# Linear prediction with Vnmrj and Chempack

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Linear prediction (LP) is a mathematical procedure where the future behavior of a periodic time function is estimated as a linear function of its previous behavior. It works by extrapolating the behavior of a "good" portion of the fid to calculate the intensities of bad data points. It has been in use in NMR spectroscopy for several years[1] to correct some anomalies that may appear in the free induction decay signals (FID) collected in an NMR experiment. If not corrected, these anomalies will result in distortions of the spectrum after the FID is Fourier transformed. The most common of these are: a) corruption of the first few data points of the FID due to instrumental imperfections and b) truncation of the FID due to a too short acquisition time. The former results in severe distortions of the spectrum's baseline, while the latter produces symmetrical ringing patterns (sinc wiggles) around the base of all resonances.
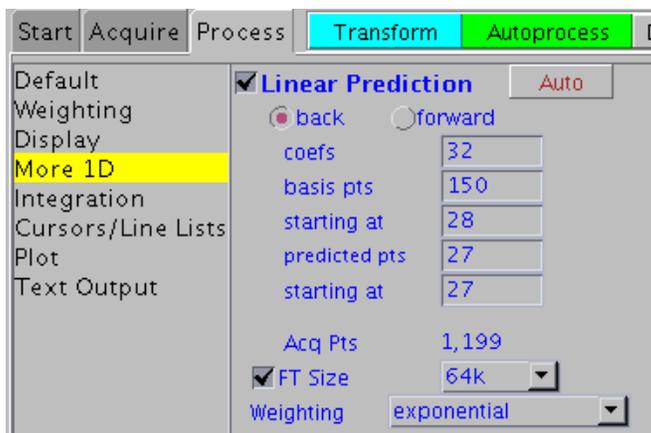
Backward linear prediction

When acquiring a spectrum with a very large spectral width, as is necessary with nuclei like ^{19}F, ^{195}Pt or ^{199}Hg, it is common to find severe distortions of the baseline. These are due to acoustic ringing and/or pulse breakthrough (see the separate heading later in this write up). As a consequence, the first few data points of the FID have anomalous intensities. The following figure shows an example ^{199}Hg FID of a metalloprotein (89 MHz, sw=120 kHz, at=20 ms) where it is clearly observed that the region before 0.00015 s contains abnormally large data points. The actual FID can be seen between 0.00015 and 0.0013 seconds approximately; after that point, it is mostly noise.
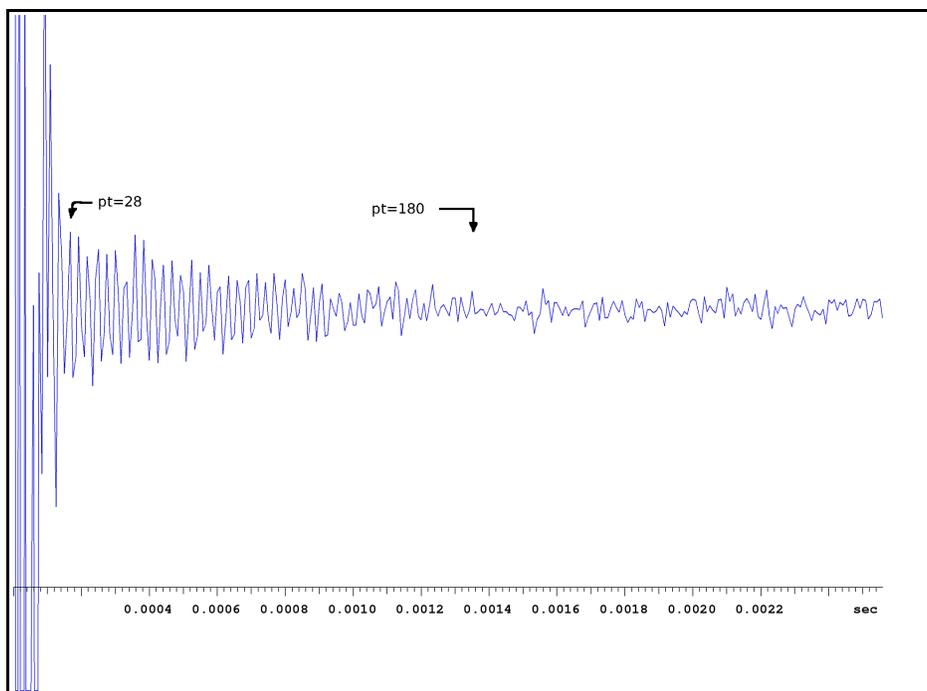
Backward linear prediction can be used to calculate and substitute the corrupted data points. First we need to know how many points are bad. Display the FID with df, expand the region at the beginning of the FID and position the cursor where you think the bad points end and type UMpoint. This macro displays, in the

command line, the number of the data point at the cursor's position. Or type `dotflag='y'` and count the number of points from time zero to the cursor position (make sure the FID is displayed from time zero). In our example this occurs around point 28. Following the same procedure we find that the FID signal decays to noise around point 180. In Vnmrj open the Process, More 1D panel as shown in the next figure. Select "Linear Prediction" and the "back" (backward) options.   Enter the parameters as follows:

- **coefs** is the number of coefficients used in the calculation. Use the default value.

- **basis pts** is the number of good points whose behavior will be extrapolated. In our example, the FID ends around point 180. After this there is mostly noise (see the previous figure). And of these 180 roughly the first 30 are bad, so we will use 150 in the calculation. The exact number is not very important.

- **starting at** indicates the position where the basis points start, 28 in our example.

- **predicted pts** is the number of points to calculate, 27 in our example. It should be one point less than the previous "starting at".

- **starting at** indicates where the bad points start. Since this is a backward prediction we start at point 27 and end in point 1. In a forward prediction, we start at the end of the FID and end some point to the right of the FID. In a backward prediction this value should be the same as the number of predicted points.


After entering the parameters, transform the FID as usual with `wft`, or click the Transform button. The resulting spectrum in our example is shown below. The upper trace shows the spectrum without linear prediction; the baseline is heavily distorted and the peak is very difficult to recognize. The lower trace shows the spectrum with linear prediction and a line broadening equal to the linewidth at half height (`lb=300`). A baseline correction like this is difficult if not impossible to obtain by other means.

In general, you will have to play a bit with the parameters. Use the minimum number of predicted points that gives you a flat baseline (of course you have to readjust the related parameters "starting at"). Then change the number of basis points; make it small (the minimum is two times the number of predicted points), and then make it larger and see if it improves signal to noise or baseline flatness. Finally change the number of coefficients. Try for example 16, 24, 30, 40 but beware of artifacts that may arise from the calculation.

The optimum parameters for LP are very dependent on the acquisition parameters and other experimental conditions and it is impossible to offer a good set of "typical" parameters. You have to examine the FID as explained before and locate the bad points. Figure out approximately how many points are bad, and how many

good points can be used before they disappear in the noise.
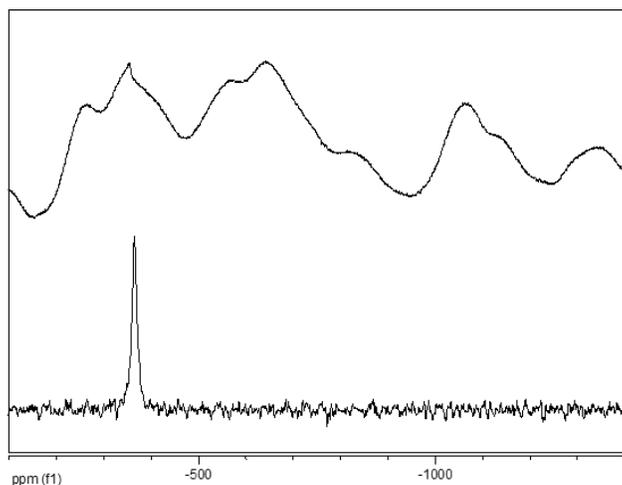
Forward linear prediction

Another common artifact occurs when the FID does not decay completely before data acquisition stops, i.e. when the acquisition time was too short. The tail of the FID is truncated and the resulting spectrum after Fourier transformation shows ringing patterns or wiggles at the base of the peaks. These are more easily seen on those peaks with the longest relaxation times, like methyl groups. Forward linear prediction can be used to remove these artifacts by extrapolating to zero the points just before the end of the FID. This is used mainly in 2D spectroscopy, where the acquisition times are necessarily very short. For example, the figure below shows the COSY spectrum of atropine in CDCl$_3$. The spectrum on the left shows the spectrum without linear prediction; the one on the right shows the same spectrum with linear prediction. Severe distortions along the F1 dimension around the base of the peaks can be seen when LP is not used.
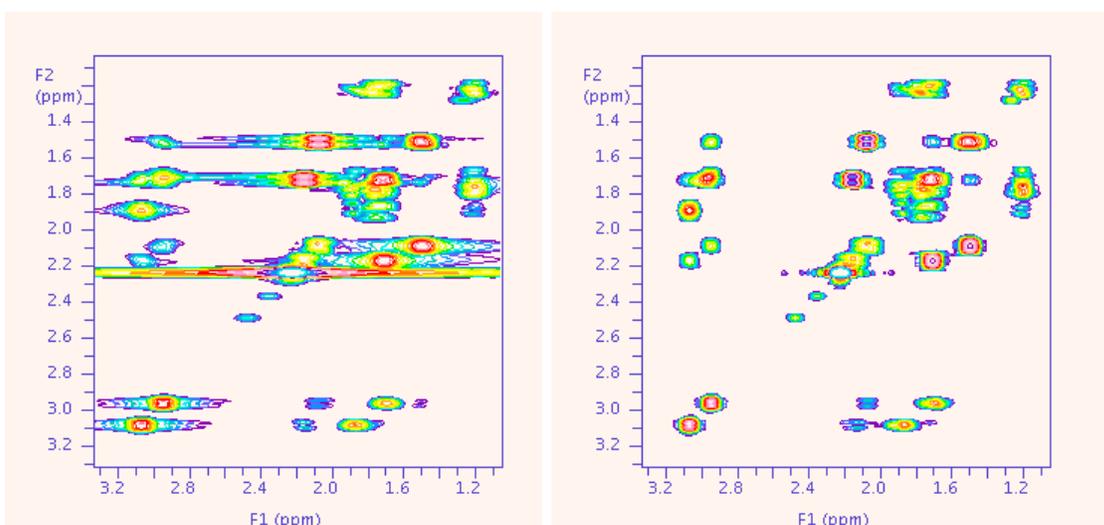
Vnmrj always tries to add appropriate forward linear prediction parameters during setup of a 2D experiment, so you should not worry about them. But if you need or want to modify them, they are found in the Process, More 2D parameter panel.

Using linear prediction in the middle of the FID

Very infrequently, data points in the middle of an FID can be corrupted due to hardware malfunctions. It it still possible to correct these points using linear prediction. To find out the bad points, display the FID with `df`, expand the region around the bad points and read the cursor position in seconds with `crf`. The bad point(s) will be located at `crf*(np/2)/at`. For this example we will assume that the FID contains two bad points at 12416 and 12420. These can be restored either with forward prediction using these parameters: coefs = 32, basis pts = 256, starting at = 12415, predicted pts = 5, starting at = 12416; or with backward prediction with these parameters: coefs = 32, basis pts = 256, starting at = 12421, predicted pts = 5, starting at = 12420.

Avoiding detection of acoustic ringing and pulse breakthrough.

When a pulse is applied to an NMR probe in a strong magnetic field, the oscillating rf current in the circuit induces mechanical (acoustic) oscillations in metal parts of the probe. These mechanical oscillations in turn generate rf signals that are detected by the coil. This so called "acoustic ringing" can be seen at the beginning of the FID as a strong "noise" or as data points with distorted intensity, and usually decays within several tens to hundreds of microseconds after the pulse. It is more of a problem at high fields, high pulse powers and lengths, and low frequencies and a particular problem when wide spectral widths are employed. The acoustic ringing may impede the observation of very broad lines and cause baseline and phasing problems when observing multiple-peak spectra with large spectra widths[2,3].

Although linear prediction can usually correct the problems caused by acoustic ringing <u>after</u> data collection, it cannot prevent other problems that may happen <u>during</u> acquisition. For example, with low sensitivity nuclei, the corrupted points may be so strong that after just a few hundreds or thousands of scans, the acquisition may stop with a "maximum transients accumulated" error. Thus, it is best to avoid collecting the bad points altogether, by delaying the acquisition of the FID.

On older Varian consoles, three delays are executed between the end of the pulse and the beginning of data collection: `rof2`, `alfa` and a machine dependent delay. If you want to increase the delay by 100 μs, all you need to do is increase `rof2` or `alfa`. But this introduces a new problem: phasing a spectrum with more than one peak becomes very difficult. The solution is to right-shift the FID to introduce a number of empty, or zero value data points at the beginning of the FID equal to the number of points lost during the delay, and to use linear prediction to restore their intensity. This is better accomplished with the `delacq` macro. For example, in our ^{199}Hg example shown above, we can see that the first 150 μs of the FID are corrupted. Typing `delacq(150)` sets up a pre-acquisition delay of 150 μs, right-shifts the FID and sets up appropriate linear prediction parameters.

On last generation Varian consoles, the digital receiver allows a more elegant solution. The parameters `rof2` and `alfa` are still present, but they are now added to form a parameter called `ddrtc` (direct digital receiver time constant), which is the overall pre-acquisition delay. The exact value of `ddrtc` is chosen (by the `setddrtc` macro) in such a way that the resulting spectrum requires very little phase correction and no right-shift of the FID. To increase the delay, go to the **Acquire, Flags** parameter panel and notice the values of `rof2`, `alfa` and `ddrtc`. Increase `rof2` to the desired value and click the **ddrtc** button or type `setddrtc` on the command line.

To set up the pre-acquisition delay, a simplified macro was developed in our facility that is independent of the console architecture. Simply type, for example, `UMdelayacq(150)` to set up a delay of 150 μs.

In general, for low frequency, low sensitivity nuclei like ^{199}Hg that require large spectral widths, a delay of 80 to

150 µs is usually adequate. Notice that by delaying the acquisition more than 150 µs, the detection of very wide peaks (width at half height > 2000 Hz) will be difficult.

References

1. J. J. Led and H. Gesmar. *Application of the Linear Prediction Method to NMR Spectroscopy*. *Chem. Rev*. **91**, 1413-1426 (1991)

2. M. L. Buess and G. L. Petersen. *Acoustic ringing effects in pulsed nuclear magnetic resonance probes*. *Rev. Sci. Instrum*. 49, 1151-1156 (1978)

3. Glenn Facey's blog: http://u-of-o-nmr-facility.blogspot.com/2008/05/acoustic-ringing.html