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On the number of spin functions in the first order interaction space

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A proof is given that in a configuration interaction method the first-order interaction space contains at most only twice as many spin functions as the zeroth-order space. This allows for a dramatic reduction of the size of CI expansion. For most of the high-spin systems only two spin functions for each configuration are needed.

Key words: Configuration interaction method—configuration selection—high-spin systems

The concept of the Hartree-Fock interacting space, used by Bunge [1], Bender and Schaefer [2], and extended to a more general concept of the first-order interaction space (FOIS) by Liu and McLean [3], plays an important role in the selection of functions in configuration interaction (CI) expansions. The length of this expansion for most open-shell systems excludes the possibility of making high-quality calculations without a clever method of selection of only the most important configuration functions (CFs). The concept of the FOIS is well justified by an analysis of the contributions of CFs based on the Reyleigh-Schrödinger perturbation theory [3] and is frequently used as a selection scheme.

In the usual classification of the CI configuration functions first a number of reference CFs is selected, spanning the zeroth-order N-particle space and covering all dominant terms in the final expansion. The space of CFs interacting through the Hamiltonian with the zeroth-order space is called the first-order interaction space. Obviously it includes singly and doubly excted CFs relatively to reference

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configuration functions, but it does not include all components of the CFs corresponding to the excited configurations. Here a configuration means a subset of N orbitals (some of them appearing twice) of the total n-dimensional orbital set, while CF refers to a function constructed from these orbitals, a function properly antisymmetrized, being an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$ operators. Considering the role of spin functions in FOIS we shall use the symmetric group approach (SGA) [4–9] to calculate matrix elements, because in this approach the spin and the orbital parts of CFs are well separated from the beginning. The same results may be derived within the unitary group approach theory, as described by Paldus [10] and Shavitt [11], but UGA graphs are more complicated than the spin diagrams used here. The readers more familiar with UGA techniques are encouraged to re-derive the result given below in an alternative way.

In SGA one separates the spin and the orbital part of a spin-adapted CF writing it in the form:

$$|\lambda, SM, k\rangle = \hat{A}(|\lambda\rangle|SM, k\rangle), \tag{1}$$

where $\hat{A}$ is the normalized symmetrizer, $|\lambda\rangle$ is a product of orbitals appearing in configuration λ, $|SM, k\rangle$ are the spin functions for the desired value of total spin S and spin projection M; finally $k = 1, 2, \ldots f(s, S)$ distinguishes independent spin functions. The number $f(s, S)$ of these functions for a given number of singly occupied orbitals s is given by the formula:

$$f(s, S) = \frac{(2S+1)s!}{((s/2)+S+1)!((s/2)-S)!}. \tag{2}$$

Thus there are $f(s, S)$ spin functions associated with each orbital configuration. To appreciate how rapidly this number grows with the number of open shells, one should look at the branching diagram [12], Fig. 1. For high-spin systems,

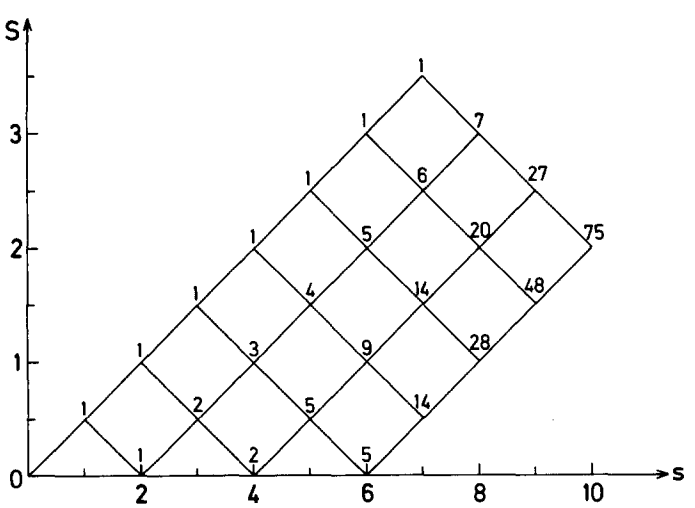

Fig. 1. Branching Diagram for 10 spins coupled to the total spin $S = 2$

even if $s = 2S$ in the reference configuration functions, taking CFs corresponding to the doubly excited configurations results in 14 spin functions for quartets, 20 for quintets, etc. No wonder that CI calculations on such systems, difficult to perform because of the complexity of high spin systems in the first place, are hard to find in the literature. Restricting ourselves to the FOIS we find in the above cases that only 2 spin functions are actually needed. We hope that this fact will stimulate CI calculations on the high-spin systems that are at present treated by less accurate methods (cf. [13–15]).

We shall now prove the following theorem:

If the number of spin functions associated with the reference configurations is $f(s, S)$ then, for the configurations doubly excited from these references, out of $f(s+4, S)$ spin functions no more than $2f(s, S)$ belong to the first-order interaction space.

Proof: First, we will identify 5 types of CF that may increase the number of open shells in a reference CF. Second, we will calculate matrix elements between each of these 5 types of CF and the reference, finding the spin functions that give non-zero elements, i.e. belong to the first order interaction space.

Let's designate the open-shell orbitals (singles) in a given reference configuration by $a_1, a_2, \ldots$, closed-shell orbitals (doubles) by $d_1, d_2 \ldots$ and the unoccupied orbitals (virtuals) by $v_1, v_2 \ldots$ Doubly excited configurations are made by replacing a_1a_2 or a_1d_1 or d_1d_2 or d_1d_1 orbitals by a_3a_4 or a_3v_1 or v_1v_2 or v_1v_1 orbitals in the reference configurations. Out of 16 configuration types which can thus be formed only 5 increase the number of open shells: 4 configuration types $|a_1d_1 \to v_1v_2\rangle$, $|d_1d_2 \to a_3v_1\rangle$, $|d_1d_2 \to v_1v_1\rangle$ and $|d_1d_1 \to v_1v_2\rangle$ add two open shells and one type of configuration, $|d_1d_2 \to v_1v_2\rangle$, adds four open shells. We have to calculate matrix elements between each of these 5 types of configurations and the reference state and check which of the $f(s+2, S)$ or $f(s+4, S)$ spin functions interact with the functions corresponding to the reference configuration.

Let's assume the following order of orbitals in configuration λ: first doubles in an arbitrary order, then virtuals ($v_1 < v_2$ if present) and then singles $a_1 < a_2 \ldots$. We shall also assume that the spin functions are built according to the geneaological scheme [4, 12]. Therefore the paths in the branching diagram and the spin functions are in one-to-one correspondence and no confusion will arise if we shall talk about the interacting paths instead of interacting spin functions.

In SGA matrix elements depend on the line-up permutations, bringing orbitals in the two configurations into maximum coincidence. We can easily find the line-up permutations for matrix elements between the CF types listed above and an arbitrary reference configuration. Consider first the element $\langle d_1a_p \to v_1v_2|\hat{H}|0\rangle$. The orbitals in the two configurations appear in the following order:

$$\begin{aligned} &d_2d_2d_1d_1a_1a_2a_3 \ldots a_{p-1}a_p && \text{in } |0\rangle \\ &d_2d_2d_1v_1v_2a_1a_2 \ldots a_{p-2}a_{p-1} && \text{in } |d_1a_p \to v_1v_2\rangle \\ &1\ 2\ 3\ 4\ 5\ 6\ 7\ \ldots p+3p+4 && \text{positions of orbitals} \end{aligned} \tag{3}$$

where for simplicity we have not numbered the positions of the doubles which will not appear in our excitations. In this case there are 2 line-up permutations bringing the orbitals of the excited configuration into maximum coincidence with orbitals of the reference: a cycle $P_1=(56\ldots p+4)$ placing v_2 at $p+4$ position and moving $a_1,\ldots,a_{p-1}$ to the left, or $P_2=(45\ldots p+4)$, placing v_1 at $p+4$ position. The first permutation leads to $(d_1v_1|a_pv_2)$ and the second to $(d_1v_2|a_pv_1)$ two-electron integral. According to [5, 7, 9] it is always enough to find the line-up permutations of singly occupied orbitals only. In the case of the $\langle d_1d_2\to a_pv_1|\hat{H}|0\rangle$ element these line-up permutations are: $P_2=(45\ldots p+4)$ and $P_3=(34\ldots p+4)$. For $|d_1d_2\to v_1v_1\rangle$ and $|d_1d_1\to v_1v_2\rangle$ CFs reordering of the singles is not needed, $P=I$, so that only diagonal elements are different from zero. Therefore the spin FOIS for these configuration types is identical with zeroth-order spin space.

For the first two types of configurations finding the interacting spin functions is reduced to the determination of non-zero matrix elements $\langle SM,k|P|SM,l\rangle$, where $|SM,l\rangle$ is a function belonging to the zeroth-order spin space (Fig. 2). The interacting functions may be found using the original method of Kotani et al. [4], but a method described in [16] is simpler in this case. The method can be used to evaluate the actual values of spin integrals and thus our matrix elements, but now we are only interested in determining which paths do interact with the reference one. Writing a cycle as a product of elementary transpositions $(k\,k+1)$:

$$(345\ldots p+4)=(34)(45)\ldots(p+3p+4), \tag{4}$$

we can find all the interacting paths on the branching diagram using a simple rule [16]: the two path interact through $(kk+1)$ if they differ at most in the k and $k+1$ arcs, i.e. the paths must be the same except for $\wedge$ in one and $\vee$ in the other. Spin functions corresponding to the reference state have a singlet

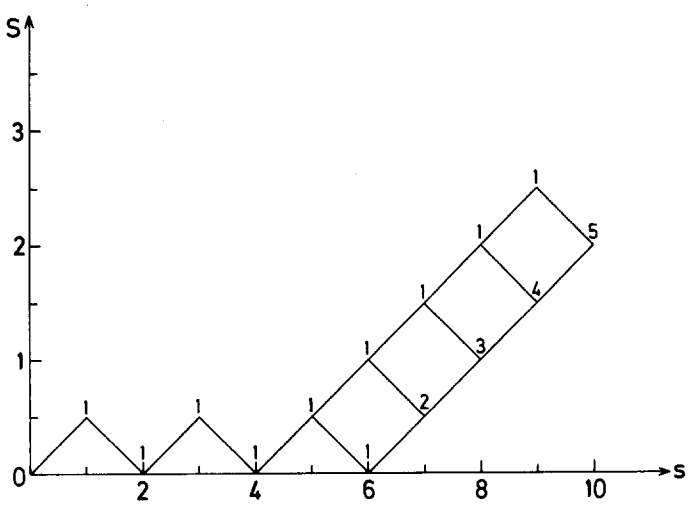

Fig. 2. Zeroth-order spin space for $S=2$, $s=6$ (at least in one reference configuration six open shells must be present). It is also spin FOIS for the configuration functions of $|d_1d_2\to v_1v_1\rangle$ and $|d_1d_1\to v_1v_2\rangle$ type

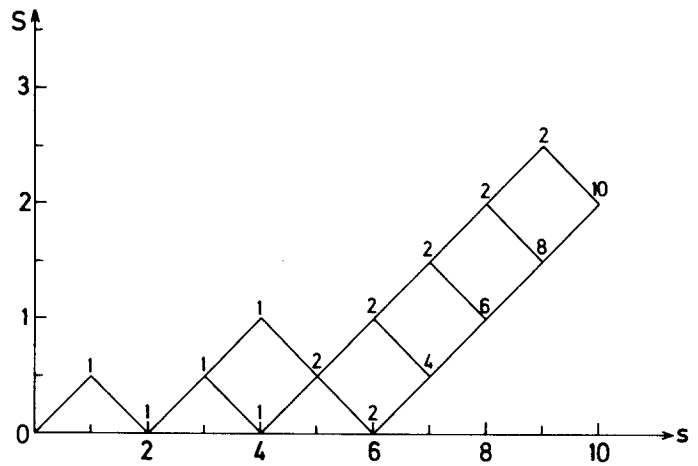

Fig. 3. Spin FOIS for configuration functions of $|d_1 a_p \to v_1 v_2\rangle$ and $|d_1 d_2 \to a_p v_1\rangle$ type. Instead of $f(8,2) = 20$ functions only $2f(6,2) = 10$ are needed

pair at the position 1, 2 and 3, 4 i.e. they are of the form  where only first five segments were drawn. Acting on any path chosen from the zeroth-order spin space with $(p+1\,p+2)$, $(pp+1)\ldots(56)$ transpositions we may produce only the paths belonging to the zeroth-order space. Permutations (45) and (34) (45) add a new possibility: they couple functions with a singlet pair at the position 3, 4 (path ) to functions with a triplet pair at this position (path ). Thus FOIS consist of the functions with the singlet and the triplet at 3, 4 position, a total of $2f(s, S)$ functions (Fig. 3).

Turning now to the case of $|d_1 d_2 \to v_1 v_2\rangle$ configuration type we find, that the two line-up permutations are in this case (23) and (123). The interacting paths may

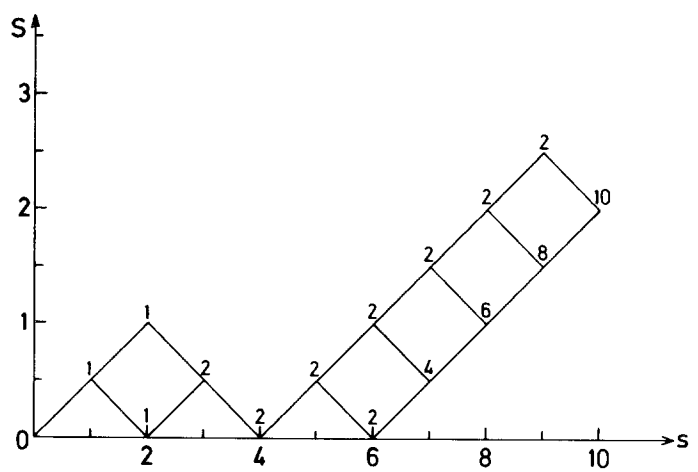

Fig. 4. Spin FOIS for configuration functions of $|d_1 d_2 \to v_1 v_2\rangle$ type. Instead of $f(10,2) = 75$ functions (Fig. 1) only $2f(6,2) = 10$ are needed

therefore differ only in the second and third arc, as shown in Fig. 4. Thus only $2f(s, S)$ spin functions are needed at most for every doubly excited CF, and from the analysis given above we know which functions (paths) should be retained. This completes our proof.

Singly excited configurations are in many cases unimportant (e.g. SCF reference states) and there are not many of them. This is a rather fortunate fact, because configurations of $|d \to v\rangle$ type give non-zero matrix elements $\langle d \to v|\hat{H}|0\rangle$ (interacting through the exchange integrals) for all $f(s+2, S)$ functions. However, in any practical case singly excited CFs should not create a serious problem.

The simple procedure described here not always leads to the minimal FOIS [3], but usually is quite close to the optimum (cf. [17]). The number of interacting spin functions may be lowered by assuming more specialized spin-coupling schemes and orbital orderings. Therefore $2f(s, S)$ spin functions per CF should be treated as an upper limit. In the example given by McLean and Liu [3] and in the example described by Brooks and Schaefer [18] the reference state is a doublet with one open shell, while doubly excited configurations have at most 5 open shells. Out of $f(1/2, 5) = 5$ spin functions only $2f(1/2, 1) = 2$ are interacting, as was indeed verified by these authors.

Both the unitary group approach [10, 11, 19–21] and the symmetric group approach [5–9, 22] are very well suited to utilize the nice property of the FOIS proved in this paper. In UGA it is enough to delete certain paths from Shavitt's graph while in SGA one has to use the simplified branching diagrams, like those in Fig. 2–Fig. 4. Such diagrams are used in a systematic and practical way (the ordering of the orbitals assumed for the purpose of the proof given above is not useful in practice) in [22]. As results from [16, 22], the FOIS spin functions which are not present in the zeroth-order space introduce at most a factor $\pm 1/2$ or $\pm\sqrt{3}/2$ in the matrix element formulas.

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