

Linear Prediction in 2D NMR SPECTROSCOPY

(Xwinmr 3.5 patchlevel 6 , Windows XP)

**DPX200
DPX300
DRX500**

and

Processing computers



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Log in and start xwinnmr. You should also know how to zero fill 2D spectra before using this manual.

Linear prediction is a mathematical procedure where a missing part of a FID can be constructed. Most linear prediction procedures are based on "singular value decomposition" (LPSVD), a digital processing technique which presupposes that the signal is composed of exponentially damped sinusoid curves. The information (frequencies, phases, amplitudes) in the part of the FID (t2, F2 dimension) or INTERFEROGRAM (the "FID" in the t1, F1 dimension) that does exist is used to calculate the part(s) that is missing. The calculated part is then added to the end of the original real existing FID/INTERFEROGRAM and the new combined "FID/ INTERFEROGRAM" are then used in the Fourier transform process. This is a much better way of processing "bad" data than simply zero filling the missing portion. Linear prediction can be used forward in time (the last part of the FID is missing) or backwards in time (the first part of the FID is missing). Linear prediction is extremely useful in 2D NMR as a way of reducing experiment time and/or improving the quality of already existing data sets. In our laboratory the linear prediction is routinely used in for 2D spectra acquired at the DRX 500 instrument for the following types of 2D spectra: HMQC, HMBC, COSY, TOCSY, NOESY, ROESY, COLOC and XHCORR. Linear prediction is mostly used in 2D NMR in the t1, F1 dimension. In the t2, F2 dimension it is fairly easy to acquire enough data points without adding to much time to the experiment. In the t1, F1 dimension each addition of an increment adds a large amount of time to the experiment. Why? This is an excellent examination question. The number of points TD (time domain) in the t2 domain is usually 1024 (1k) or 2048 (2k). In the t1 dimension the number of points in TD is usually a small number: 64 or 128 is often used. This means that the digital resolution is bad (peaks are broad/long) in this dimension (^{13}C dimension in the ^1H detected spectra and the ^1H dimension in the ^{13}C detected spectra). Linear prediction in the t1 dimension improves the resolution enormously on the F1 frequency axis. In 2D ^1H - ^{13}C spectra of the type **XHCORR/HETCOR** and **COLOC** spectra the ^1H nuclei are on the F1 frequency axis. In 2D ^1H - ^{13}C (inverse spectra) e.g. **HMQC**, **HMBC** and **HSQC** the ^{13}C nuclei are on the F1 frequency axis. Linear prediction is therefore recommended on different nuclei depending upon what kind of experiment you are processing. Linear prediction of uncomplete data is enabled by setting the **ME_mod** to **LPfr** (forward real) or **LPfc** (forward complex). Use **LPfc** - as long as you use **xfb** to process, the computer changes to **LPfr** by itself if so needed. To summarize: Processing without LP is: baseline correction, window multiplication, Fourier transformation and phase correction. Processing **with LP** consists of: baseline correction, **linear prediction**, window multiplication, Fourier transformation and phase correction. The processing parameter **NCOEF** represents the number of coefficients used for the LP calculation. **NCOEF** should be 2-3 times the number of peaks in the dimension(s) where LP is performed.

1. Use **search** to find a 2D ^1H - ^{13}C data set. (Preferably one with low quality, few increments in the F1/t1 dimension).

2. Type **wrd**↵ This is the command for copying the dataset which is on screen to another disk (home or other place) for permanent storage and at the same time **change the ownership** of the files.

Enter target data set **NAME:** **LINEARPRE2D**↵ (use your own expname)

Enter target data set **EXPNO:** **1**↵ (use the expno seen in the top part of the xwinnmr window).

Enter target data set **PROCNO:** **1**↵ (use the procno seen in the top part of the xwinnmr window).

Enter target disk unit **DU:** **D:**↵

Enter target user name **USER:** **UIO-username**↵ (your own uio user name)

3. Use **search** to find the **LINEARPRE2D** dataset which is now owned by you, then **append** and **apply** expno1 procno 1 to show the dataset in the xwinnmr window and **xfb**↵ to Fourier transform it. You can not work properly with a dataset not owned or not processed by yourself. If the computer you are using does have another plotter attached than the one used under acquisition use **edo** (edit output) to select the new plotter. The data set does regretfully remember the plotter name connected to the computer used to acquire the spectrum.

4. Type successively **abs1**↵ and **abs2**↵ in the xwinnmr command line to improve the baselines.

5. Type **eda**↵ and write down the numeric values for **TD(F2)** and **TD(F1)** (for instance 1024 and 256) Type **edp**↵ to see processing parameters. Look for the parameter **SI** (size) in both dimensions. If SI in the F2 is in this case for instance 256 and SI in F1 is 128 - no zero filling or other tricks is performed on this data set. (When $\text{SI}=\text{TD}/2$ no zero filling has taken place.) The parameter sets used to acquire the data set might be set up with substantial zero filling as default.

6. Use **edc** to increase the **procno** (processing numbers) to **2**. Change **SI**, Select SI(F2) to 2048 and SI(F1) to 256 and. **xfb**↵ the data set. Observe any changes. You have now zero filled once in the F1 dimension.

7. Use **edc** to increase the **procno** (processing numbers) to **3**. Click on **ME_mod** in the EDP window for F1. A list of options comes up, LPfr (forward real), LPfc (forward complex), LPbr (backwards real), LPbc (backwards complex). Since we are adding the missing end of the FID LPfr and LPfc can be used. Select **LPfc** to use both the imaginary (**Im**) and real part (**Re**) of the FID in the calculations.

8. Find **NCOEF** (number of coefficients) for F1 in the edp window. The number to be put in for **NCOEF** must be larger than the number of resonances in the spectrum. Select 32. Select **LPBIN**

256. This means that linear prediction is performed from data point 128 to data point 256 in both **Re** and **Im** parts of the dataset. **xfb** ↵. Observe any changes.

9. Use **edc** to increase the **procno** (processing numbers) to **4**. Change **SI (F1)** to **1024**. **NCOEF** to **100** and **LPBIN** to **1024**. **xfb** ↵ the data. Observe any changes.

10. A combination of linear prediction and zero filling is possible if **LPBIN** is set to a lower number than **SI**. **LPBIN** (in this case) at 512 means that 128 original data points are used for regular FT, then from 129 to 512 a linear prediction is performed and from is linearly predicted and from datapoint 513 to zero filling is done. (All this is done on both **Re** and **Im** parts).

Plot the same area for all processings to clearly observe the changes. If the 1D ¹H spectrum does not appear on the F2 axis use **edg** and sub menus in **edg** to define it correctly. If the computer tells you that an unknown plotter is attached use **edo** to set correct plotter and printer. (Why are we predicting in the F1 dimension instead of the F2 dimension ?) You can of course play around with linear prediction is both dimensions.