Wave Function expansions

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1 Introduction

The present format for wave function expansions needs to be refined for large cases. There are two concerns — the way information is stored for viewing by the user and possibly also the input of information to the computer and the way in which that information is stored in memory as a data structure. Here we are concerned primarily with the former which may be thought of as the external view (external to the computer) and in the computer as the internal organizations

1.1 CSFs for a list of configurations

For large cases the present external view is not meaningful for a user and consumes a great deal of disk space. A new format is proposed.

In GRASP, each CSF is defined in terms of 3 lines of data:

1) The line designating the occupied orbitals and their occupation number. Identifying keys for this line are the characters "(" or ")".

2) The J quantum number for each subshell and, for f-shells, some related data.

3) The resultant coupling, ending with the parity. The key here are the "+" of "-" characters.

In long expansions, with multiple couplings of shells, there are many duplicate lines that can be eliminated. If we introduce the notion of a "current value", then, in evaluating a list, lines 1) and possibly also 2) of the "next" CSF can be eliminated. Below is an example showing the CSFs for the $3p^4 3d^2$ configuration for $J = 3$ in the new format. Note the this includes 8 configurations in jj-coupling.

```
----------------------------------------------
CSF(s):  COMMON CORE
  3p ( 4)  3d-( 1)  3d ( 1)
              3/2       5/2
                          3+
  3p-( 1)  3p ( 3)  3d ( 2)
     1/2       3/2       2
                     1      3+
                     2      3+
     1/2       3/2       4
                     1      3+
```

```
                      2        3+
      3p-( 1)  3p ( 3)  3d-( 1)   3d ( 1)
          1/2       3/2        3/2        5/2
                              1       1/2        3+
                              1       3/2        3+
                              1       5/2        3+
                              2       1/2        3+
                              2       3/2        3+
                              2       5/2        3+
                              2       7/2        3+
      3p-( 1)  3p ( 3)  3d-( 2)
          1/2       3/2        2
                              1        3+
                              2        3+
      3p-( 2)  3p ( 2)  3d ( 2)
                     2        2
                                      3+
                     2        4
                                      3+
      3p-( 2)  3p ( 2)  3d-( 1)   3d ( 1)
                     0        3/2        5/2
                                      3/2        3+
      3p-( 2)  3p ( 2)  3d-( 1)   3d ( 1)
                     2        3/2        5/2
                                      1/2        3+
                                      3/2        3+
                                      5/2        3+
                                      7/2        3+
      3p-( 2)  3p ( 2)  3d-( 2)
                     2        2
                                      3+
--------------------------------------------------
```

A quick glance is sufficient to indicate the coupling of the various subshells. Essentially, every line with the $+$ or $-$ key designates a new CSF. If the preceeding line also is of type 3) then the current line 1) and line 2) are those of the preceeding CSF.

1.2   COMMON Cores of filled subshells

At present, the wave function expansion is defined in terms one set of inactive core subshells. For large atoms, with many filled subshells (Uranium has more than 20) these generate extremely long lines in the present format, too long to include in this report.

The ground state of Uranium is $5f^3 6d 7s^2$. To evaluate the stability, potential reactivity, and relaxation mechanisms on different uraninite surfaces, the state of U^+ with a hole in the $3d^{10}$ subshell is of interest [1, 2]. In such a calculation, we prefer to maintain the orbital order by the principal quantum number n. At the same time we would like to represent the hole state as $3d^9 5f^3 6d^2 7s^2$. This could be achieved because, in vector-coupling to generate CSFs the filled subshells can be included in any order. Suppose that the holes state is one obtained from the $3d \to 6d$ excitation and an expansion is needed that includes both the ground CSF and this excited CSF. A format, such as the following, could achieve this goal.

```
------------------------------------------------------------
Core subshells:
  1s   2s   2p-  2p   3s   3p-  3p   3d-  3d   4s   4p-  4p
  4d-  4d   4f-  4f   5s   5p-  5p   5d-  5d   6s   6p-  6p
Peel subshells:
```

```
   5f-  5f   6d-  6d   7s
CSF(s):   COMMON CORE - none
 5f ( 3)  6d ( 1)  7s ( 2)
     5/2       5/2
                        0       0-
 5f ( 3)  6d-( 1)  7s ( 2)
     3/2       3/2
                        0       0-
 5f-( 1)  5f ( 2)  6d ( 1)  7s ( 2)
     5/2       0       5/2
                            0       0-
     5/2       2       5/2
                  5/2       0       0-
                  3/2       0       0-
     5/2       4       5/2
                  5/2       0       0-
                  3/2       0       0-
 5f-( 2)  5f ( 1)  6d ( 1)  7s ( 2)
      2       7/2       5/2
                  5/2       0       0-
      4       7/2       5/2
                  5/2       0       0-
 5f-( 2)  5f ( 1)  6d-( 1)  7s ( 2)
      2       7/2       3/2
                  3/2       0       0-
      4       7/2       3/2
                  3/2       0       0-
 5f-( 3)  6d ( 1)  7s ( 2)
     5/2       5/2
                        0       0-
 5f-( 3)  6d-( 1)  7s ( 2)
     3/2       3/2
                        0       0-
CSF(s) :  COMMON CORE -3d
 3d-( 3)  3d ( 6)  5f ( 3)  6d ( 2)  7s ( 2)
     3/2                 7/2       2
                              2       0       0-
     3/2                 7/2       4
                              4       0       0-
     3/2                 3/2       0
                              0               0-
 ...
---------------------------------------------------------
```

Note that, in this format, in the excited CSF the $3d$-subshells $(3d-, 3d)$ are moved from the inactive COMMON core to the active set of orbitals and orbitals are coupled from the left to the outer valence shells. No re-ordering of the orbitals is needed although the angular code needs to be modified. Note that, in GRASP, angular data for contributions from the core are dealt with by formula. In particular, there are now two values of "$Ecore$" and the interaction between the two CSFs needs to deal algebraically with the interaction between $3d^{10}5d^36d7s^2$ and $3d^95f^36d^27s2$ CSFs.

Thus one idea is to move filled subsets from an inactive COMMON CORE to the active set of orbitals by redefining the core.

2 Expansions for Correlation

Some calculations for ionized atoms with a relatively few electrons have achieved excellent accuracy with a single orthonormal orbital set [4, 5]. But for heavier atoms, where outer electrons penetrate the core more significantly, correlation with the core may well play a more important role.

In heavy elements, it is clear that the occupied outer valence electrons will have different principal quantum numbers (as in Uranium) and VV expansions will be over a set of outer orbitals. The orbitals for an expansion can then be classified as:

1) The COMMON CORE shells

2) Occupied Valence orbitals (V) of the MR set, which may be subdivided into

    i) Filled (V_filled)

    ii) Unfilled (V_unfilled)

3) Virtual Valence orbitals (VV)

4) Symmetry orbitals (SO) that are used to represent symmetry adapted pair functions (SAPF) for two electrons, to be explained later.

Expansions for VV correlation are the typical GRASP expansions, consisting of a COMMON CORE orbitals and SD expansions of the type: $(ab) \rightarrow (vv)$ where a, b refer to orbitals from occupied orbitals from V of the CSF and vv from either V_unfilled or from VV. The GRASP excitation process for VV correlation does not take coupling into account and hence, CSFs are generated that do not interact directly with the parent but are CSFs with the same configuration (and hence similar energies) that may be more likely to have a higher order effect than other TQ excitations. These CSFs can be removed using the RCSFinteract code, when appropriate.

The SO orbitals are basis orbitals for two-electron, symmetry adapted functions (SAF1 for one electron and SAF2 for 2 electrons) of different LS or J symmetries that are particularly useful for core-correlation. Their principal quantum numbers are not physically meaningful and the orbitals themselves may be referred to simply as $3s3p3d2f1g$, for example, where the digit refers to the number of orbitals of a given symmetry. In defining two-electron correlation basis states, it is convenient to let ns refer to any s orbital of the SO set and $n's$ to any second orbital from the set but with $n' > n$. Then the basis set $\{nl^2\}$ refers to all nl^2 basis states for orbitals in the SO set whereas

$$\{nln'l \ LS\}, n' \geq n, n = 1, \ldots$$

refers to all possible basis states from non-equivalent s-orbitals. Let us consider the case of the $3s^2$ in Mg-like systems and suppose the orbital sets are defined as follows:

1) COMMON CORE: {1s, 2s, 2p}

2) Occupied orbitals {3s, 3p, 3d} of the $3s^2, 3p^2, 3d^{21}$ MR set.

    i) Filled {3s}

    ii) Unfilled {3p, 3d}

3) Virtual orbitals {4s, 4p, 4d, 4f }

4) SO: {3s3p3d2f1g}

In any internal organization, the SO orbitals might then be assigned quantum numbers following the largest in VV as in: 5s, 6s, 7s, 5p, 6p, 7p, 5d, 6d, 7d, 5f, 6f, 6g. In other words, SO orbitals are ordered by symmetry, and then by principal quantum number. Thus

$$nsn's\ ^1S \in \{5s6s, 5s7s, 6s7s\}^1S$$

where the latter my be viewed as an upper triangular array. Because there are different angular factors for equivalent electrons, we have separated the two sets but pair correlation functions are expansions over both. When the angular quantum numbers differ, the set of 2-electron basis states is rectangular and the traditional order of $l \le l'$ is retained but not $n \le n'$. So, $np\ n'd\ LS$ for the SO set of our example is a set that may be viewed as an array:

```
5p5d 5p6d 5p7d
6p5d 6p6d 6p7d
7p5d 7p6d 7p7d
```

In FORTRAN, such two-dimensional arrays are linearized in column order to become part of the vector defining the wave function.

2.1 A generalized GRASP expansion

Another possibility is to continue with the current process as implemented in GRASP (coupling from left to right) and introduce some new features such as varying the active set of orbitals and modifying the external format of the expansion as well as the internal format.

Let us consider the Mg-like case for $3s^2\ ^1S$. The script

```
rcsfgenerate <<EOF
*
0
1s(2,i)2s(2,i)2p(6,i)3s(2,*)

3s, 3p, 3d
0, 0
2
y
1s(2,*)2s(2,*)2p(6,*)3s(2,*)

4s, 4p, 4d, 4f
0,0
2
n
EOF
```

generates an expansion that includes CSFs from SD excitations for all subshells – core and valence, but there is a file 'clist.new' that includes all the CSFs that are generated when any of the core orbitals participate in the excitation process. So, if we think of the contribution from the first JJGEN run as defining the MR set, and the second that of adding correlation, the parts of clist.new that have excitations from the core, represent CV + CC. For CC interactions, as mentioned before, there are simplifications and by coupling excitations to virtual orbitals (unoccupied) the expansions can be restricted to those that interact with the MR set.

Let us analyze the structure for the core contributions from traditional expansions. Basically, there are two types of excited orbitals – unfilled and virtual. In our Mg, example. although we are exciting only from one CSF, let us assume that the MR set includes $3s^2, 3p^2, 3d^2$ so that $3p, 3d$ orbitals are unfilled and that $4s, 4p, 4d, 4f$ are virtual orbitals. As a result, there are two types of S-excitations: core $\rightarrow$ unfilled, or core $\rightarrow$ virtual and three types of D-excitations: core-core $\rightarrow$ unfilled-unfilled, unfilled-virtual, or virtual-virtual. The excitations that involve virtual orbitals (one or two) can be generalized to sets of CSFs, but excitations to unfilled are specific to the parent CSF. The list below shows the structure of an expansion in which the COMMON CORE is changed systematically. Not shown are the expansions contribution from the virtual orbitals. Note that, in order to generated all CSFs in general, two layers of virtual orbitals would be needed. Even though most excitations with be from a pair of equivalent electrons from the core, the excited (virtual) orbitals do not need to be equivalent.

```
Core subshells:
  1s   2s   2p-  2p
Peel subshells:
  3s   3p-  3p   3d-  3d   4s   4p-  4p   4d-  4d   4f-  4f
CSF(s):  COMMON CORE
  ...
  (CSFs of the MR set and VV correlation)
  ...
CSF(s):  COMMON CORE -2p
  2p-( 1)  2p ( 4)  3s ( 2)  3p-( 1)
     1/2                        1/2
                                    0+
  2p-( 2)  2p ( 3)  3s ( 2)  3p ( 1)
               3/2                3/2
                                    0+
  2p ( 4)  3s ( 2)  3p ( 2)
                         0
                            0+
  2p ( 4)  3s ( 2)  3p-( 2)

                            0+
  2p ( 4)  3s ( 2)  3d ( 2)
                         0
                            0+
  2p ( 4)  3s ( 2)  3d-( 2)
                         0
                            0+
  2p-( 1)  2p ( 3)  3s ( 2)  3p ( 2)
     1/2       3/2                2
                      2             0+
  2p-( 1)  2p ( 3)  3s ( 2)  3p-( 1)  3p ( 1)
     1/2       3/2                1/2       3/2
                      1              3/2       0+
                      2              3/2       0+
  2p-( 1)  2p ( 3)  3s ( 2)  3d ( 2)
     1/2       3/2                2
                      2             0+
  2p-( 1)  2p ( 3)  3s ( 2)  3d-( 1)  3d ( 1)
     1/2       3/2                3/2       5/2
                      1              5/2       0+
                      2              5/2       0+
  2p-( 1)  2p ( 3)  3s ( 2)  3d-( 2)
     1/2       3/2                2
                      2             0+
```

```
2p-( 2)  2p ( 2)  3s ( 2)  3p ( 2)
                        0             0
                                            0+
2p-( 2)  2p ( 2)  3s ( 2)  3p ( 2)
                                      2                        2
                                            0+
2p-( 2)  2p ( 2)  3s ( 2)  3p-( 1)  3p ( 1)
                  2                  1/2       3/2
                                            3/2       0+
2p-( 2)  2p ( 2)  3s ( 2)  3p-( 2)
                        0


                                            0+
2p-( 2)  2p ( 2)  3s ( 2)  3d ( 2)
                        0             0
                                            0+
                  2                  2
                                            0+
2p-( 2)  2p ( 2)  3s ( 2)  3d-( 1)  3d ( 1)
                  2                  3/2       5/2
                                            5/2       0+
2p-( 2)  2p ( 2)  3s ( 2)  3d-( 2)
                        0             0
                                            0+
                  2                  2
                                            0+
CSF(s):  COMMON CORE:   -2s, -2p
 2s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p ( 1)  3d ( 1)
     1/2       1/2                      3/2       5/2
                  1                              5/2       0+
 2s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p ( 1)  3d-( 1)
     1/2       1/2                      3/2       3/2
                  0                              3/2       0+
                  1                              3/2       0+
 2s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p-( 1)  3d-( 1)
     1/2       1/2                      1/2       3/2
                  1                              3/2       0+
 2s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p ( 1)  3d ( 1)
     1/2               3/2              3/2       5/2
                              1                  5/2       0+
                              2                  5/2       0+
 2s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p ( 1)  3d-( 1)
     1/2               3/2              3/2       3/2
                              1                  3/2       0+
                              2                  3/2       0+
 2s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p-( 1)  3d ( 1)
     1/2               3/2              1/2       5/2
                              2                  5/2       0+
     1/2               3/2              1/2       3/2
                              1                  3/2       0+
 2s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p-( 1)  3d-( 1)
     1/2               3/2              1/2       3/2
                              2                  3/2       0+
CSF(s)  COMMMON CORE -2s
 3s ( 2)  3p ( 2)
                  0
                     0+
 3s ( 2)  3p-( 2)


                     0+
```

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```
    3s ( 2)  3d ( 2)
                  0
                     0+
    3s ( 2)  3d-( 2)
                  0
                     0+
CSF(s):    COMMON CORE -1s  -2p
  1s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p ( 1)  3d ( 1)
      1/2      1/2                         3/2      5/2
                        1                         5/2       0+
  1s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p ( 1)  3d-( 1)
      1/2      1/2                         3/2      3/2
                        0                         3/2       0+
                        1                         3/2       0+
  1s ( 1)  2p-( 1)  2p ( 4)  3s ( 2)  3p-( 1)  3d-( 1)
      1/2      1/2                         1/2      3/2
                        1                         3/2       0+
  1s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p ( 1)  3d ( 1)
      1/2               3/2                3/2      5/2
                        1                         5/2       0+
                        2                         5/2       0+
  1s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p ( 1)  3d-( 1)
      1/2               3/2                3/2      3/2
                        1                         3/2       0+
                        2                         3/2       0+
  1s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p-( 1)  3d ( 1)
      1/2               3/2                1/2      5/2
                        2                         5/2       0+
      1/2               3/2                1/2      3/2
                        1                         3/2       0+
  1s ( 1)  2p-( 2)  2p ( 3)  3s ( 2)  3p-( 1)  3d-( 1)
      1/2               3/2                1/2      3/2
                        2                         3/2       0+
CSFs:    COMMON CORE -1s
  3s ( 2)  3p ( 2)
                  0
                     0+
  3s ( 2)  3p-( 2)

                     0+
  3s ( 2)  3d ( 2)
                  0
                     0+
  3s ( 2)  3d-( 2)
                  0
                     0+
------------------------------------------------------------------
```

The expansions can be analyzed according to the COMMON CORE as shown here for excitations to the $n = 3$ set of orbitals that define V+VV. Some patterns are observed.

1) The order of COMMON CORE redefinition is given as (2p, 2s2p, 2s, 1s2p, 1s2s, 1s) provided excitations from (ml nl')include only excitations in which one ml orbital and one nl orbital are included in this set where nl (by itself) included single and double excitations.

2) The excitations for the (1s) COMMON CORE are exactly the same as the excitations for (2s).

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3) The excitations for (2s 2p) are exactly the save as those for (1s 2p) provided 2s is replaced by 1s in the CSFs.

This implies that symbolic templates may be defined for expansions. For a Neon-like core where cores subshells are 1s, 2s and 2p, symbolic expansions are needed for ns, np and $msns, msmp$.

2.2 The problem of CSFs that do not interact

The present algorithm introduces many CSFs that do not interact with the referenced CSF. Below is an expansion for $3s^2 3d^2$, $J = 0$ and $3p^2 3d^2$, $J = 0$, namely

```
-------------------------------------------
CSF(s):
 3s ( 2)   3d ( 2)
                 0
                   0+
 3s ( 2)   3d-( 2)
                 0
                   0+
 3p ( 2)   3d ( 2)
         0         0
                   0+
         2         2
                   0+
 3p ( 2)   3d-( 1)   3d ( 1)
         2       3/2       5/2
                   5/2       0+
 3p ( 2)   3d-( 2)
         0         0
                   0+
         2         2
                   0+
 3p-( 1)   3p ( 1)   3d ( 2)
     1/2       3/2         2
                   2       0+
 3p-( 1)   3p ( 1)   3d-( 1)   3d ( 1)
     1/2       3/2       3/2       5/2
                   1       5/2       0+
                   2       5/2       0+
 3p-( 1)   3p ( 1)   3d-( 2)
     1/2       3/2         2
                   2       0+
 3p-( 2)   3d ( 2)
                 0
                   0+
 3p-( 2)   3d-( 2)
                 0
                   0+
-------------------------------------------
```

But only CSFs which couple to a $J = 0$ state with the coupled first two orbitals will interact through the $(3s3s => 3p3p)$ $J = 0$ excitation. The others are CSFs that contribute to the energy through a higher-order correction to the wave function. The RCSFinteract program produces the list to the following output.

```
------------------------
 3s ( 2)   3d ( 2)
```

```
                 0
                   0+
    3s ( 2)   3d-( 2)
                 0
                   0+
    3p ( 2)   3d ( 2)
          0        0
                   0+
    3p ( 2)   3d-( 2)
          0        0
                   0+
    3p-( 2)   3d ( 2)
                 0
                   0+
    3p-( 2)   3d-( 2)
                 0
                   0+
------------------------
```

For $J = 0$ it was easy to select the interacting states. In the case of the $4d^{10}4f^2$ and $4d^8 4f^4$ interaction, things are not nearly as simple, even for $J = 0$ shown here.

```
-----------------------------------------------
  4d-( 4)   4d ( 6)   4f ( 2)
                            0
                              0+
  4d-( 4)   4d ( 6)   4f-( 2)
                            0
                              0+
  4d-( 2)   4d ( 6)   4f ( 4)
        0                   0
                              0+
        2              2;    2
                              0+
        2              4;    2
                              0+
  4d-( 2)   4d ( 6)   4f-( 1)  4f ( 3)
        2                 5/2      7/2
                            7/2        0+
  4d-( 2)   4d ( 6)   4f-( 2)  4f ( 2)
        0                 0        0
                                     0+
        2                 0        2
                                     0+
        2                 2        0
                            0        0+
  4d-( 2)   4d ( 6)   4f-( 3)  4f ( 1)
        2                 5/2      7/2
                            7/2        0+
  4d-( 2)   4d ( 6)   4f-( 4)
        0                   0
                              0+
        2                   2
                              0+
  4d-( 3)   4d ( 5)   4f ( 4)
      3/2       5/2   2;    2
                       2        0+
      3/2       5/2   2;    4
                       4        0+
      3/2       5/2   4;    2
```

```
                        2       0+
        3/2       5/2   4;   4
                        4       0+
4d-( 3)  4d ( 5)  4f-( 1)  4f ( 3)
   3/2       5/2       5/2       7/2
                        1      7/2       0+
                        2      7/2       0+
                        3      7/2       0+
                        4      7/2       0+
4d-( 3)  4d ( 5)  4f-( 2)  4f ( 2)
   3/2       5/2        0         2
                        2                 0+
   3/2       5/2        0         4
                        4                 0+
   3/2       5/2        2         0
                        2         0       0+
   3/2       5/2        4         0
                        4         0       0+
4d-( 3)  4d ( 5)  4f-( 3)  4f ( 1)
   3/2       5/2       5/2       7/2
                        1      7/2       0+
                        2      7/2       0+
                        3      7/2       0+
                        4      7/2       0+
4d-( 3)  4d ( 5)  4f-( 4)
   3/2       5/2        2
                        2       0+
   3/2       5/2        4
                        4       0+
4d-( 4)  4d ( 4)  4f ( 4)
             0         0
                        0+
             2    2;   2
                        0+
             2    4;   2
                        0+
             4    2;   4
                        0+
             4    4;   4
                        0+
4d-( 4)  4d ( 4)  4f-( 1)  4f ( 3)
             2        5/2       7/2
                        7/2       0+
             4        5/2       7/2
                        7/2       0+

             0         0         0
                                  0+
4d-( 4)  4d ( 4)  4f-( 2)  4f ( 2)
             2         0         2
                                  0+
             2         2         0
                        0         0+
             4         0         4
                                  0+
             4         4         0
                        0         0+
4d-( 4)  4d ( 4)  4f-( 3)  4f ( 1)
             2        5/2       7/2
                        7/2       0+
```

```
                4       5/2      7/2
                        7/2         0+
   4d-( 4)  4d ( 4)  4f-( 4)
                  0         0
                            0+
                  2         2
                            0+
                  4         4
                            0+
-------------------------------------------
```

Of the 121 CSFs for the $4d^8 4f^4$ $J = 0$ configuration, only 45 interacted with the two $4d^{10} 4f^2$ $J = 0$ CSFs whereas for $J = 4$, 610 CSFs are reduced to 89 CSFs.

3   A procedure for generating CFS that interact

3.1   Expansions for one and two electrons in partial waves

In a study of correlation in an N-electron system, Jankowski *et al.* [?] expressed correlation contributions to the wave function in terms of orbital configurations, of one-electron functions, and of symmetry-adapted pair functions in the form of partial-wave (PW) expansions. In this section we will use the excitation process to determine these functions.

The basic one-electron symmetry adapted one-electron function (SAF1) is

$$\Psi(ml \; \nu LS) = \sum_n c_n \Phi(nl \; \nu LS) \tag{1}$$

where $\Phi(nl; LS)$ are one-electron orbitals and Ψ is a partial wave (PW). Similarly, the symmetry adapted pair function (SAF2) for $LS = {}^1 S, {}^3 P$ with even parity is

$$\Psi((ml)^2 \; \nu LS) = \sum_{(l \geq L)} \left(\sum_n c_n^l \Phi(nl)^2 \; \nu LS) \right) \tag{2}$$

$$+ \sum_{(l \geq L)} \left(\sum_{n < n'} c_{nn'}^l \Phi(nln'l \; \nu LS) \right) \tag{3}$$

where now the partial wave for two equivalent electrons is expressed in terms of a sum of CSFs for two electrons. So the PW for an SAF2 consists of a number of symmetry order primals (SOP's) that are sums over principal quantum numbers $\{nlnl\}$ for equivalent electrons or double sums $\{nl, n'l'\}$, $l' = l$ that are triangular for non-equivalent electrons. In the case of $\Phi((ml)^2 \; {}^1 D)$, in addition to the above SOP's there is the sum

$$\sum_{(l \geq 0)} \left(\sum_{n,n'} c_{nn'}^l \Phi(nln'l' \; \nu LS) \right), \; l' = l + 2. \tag{4}$$

An important SAF2 is for the two-electron odd symmetry

$$\Psi \left(msm'p \; {}^{1,3}P^o \right) = \sum_l \left(\sum_{n,n'} c_{nn'}^l \Phi(nln'l' \; {}^{1,3}P^o) \right), \; l' = l + 1 \tag{5}$$

Rules can readily be defined for pairs of electrons. In the above, the range of summation has not been mentioned, the upper limit would be a parameter for a calculation. The lower limit is determined by the electrons present in the remaining $N-2$ part of the configuration state function.

In non-relativistic theory, all these sums over n for equivalent or n, n' non-equivalent have the same spin-angular factor and can be expressed simply are sums over radial functions times a single spin-angular factor. Using these relations it was possible to compute He-like energies in a B-spline basis without ever generating angular data or computing the interaction matrix citeref:cff-1991 in terms of vector processing.

3.2 Core Core Correlation

Let us present our various concepts in LSJ notation and apply them to core correlation for Mg-like systems.

The SD excitations from a $1s^2 2s^2 2p^6 3s^2$ CSF consist of all excitations of the type $(ab)LSP \rightarrow (vv)LSP$ where a, b are orbitals occupied in the reference CSF and P designates the parity of the pair of orbitals, and vv is any pair of unfilled or virtual orbitals. Notice that we couple the pair of electrons before coupling them to the valence shells. The type of (ab) orbitals determines the type of correlation – VV, CV, or CC

For CC correlation, we are only interested in the case where a, b are orbitals in the closed shells, either the same shell or different. Put another way, making a single subshell active, allows S and D excitations, whereas two-different subshells imply only D excitations, with one orbital from each shell.

In general, assume we have a closed shell $|l^{2l+1\,1}S\rangle$ coupled (left to right) to a valence CSF $|\gamma LS\rangle$. For CC, the pair $(ab)LSP \equiv (l^2)LSP$ couples with the remaining closed shell orbitals, $(l^{2l-1})LSP$. Assume the pair couples to the right of the remaining closed shell orbitals. So we have

$$|l^{2l-1\,1}S\rangle \cdot |l^2 LS\rangle(^1S) \cdot |\gamma LS\rangle.$$

The excitation process replaces the l^2 core orbitals with vv orbitals. But for these excited CSFs to interact with the original "parent" CSF, the LSP for the pair must be the same as the LSP of the uncoupled orbital pair l^{2l-1} and couple to form a ^1S state. In this D excitation process, the orbitals for the coupled pair are replaced without a change in the total coupling. Note the the coupling of (ab) may have a number of possibilities and usually there are many possibilities for replacing orbitals. Thus CC expansions increase rapidly in size both with the number of orbitals in SO and the number of closed subshells that are considered.

In order to understand this process, let us consider the case of a single closed shell, namely 2p so the active CSF in our Mg example, becomes $2p^6 3s^2$. Uncoupling a pair of $2p^2$ orbitals yields

$$2p^6 3s^2 \, {}^1S \rightarrow \sum_{LS} (\ ) 2p^4\{LS\} 2p^2\{LS\} \, (^1S) 3s^2 \text{ where } LS = \{{}^3P, {}^1D, {}^1S\}.$$

The substitution $2p^2 \rightarrow 3s^2$ yields a null value upon recoupling with the valence function since the $3s$ subshell is already filled. In general, excitations to occupied orbitals nullify some excitations from the core. On the other hand, excitations to other Valence Valence orbitals may be allowed. But nothing interferes with excitations when the v or vv orbitals are from the SO set.

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Note that, with this order of uncoupling and replacement, the core-correlation CSFs are not specified in the usual order for orbitals, but it is extremely convenient that the coupling of the outer valence shells is unaffected. The remaining core orbitals and the replacement pair always couples to a ^1S state.

3.3   Core correlation in Mg I

```
#!/bin/sh

rcsfgenerate << EOF
 * ! Orbital order
1  ! Selected core
2s(2,i)2p(6,i)3s(2,*)
2s(2,i)2p(6,i)3p(2,*)
2s(2,i)2p(6,i)3d(2,*)
*
3s, 3p, 3d
0            8  ! Lower and higher 2*J
0  ! Number of excitations
n
EOF

cp rcsf.out Mg.MR.c
mv rcsf.out rcsfmr.inp

rcsfgenerate << EOF
 * ! Orbital order
1  ! Selected core
2s(2,*)2p(6,*)3s(2,i)
2s(2,*)2p(6,*)3p(2,i)
2s(2,*)2p(6,*)3d(2,i)
*
4s, 4p, 4d, 4f
0            8  ! Lower and higher 2*J
2  ! Number of excitations
n
EOF

mv rcsf.out rcsf.inp
rcsfinteract << EOF
1
EOF
mv rcsf.out Mg.cc.c
```

The first expansion defines the MR that includes only VV correlation. The second correlates the core but, inspite of the fact that the $n = 3$ orbitals are inactive, excitations to $n = 3$

orbitals are present in the expansion. All CSFs with more than two $n = 3$ orbitals need to be deleted. The final expansions will then include only excitations of the form $2l2l' \rightarrow 4l''4'''$, where the $n = 4$ orbitals are virtual orbitals, in this case.

Computing first the MR wavefunction and then the expansion with CC correlation, we see that the total energies of all states are reduced significantly. In particular, the $J = 0$ state has been reduced by 0.228725 Hartrees. The spectrum has changed hardly at all as shown in the table below. This calculation included only double (D) excitations, including $2p^2 \rightarrow 4s4d$ and possibly others. The last column shows the difference in the two spectra.

Pos	J	Energy Total 3s2+3p2+3d2 (a.u.)	Levels	Configuration (cm^-1)	Energy Total + D n=4 (a.u.)	Levels (cm^-1)	Diff (cm^-1)
1	0	-199.9588626	0.00	3s(2)_1S0	-200.1875882	0.00	0.0
2	0	-199.7067269	55337.39	3p(2)_3P2	-199.9354545	55336.95	-0.44
1	1	-199.7066136	55362.26	3p(2)_3P2	-199.9353413	55361.79	-0.47
1	2	-199.7063727	55415.13	3p(2)_3P2	-199.9351004	55414.65	-0.48
2	2	-199.6807655	61035.27	3p(2)_1D2	-199.9095290	61026.93	-8.34
3	0	-199.6335435	71399.30	3p(2)_1S0	-199.8623339	71385.06	-14.24
3	2	-199.4555889	110455.80	3d(2)_3F2	-199.6840751	110508.34	52.54
1	3	-199.4555688	110460.22	3d(2)_3F2	-199.6840549	110512.78	52.56
1	4	-199.4555410	110466.33	3d(2)_3F2	-199.6840269	110518.92	52.59
4	2	-199.4404961	113768.30	3d(2)_1D2	-199.6689880	113819.59	50.29
4	0	-199.4388766	114123.73	3d(2)_3P2	-199.6673698	114174.74	51.01
2	1	-199.4388744	114124.21	3d(2)_3P2	-199.6673676	114175.22	51.01
5	2	-199.4388674	114125.76	3d(2)_3P2	-199.6673604	114176.79	51.03
2	4	-199.4380889	114296.61	3d(2)_1G2	-199.6665779	114348.53	51.92
5	0	-199.3919496	124423.02	3d(2)_1S0	-199.6204692	124468.22	45.20

This table shows that, when doubles from core-correlation are included for every CSF of a valence expansion *and* the excitations are to orbitals not occupied in the valence expansion, the spectrum (which is an energy difference) will not be affected although the wave function is modified. The latter may affect other properties but not the spectrum. The larger components of the Mg ground state becomes:

```
    1    0    +           -200.187588165       99.986%
      0.95778215    0.91734664    2s(2).2p(6).3s(2)_1S
      0.26157160    0.06841970    2s(2).2p(6).3p(2)1S0_1S
      0.04689358    0.00219901    2s(2).2p(4)1D2_1D.3s(2).4p(2)1D2_1S
     -0.04624983    0.00213905    2s(2).2p(4)3P2_3P.3s(2).4d(2)3P2_1S
      0.04206192    0.00176921    2s(2).2p(4)3P2_3P.3s(2).4p(2)3P2_1S
     -0.03643618    0.00132760    2s(2).2p(4)1D2_1D.3s(2).4d(2)1D2_1S
      0.03515155    0.00123563    2s.2p(5)_1P.3s(2).4s_2P.4p_1S
      0.03373344    0.00113794    2s(2).2p(4)1S0_1S.3s(2).4d(2)1S0_1S
```

Note that the double excitations may involve different subshells.

4   Summary of changes

Currently, expansions are obtained using the program JJGEN and its wrapper that defines RCSFgenerate. Several changes are needed.

1) CSF order. At present the program tries to prepare an expansion for CSFs in order of energy. Possibly this is related to finding duplicates using a fast binary search. More

useful would be an order in which the maximum principal quantum number of a CSF increases. If a CSF is classified "by n", confirming whether a recently generated CSF is different could still be fast in that only CSFs in the same class would need to be searched

2) Replacing newly generated CSFs by the "add" option available in JJGEN rather than the "merge" option used by RCSFgenerate. Such an order would make it possible to "add" new $n = 6$ CSFs, for example, to an expansion for $n = 5$ that had been optimized in some way and defined the zero-order set.

3) Multiple COMMON Closed shells.

4) Read/Write algorithms are needed for dealing with the proposed format.

The first step would be to deal with one COMMON CORE in the new format.

References

[1] J. Li and U. Becker, *private communication—*

[2] F.N. Skomerski *et al.* Am. Minerologist, J. Earth and Planetery Materials, **91**(11), 2006.'

[3] M.S. Safronova and W. R. Johnson, Adbances AMOP, **55**, 192-233 (2008).

[4] P. Jönnson *et al.*, ADNDT, **100**, 1-154 (2014).

[5] R. Si *et al*, Ap. J. Supplement Series, **227**, 2016.

[6] K. Jankowski and P. Malinowski, Phys. Rev. A **21**, 45 (198)

[7] C. Froese Fischer, Int'l J. High Performance Computing Applications, **5**, 5-20 (1991).