Novel Data Evaluation Algorithms:
The J-Correlator™ (JC)

Carlos Cobas [1], Nikolay Larin[1], Pablo Monje[1], Santiago Fraga[1], Stanislav Sýkora [2]

[1] Mestrelab Research, Xosé Pasín 6, Santiago de Compostela, 15706 Spain; carlos@mestrec.com
[2] Extra Byte, Via Raffaello Sanzio 22/C, Castano Primo (Mi), Italy I-20022; sykora@ebyte.it

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Introduction

1D NMR spectra, especially proton spectra of organic compounds, usually consist of a number of groups of spectral lines (multiplets). Each group corresponds to one or more chemically distinct nuclides and its central position defines, at least approximately, the chemical shift(s) of the involved nuclei. Though the chemical shifts are relatively well known, both because of a large amount of accumulated empirical data and through semi-empirical prediction techniques, the number of positions of the multiplets is generally not sufficient to define the molecular structure of the compound corresponding to the NMR spectrum (provided it is a simple compound and not a mixture). Additional information required for such a molecular structure verification and/or elucidation and available in 1D NMR spectra comes from the scalar couplings (the J's) between nuclides which determine the fine structure of the individual multiplets.

When it comes to couplings, the absolute position of spectral lines becomes irrelevant. What matters are distances between their centers which we will generically called splittings. However, a splitting may be purely spurious, since *any* two spectral lines define a splitting, regardless of whether they are in any way related to a scalar coupling. Fortunately, it is possible to show that, regardless of the strengths of the couplings present in the system, the splittings which correspond to a scalar coupling come in pairs present in both coupled multiplets [a Theorem to be discussed elsewhere]. In strongly coupled systems, the values of such paired splittings need not exactly equal any of those of the J's the way it happens in weakly coupled systems but, nevertheless, they *must* be paired.

The J-Correlator is essentially a *visual tool* which helps the NMR spectroscopist to pick out the patterns of scalar couplings between all the multiplets in the spectrum. When many lines are present (example: 100), the total number of splittings (10000) is so large that an analysis of their values by a human would be an impossible chore. The J-Correlator simplifies it enormously and reduces it to a manageable task.

The J-CORRELATOR™
A New Method for Assessing Spin Connectivities in 1D NMR Spectra

JC operates on phased, real part of a **1D NMR** spectrum and generates a **2D plot** of all splittings, each corresponding to a "cross peak". For each peak, the additional (vertical) dimension of encodes the splitting value, while the horizontal position corresponds to the center of the corresponding pair of lines. It is evident that an isolated single line would not appear anywhere in the 2D plot, while any pair of lines gives rise to a cross-peak. Distinct cross peaks which share the same splitting value and thus lie on the same horizontal line indicate a possible J-coupling between the multiplets to which they belong. Vice versa, a cross peak which has no "partner" with the same splitting value is spurious and has nothing to do with any J-coupling.
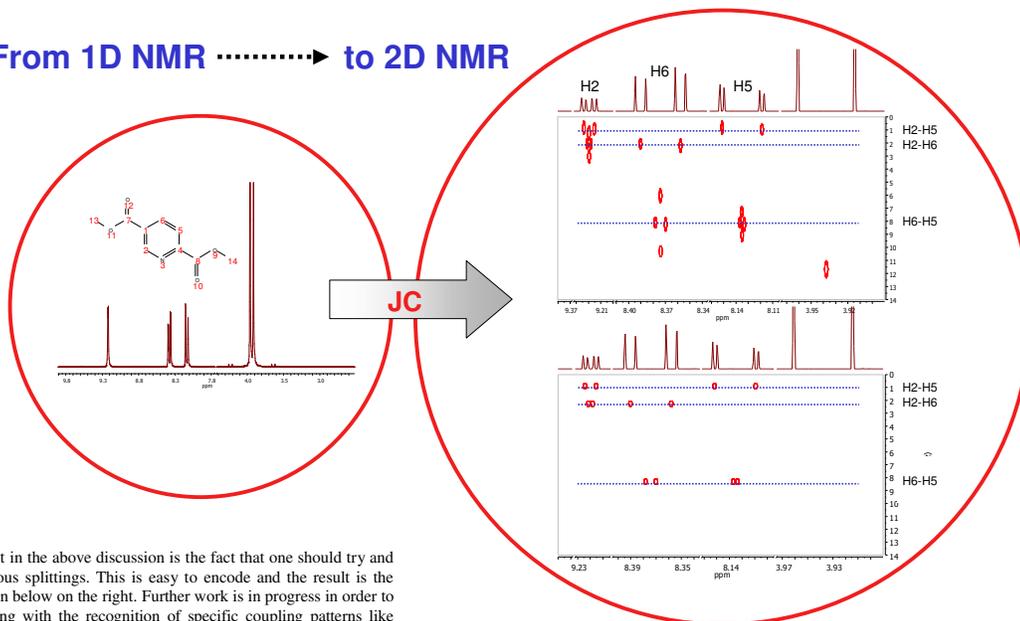
JC editing: Implicit in the above discussion is the fact that one should try and get rid of all spurious splittings. This is easy to encode and the result is the edited JC plot shown below on the right. Further work is in progress in order to combine such editing with the recognition of specific coupling patterns like triplets, quadruplets, doublet-triplet pairs, etc.

Analog and Digital JC

Routine HR NMR acquired at high-field spectrometers are often plagued by relatively low digital resolution and, consequently, limited operator attention to the magnetic field homogeneity (digital resolutions of the order of 0.5 Hz per step are sometimes considered satisfactory). Under such conditions, the "vertical" resolution of JC may be severely limited (long vertical strips). It is therefore recommended to always combine JC with with the **Resolution Booster**™ (RB) described in a separate poster.

This has the additional advantage of correcting much of the coalescence error in line-location estimates in overlapped multiplets (see the RB poster) and thus reducing the probability of false positives and false negatives (intended in terms of the presence or absence of scalar J-couplings).

Another improvement can be obtained by combining JC with an efficient peak-picking algorithm. This permits to synthesize a JC map directly from the peaks list, increasing considerably the resolution and precision of the method. We call this approach, presently under development, the **Digital J-Correlator**.

Conclusion

There is intensive work in progress on this very promising data processing method which addresses the **general problem of assigning a spin system to a 1D NMR spectrum**. We are developing an automatic wizard which will address this task but it appears reasonable to assume that completely automatic algorithms will often end in an impasse and require additional a-priori information from the User. In such case, the **J-Correlator** will represent a convenient visual bridge between the wizard and the NMR expert.