Simulation of Second Order Splitting

Simulation of Splitting Patterns

The TOPSPIN package uses the DAISY program to calculate splitting patterns. If you have a spectrum on the screen, you can input peak positions and coupling constants for the members of a spin-set. Once you have come close, the software will iterate (hopefully) towards the exact pattern, allowing calculation of the exact shift and coupling values.

The software displays the calculated spectrum above the experimental one, allowing for easy comparison. If you wish to calculate a pattern for which you don't have an FID, you can copy an existing spectrum into a dummy-file, integrate a portion of it (to keep DAISY content), then set its vertical scale low enough to not be distracting. Obviously, you can't do iteration in this case.

Using the DAISY Simulation Software

1. Display a spectrum on the screen.

2. Integrate each region to be simulated. When you iterate in step 7, DAISY will try to match the integrated regions.

3. Enter "daisy" on the command line.

4. In the DAISY window, click the spin-cone icon, ⇗, to edit the parameter tables.

    a. Under the <u>Frequencies</u> tab, fill in the chemical shifts of the nuclei and how many are in each group (eg, A vs A_2).
        Group indices are optional. Magnetically inequivalent nuclei may be designated by entering two lines (one for A and one for A') but giving them the same group index. Any changes made to the first line will be propagated to the second when you click the "Apply" button.

    b. Under the <u>Scalars</u> tab, fill in the coupling constant matrix. Equivalent coupling constants (eg, if $J_{AB} = J_{AB}$) may be designated by clicking in the appropriate matrix cell and giving the coupling a group number, similar to the chemical shift group-numbers.
        Ignore the <u>Lineshape</u> button.
        Click "OK" to exit the parameter editor.

5. Perform the simulation using the ⓢⓘⓜ button. The simulation should appear above your spectrum.

    a. To <u>scale</u> the spectra, bring the calculated (red) spectrum to some reasonable height with the mouse-wheel. Click the box in the right corner of the (blue) experimental spectrum, and use the scaling buttons (eg, $*2_S$) to make the experimental one the same size as the calculated. The buttons control the selected spectrum, whereas the mouse-wheel controls both.

    b. The <u>display mode</u> may be toggled with the ⊞↕ button (stacked *vs* superimposed).

6. Tweak the parameters for the spectrum, re ⓢⓘⓜ ulate, and repeat until the simulation approaches the experimental spectrum.

If <u>iteration</u> is desired, be sure to save the current parameters under some dummyfile name (⊟-button). If the iteration goes haywire (very likely), there is no "undo" to recover the parameters. Saving intermediate results in a check-file is especially important before you iterate on several parameters at once. Simulations run best when the input values are very close to the final ones — less chance to go astray. Try doing single couplings or peaks before combining them.

7. Re-enter the parameter editor (spin-cone icon) and enable iteration for the peak positions. Exit the parameter editor. Run the iteration with the ⓘⓣ, button. If the iteration mungs up your values, recall the saved ones.

8. In the parameter editor, disable the peak position iteration. Pick the coupling constant you have the most confidence in and select its cell in the coupling matrix under the <u>scalars</u> tab. To enable iteration of this constant, click "OK", and iterate. Progressively add more *J*s to the iteration, saving check-files along the way.

   If you run into a dead end, try changing the sign of a coupling constant.

9. If the simulation gives several closely-spaced lines where the observed spectrum only has one, try increasing the linewidth setting (LB value) in the <u>lineshapes</u> tab of the simulator.