integral over all MAS sideband Lorentzian peaks from the left edge ν_+ of a spectrum to a given frequency νs, using

$$\mathcal{U} = 2 \cdot \text{fwhm} \cdot (\nu_+ - \nu) \tag{38}$$

$$\mathcal{V}_n = \text{fwhm}^2 + 4 \cdot (\nu_0 + n \cdot \nu_r - \nu_+)(\nu_0 + n \cdot \nu_r - \nu) \tag{39}$$

$$= \text{fwhm}^2 + 4 \cdot \nu_0^2 + \nu_0 \cdot 4 \cdot (2 \cdot n \cdot \nu_r - \nu_+ - \nu) + 4 \cdot (i^2 \nu_r^2 - n \cdot \nu_r(\nu + \nu_+) + \nu_r \cdot \nu) \tag{40}$$

$$\int_{\nu_+}^{\nu} S_{\nu_r}(\nu) = I_{\nu_r}(\nu) = \sum_{n \neq -1} \frac{A_n}{\pi} \cdot \tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_n}\right\} + \frac{1}{\pi}\tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_{-1}}\right\}\left(\sum_{n \neq -1} n \cdot A_n\right) \tag{41}$$

$$= \frac{1}{\pi}\sum_{n \neq -1} A_n \left(\tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_n}\right\} + n \cdot \tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_{-1}}\right\}\right) \tag{42}$$

$$= \frac{1}{\pi}\sum_{n \neq -1} A_n \tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_n}\right\} + \frac{1}{\pi}\tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_{-1}}\right\}\sum_{n \neq -1} n \cdot A_n \tag{43}$$

6.6.1 Partials

$$\frac{\partial I_{\nu_r}(\nu)}{\partial A_n} = \frac{1}{\pi} \cdot \left(\tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_n}\right\} + n \cdot \tan^{-1}\left\{\frac{\mathcal{U}}{\mathcal{V}_{-1}}\right\}\right) \tag{44}$$

$$\frac{\partial I_{\nu_r}(\nu)}{\partial \nu_0} = -\frac{4 \cdot \mathcal{U}}{\pi}\sum_n A_n \cdot \left(\frac{1}{\mathcal{U}^2 + \mathcal{V}_n^2}\right)(2 \cdot \nu_0 + 2 \cdot n \cdot \nu_r - \nu_+ - \nu) \tag{45}$$

$$\frac{\partial I_{\nu_r}(\nu)}{\partial \text{fwhm}} = \frac{\mathcal{U}}{\pi}\sum_n A_n \left(\frac{1}{\mathcal{U}^2 + \mathcal{V}_n^2}\right)\left(\frac{\mathcal{V}_n}{\text{fwhm}} - 2 \cdot \text{fwhm}\right) \tag{46}$$

6.7 Derivative of Lorentzian MAS manifold

Derivative of Lorentzian manifold of MAS peaks with respect to ν, using

$$\mathcal{U}_n = 8 \cdot \text{fwhm} \cdot (\nu_0 + n \cdot \nu_r - \nu) \tag{47}$$

$$\mathcal{V}_n = \text{fwhm}^2 + 4(\nu_0 + n \cdot \nu_r - \nu)^2 \tag{48}$$

$$\frac{\mathrm{d}}{\mathrm{d}\nu} S_{\nu_r}(\nu) = D(\nu) = \frac{1}{\pi} \cdot \sum_{n \neq -1} A_n \left(\frac{\mathcal{U}_n}{\mathcal{V}_n^2} + n \frac{\mathcal{U}_{-1}}{\mathcal{V}_{-1}^2} \right) \tag{49}$$

$$= \frac{1}{\pi} \left(\sum_{n \neq -1} A_n \frac{\mathcal{U}_n}{\mathcal{V}_n^2} \right) + \frac{1}{\pi} \left(\frac{\mathcal{U}_{-1}}{\mathcal{V}_{-1}^2} \sum_{n \neq -1} n \cdot A_n \right) \tag{50}$$

6.7.1 Partials

$$\frac{\partial D(\nu)}{\partial A_{n \neq -1}} = \frac{1}{\pi} \cdot \left(\frac{\mathcal{U}_n}{\mathcal{V}_n^2} + n \frac{\mathcal{U}_{-1}}{\mathcal{V}_{-1}^2} \right) \tag{51}$$

$$\frac{\partial D(\nu)}{\partial \nu_0} = \frac{2}{\pi} \sum_n A_n \left(\frac{1}{\mathcal{V}_n^2} \right) \left(4 \cdot \text{fwhm} - \frac{1}{\text{fwhm}} \frac{\mathcal{U}_n^2}{\mathcal{V}_n} \right) \tag{52}$$

$$\frac{\partial D(\nu)}{\partial \text{fwhm}} = \frac{1}{\pi} \sum_n A_n \frac{\mathcal{U}_n}{\mathcal{V}_n^2} \left(\frac{1}{\text{fwhm}} - \frac{4 \cdot \text{fwhm}}{\mathcal{V}_n} \right) \tag{53}$$