Coupling Schemes Algorithm

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The seven Fe atoms of FeMo-co are arranged in space in such a way that the nearest neighbors of each iron are those listed in Figure 1. When obtaining broken symmetry density functional theory (BS-DFT) wavefunctions for a system such as FeMo-co, a spin coupling scheme is required to make sense of the results from these calculations. A spin coupling scheme is obtained by deciding which pairs of spins (which can be alpha or beta) are added together linearly to give a combined spin, which can then be pairwise coupled to other combined or individual spins in the system until the total spin is obtained.

The Fe atoms in FeMo-co

	1	
2	3	4
6	7	5

Nearest neighbors:

Fe1: [2, 3, 4]
Fe2: [1, 3, 4, 6]
Fe3: [1, 2, 4, 7]
Fe4: [1, 2, 3, 5]
Fe5: [4, 6, 7]
Fe6: [2, 5, 7]
Fe7: [3, 5, 6]

Figure 1: The spatial position of the Fe atoms, along with the nearest neighbors of each Fe.

I claim that every single possible coupling scheme can be associated with two permutations, one of the numbers from 1 to 7 and one of the numbers from 1 to 6. This assignment is not unique, but if we generate all possible coupling schemes and some repeat themselves it will be easy then to decide which ones occur more than once and eliminate them. The first kind of permutation required to define a coupling scheme is a permutation of the numbers 1-7 in which all numbers are ”connected”, meaning that each iron needs to be preceded by and also succeeded by one of its nearest neighbors. For example, 1234567 is such a permutation, but 1765432 is not a ”connected” permutation because 1 and 7 are not nearest neighbors. The second permutation needed to generate a coupling scheme can be any possible permutation of the numbers from 1 to 6.

To see how two permutations, one ”connected” and one random, generate a coupling scheme let’s look at a specific example. Let’s take a very messy ”connected” permutation, [4132675] and a random permutation [165243]. The first number in the random permutation, 1, tells us that in the last step of the coupling, spin S_4 couples to S_{132675}. The second number in the permutation, 6, tells us that in the last but one coupling step, S_{13267} will couple to S_5. So the random permutation tells us how to trace the coupling scheme all the way back to individual uncoupled spins. The coupling scheme resulting from the two permutations [4132675] and [165243] is represented graphically in Figure 2.

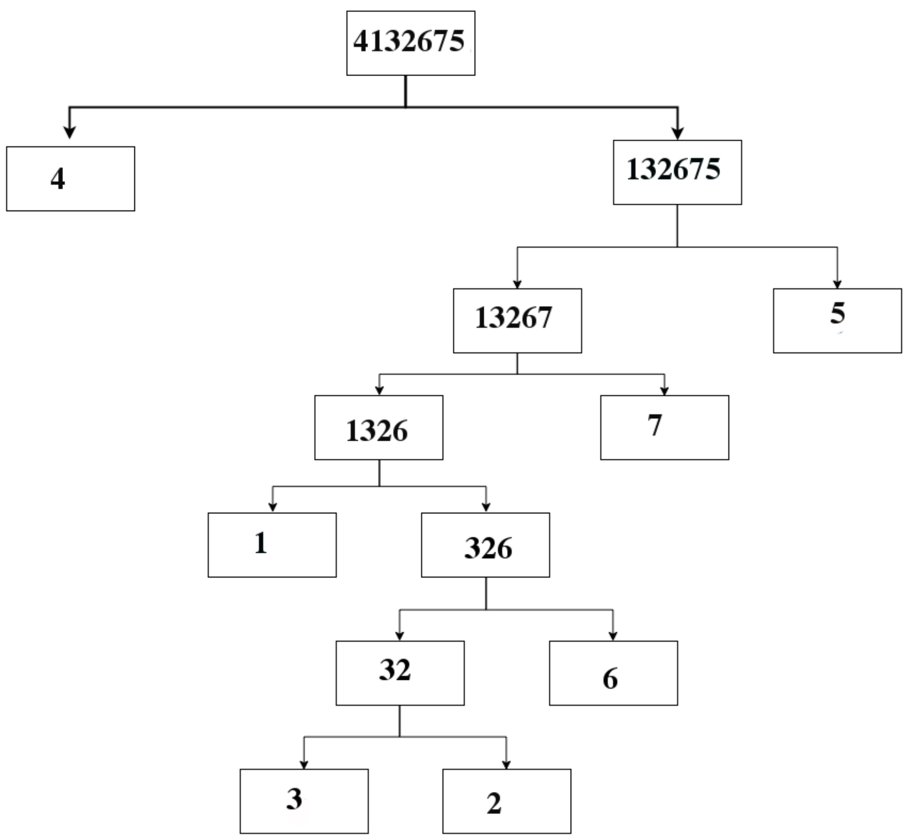

Figure 2: The coupling scheme corresponding to the permutations [4132675] and [165243]

Clearly any two such permutations give a single, although not unique, coupling scheme. It is now only left to prove that every single coupling scheme can be represented by two such permutations. This is however, trivial, since any coupling scheme is eventually written as a tree of the type in Figure 2. Clearly the ”parent” of the tree is a ”connected” permutation, and the way that the ”children” are obtained is by choosing a position at which to cut the parent at each step. Since there are six such positions, the order in which the cutting happens is represented by a permutation of the numbers from 1 to 6.

The algorithm to get all possible coupling schemes is thus very simple:

Step 1:

Generate all ”connected” permutations. Easiest way would be to generate all possible permutations of the numbers from 1 to 7 and then check which are not ”connected” and eliminate them.

Steps 2 and 3:

Generate all possible permutations of the numbers form 1 to 6. Then, generate all combinations of the permutations in Steps 1 and 2. These combinations will give all possible coupling schemes but with a lot of repetitions.

Step 4:

Write every single coupling scheme in step 3 as 7 lists showing the coupling history of each atom. For example the coupling scheme in Figure 2 would be written as:

Fe1: [1, 1236, 12367, 123567, 1234567]
Fe2: [2, 23, 236, 1236, 12367, 123567, 1234567]
Fe3: [3, 23, 236, 1236, 12367, 123567, 1234567]
Fe4: [4, 1234567]
Fe5: [5, 123567, 1234567]
Fe6: [6, 236, 1236, 12367, 123567, 1234567]
Fe7: [7, 12367, 12567, 1234567]

Note that I ordered the numbers in each group, so that such a representation of a coupling scheme is indeed unique. Using this unique representation we can eliminate all repeating coupling schemes.

Note: For example one of the coupling schemes we have used so far, [[[[2 3] [6 7]] 5] [1 4]] can be represented by the ”connected” permutation [2376541] and any one of the following random permutations: [564213] , [564231], [546213] , [546231], [542613], [542631], [542361], [542163], [542136], [542316]. This is because for example in the case of the pair 1 and 4 it doesn’t matter when we separate then (which corresponds to the number 6 in the random permutation) as long as it is after we have separated 41 from 23765, which corresponds to the number 5 in the random permutation. Same applies for separating 2 and 3 and 6 and 7.