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Spin-Spin Simulation with wxNUTS

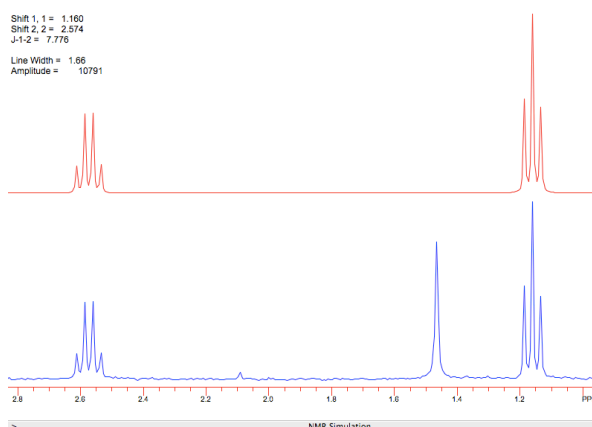
The spin-spin simulation routines used in wxNUTS are based on the time proven routines in the original NUTS program. There have been several advancements in the wxNUTS routines, mostly in areas to aid in Simplex optimization of chemical shifts and coupling constants:

- Identical individual spins can be grouped into “Spin Groups” with a multiplicity number. For example, a methyl group’s three spins are grouped into one Spin Group with a multiplicity number of three.
- The chemical shift of any Spin Group can be locked so it will not be iterated in a Simplex optimization process.
- The chemical shift of any Spin Group can be locked to the chemical shift of another Spin Group so that they will be iterated together in the Simplex optimization process.
- Coupling constants are entered as the J value in Hertz between Spin Groups.
- Any coupling constant can be locked so it will not be iterated in a Simplex optimization process.
- Any coupling constant can be locked to another coupling constant so that they will be iterated together in the Simplex optimization process.

These changes greatly improve the usefulness of the Simplex optimization routine.

Ethyl Group

A simple example of the spin-spin simulation used in wxNUTS is the ethyl group of Ethyl Benzene. In traditional NMR nomenclature, this is an A_3X_2 spin system. The 3 A spins comprise one Spin Group, and the 2 X spins comprise a second Spin Group.



The actual spectrum is shown in blue, and the simulation in red.

A section of the saved simulation file shown on the next page can be used to illustrate some of the changes made to wxNUTS from the original NUTS version. In NUTS, we would have entered 5 spins - three for the CH_3 and two for the CH_2 . In wxNUTS, we enter two Spin Groups - the CH_3 with a quantity of 3 and the CH_2 with a quantity of two.

Ethyl Group Simulation File

```
wxNUTSsimulation
TotalSpins = 5
SpinGroups = 2
Nuclei = HH
Scale = 10917.988281
Spectrometer Frequency = 300.152374
LineWidth = 1.560436 Hz
Min Ht = 0.000100
```

```
Spin# = 1
SpinLabel = CH3
Quantity = 3
ChemicalShift = 1.161
ShiftLockedTo = 0
; Couplings Locked To 0 = unlocked
EndJs
```

```
Spin# = 2
SpinLabel = CH2
Quantity = 2
ChemicalShift = 2.572
ShiftLockedTo = 0
; Couplings Locked To 0 = unlocked
; From To From To Value
1 2 0 0 7.817 Hz
EndJs
```

In this simulation, we have a total of 5 spins in two Spin Groups for the calculation. Each Spin Group has its chemical shift locked to 0 (zero). This means it is unlocked during any Simplex optimization. If we had locked Spin #1 to Spin #1 (locked to itself), then its chemical shift would not be iterated.

The second Spin Group shows that we have a coupling from Spin Group 1 to Spin Group 2 with a value of 7.817 Hz. The two zeros after the 1 and 2 in this line indicate that this coupling constant is also unlocked during any Simplex optimization. The use of locking chemical shifts and coupling constants is a powerful change in wxNUTS from the original NUTS.

The use of Spin Groups in wxNUTS means that the three spins of the CH₃ and the two spins of the CH₂ will be iterated together during any Simplex optimization. In NUTS, the three spins of the CH₃ would be iterated independently as would the two spins of the CH₂. The process of iterating those spins independ-

ently leads to undesired corruption of the simulation during any Simplex optimization.

ODCB

The spin-spin simulation of *ortho*-dichlorobenzene makes good use of the chemical shift and coupling constant locking to simulate the AA'BB' system. Because of the symmetry, the chemical shifts of A and A' must remain the same. Likewise, the chemical shift of B and B' must remain the same. J(A, B) must always be equal to J(A', B'), and J(A, B') must always be equal to J(A', B).

```
wxNUTSsimulation
TotalSpins = 4
SpinGroups = 4
Nuclei = HHHH
Scale = 100000.000000
Spectrometer Frequency = 399.784607
LineWidth = 0.281250 Hz
Min Ht = 0.000100
```

```
Spin# = 1
SpinLabel = A
Quantity = 1
ChemicalShift = 7.695
ShiftLockedTo = 0
EndJs
```

```
Spin# = 2
SpinLabel = A'
Quantity = 1
ChemicalShift = 7.695
ShiftLockedTo = 1
1 2 0 0 0.340 Hz
EndJs
```

```
Spin# = 3
SpinLabel = B
Quantity = 1
ChemicalShift = 7.485
ShiftLockedTo = 0
1 3 0 0 8.080 Hz
2 3 0 0 1.520 Hz
EndJs
```

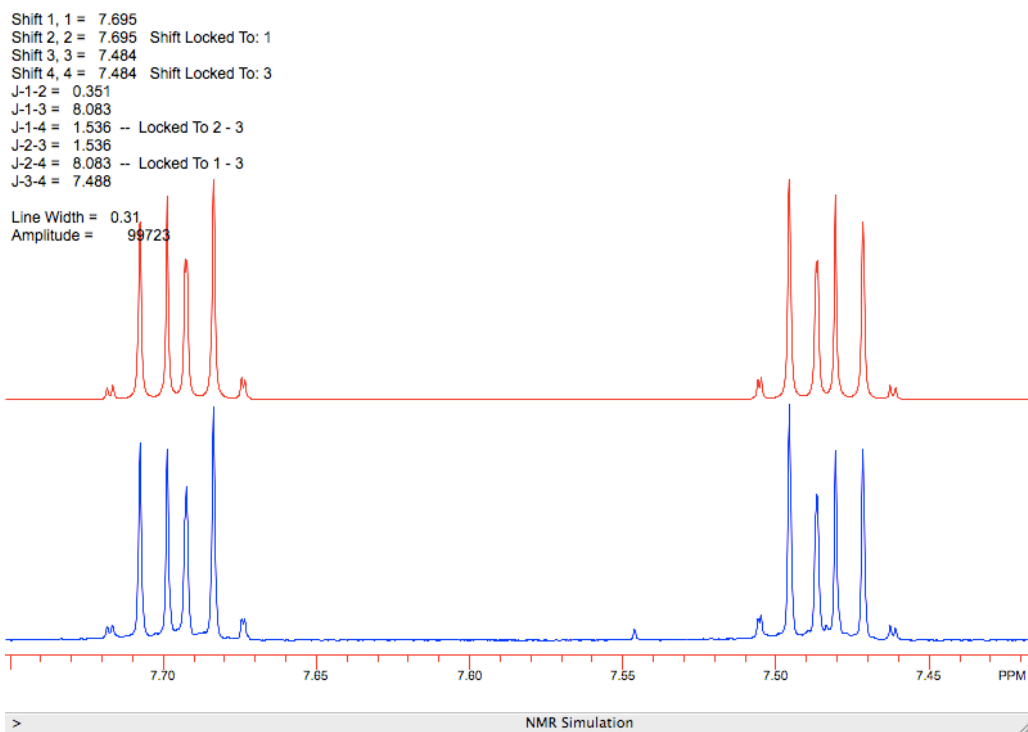
```
Spin# = 4
SpinLabel = B'
Quantity = 1
ChemicalShift = 7.485
ShiftLockedTo = 3
1 4 2 3 1.520 Hz
2 4 1 3 8.080 Hz
3 4 0 0 7.490 Hz
EndJs
```

As can be seen in this simulation file, the chemical shifts of Spin Group #1 (A) and Spin Group #3 (B) are not locked. The chemical shift of Spin Group #2 (A') is locked to Spin Group #1 (A). The chemical shift of Spin Group #4 (B') is locked to Spin Group #3 (B).

Because we want to keep $J(A', B')$ equal to $J(A, B)$, the coupling constant between spins 2 and 4 is locked to the coupling constant between spins 1 and 3. To keep $J(A', B)$ equal to $J(A, B')$, the coupling constant between spins 1 and 4 is locked to the coupling constant between spins 2 and 3.

All other coupling constants are unlocked.

All this locking and unlocking allows the Simplex optimization to maintain the necessary symmetry of the AA'BB' system. This additional capability greatly increases the utility of the Simplex optimization process in the spin-spin simulations.



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