BCMB/CHEM 8190 LAB EXERCISE: PRODUCT OPERATORS BY MAPLE
February 21, 2014

The product operators that we have introduced, and transformations that they undergo in the presence of scalar coupling, chemical shift offsets and rf pulses, represent an algebra that can be coded and applied in the environment of a symbolic problem solver on various computer platforms. Packages such as Mathematica and Maple are capable of symbolic manipulation as well as evaluation of various functions in interactive algebra, graphics and discrete math. In 1993 Peter Guntert *et al* produced POMA (Product Operators in Mathematica) (JMR A 101, 103-105 (1993)) and Kanters *et al* produced a similar treatment run under Maple (JMR A 101, 23-29 (1993)). These groups wrote notebooks or procedure files that define various functions such as pulse(target, spins, angle) that transform variables (product operators) according to the transformation rules we have introduced. We will learn to use one of these packages (Kanters' Maple package, pof (product operator functions)) to analyze various 1D and 2D NMR experiments.

1) Getting Started:

You can log onto one of the computers in the computer lab which has Maple installed for these exercises. For Red Hat Linux users: simply type "xmaple" in the terminal window. The Maple 13 graphical interface will start and open a blank worksheet.

We introduced some of the Maple utilities in the last laboratory, but if you need a "refresher" you can find useful tutorials under the 'help' button on the maple menu bar. One major addition for those needing to set up Maple on there own computes is that you may need to load the 'share' library that contains the 'pof' procedures used in this exercise. A version of this library was once available from the application center of the Maple web site (http://www.maplesoft.com/applications/) but no longer seems to be available. We have archived a version of this share library with the product operator formalism (pof) on our web site. You don't need to retrieve this if you are using a teaching lab computer, but if you wish to install pof on your personal computer, the direct link to Maple share tar.gz file is: http://tesla.ccrc.uga.edu/ShortTermStorage/maple.share.tar.gz. The file maple.share.tar.gz should be untar'd (tar zxf maple.share.tar.gz) and the resulting "share" directory placed in the Maple home directory. There will be an error message when you try to use it but that can be ignored (pof does work).

2) Using Product operator Formalism:

Kanters has defined procedures for rf pulse effects and evolution of density matrices represented as linear combinations of product operators, and put these in a library called 'pof'. Worksheets giving examples of application are available at http://www.maplesoft.com/applications . Search for 'kanters' and several example worksheets should appear. These can be downloaded by simply clicking on the title of the worksheet and then "Download Maple Document" on the subsequent page. We have also provided copies of similar sheets on our class website and they should already be on the computer you'll use to run Maple. For the Linux users, the files will be in your home directory. The two worksheets we'll use today are named: **chemical_shift_refocusing.mws** and **COSY.mws**.

Worksheet 1: chemical_shift_refocusing.mws

Open the worksheet in Maple. This worksheet illustrates the effect of a 90-tau-180-tau sequence, the same sequence that removes the effects of chemical shift evolution and can generate a t1 point for a 2D J resolved spectrum. It is illustrated for both an isolated spin and a coupled pair of spins. The following explains some of the operations in the worksheet. Remember that you need to put your cursor behind each command and hit return to execute statements.

restart - clears variables in Maple and starts with a clean sheet.

with(share): with(pof); - tells Maple to look in the share library and that we are going to use procedure definitions provided by Kanters in the pof library (ignore the error message you may get at this point – the library will work for our purposes). The ':' suppressed output from the first command, the ';' let the functions be listed.

step1:=spinsystem([X]); defines this to be a one spin system, defines the basis set for the computation and assigns the variable step1 to the equilibrium density matrix. Note that this is given in terms of the product operator IzX.

step2:=ypulse(step1, {X}, Pi/2); applies rotation operators for a 90y pulse to the X spin represented by the density matrix step1. Note that the result is given in terms of the product operator IxX.

The following steps show evolution under chemical shift for period tau, evolution under a 180x pulse, and evolution for tau. Note that each operates on the density matrix from the previous operation. At the end the density matrix is simply IxX. Note that there has been no net evolution due to chemical shift although there was evolution at intermediate steps.

Next, the sequence is restarted for a two spin system, assuming they are coupled with coupling constant J. Note that the final result, step5, now contains evolution under the coupling constant J, but not chemical shift offsets from either spin. This is the basis of J resolved spectroscopy when tau is incremented as the indirect dimension in a 2D experiment.

Worksheet 2: COSY.mws

Now open and examine COSY.mws. This describes the basic 90-t1-90-t2 COSY experiment. Operations are similar to those described above until step5 where the observe function generates evolution in a second time domain, t2. In step6 the evalc function returns the result of Fourier Transformation (in algebraic form) in both dimensions. Note that there are 32 terms offset by chemical shifts of A and X and by +/- J/2 in both dimensions. They describe line shapes (absorption or dispersion) in each dimension (v1 or v2). These are the auto and cross peaks expected for the AX spin system. The table definitions set values for T2 relaxation times, chemical shifts and coupling constants to be used in subsequent plot functions. A couple of different plotting functions are illustrated. The variables in the plot functions set boundaries of the regions to be plotted and the number of points to be used. In the first instance you are only plotting one crosspeak (note the range of the v1 and v2 variables). You can interactively rotate the spectrum to see it more clearly. The second example plots the entire spectrum. These particular plotting functions are part of the share library so no help descriptions are available. There are also extensive plotting routines available in Maple. To find some of the plotting routines open the Help utility from the icon on the right side of the second menu bar and type "plot" in the search window that opens.