COUPLING: The program for searching optimal coupling scheme in atomic theory

Example calculation: P II $3p4f$

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1 Suitability of the coupling scheme

Transformation of the atomic state functions (ASFs) from the LS coupled basis to other bases is performed by the program COUPLING. The parameter defining a *correct* and *complete* transformation is the sum of all 'weights' in an arbitrary coupling basis, i.e. $\sum_i \left| a_i^{(\text{any coupling})}(\tau) \right|^2$ which should be

$$\sum_i \left| a_i^{(\text{any coupling})}(\tau) \right|^2 = 1. \tag{1}$$

This parameter is approximately equal to 1 if the calculation was performed correctly and completely.

Evaluation of suitability of the couplings for the classification of energy spectra is performed using the methodology described in [1]. A square of the largest coefficient averaged over the states (P_s) of the considered configuration are used in the program COUPLING as the numerical parameters.

The "purity" parameter P_s is defined as

$$P_s = \frac{\sum_J P_J}{\sum_J m_J}, \tag{2}$$

where m_J is the number of atomic state functions with a given J and

$$P_J = \sum_{k=1}^{m_J} a_{max\ k}^2 \tag{3}$$

where $a_{max\ k}$ is the largest coefficient in the expansion of kth atomic state function. The averaging in (2) is over all J values. The higher the "purity" P_s value, the better the coupling scheme.

2 Coupling schemes supported by the program COUPLING

The coupling schemes outlined in Table 1 include those most frequently used in calculations of atomic structure [2,3]. Any term symbol gives the values of two angular momenta that may be coupled to give the total electronic angular

Table 1
The quantum numbers for the two vectors that couple to give the final J.

No.	According to [3]			According to [4]		Identification in the program		
							Coupling	
	Coupling scheme	Quantum numbers for vectors that couple to given J	Term symbol	Coupling scheme	Term symbol	Number of coupled shells	Labels	Expression of coupling scheme
1	LS	L, S	^{2S+1}L	LS	^{2S+1}L	2	LS	(4)
2	$J_1 J_2$	J_1, J_2	(J_1, J_2)	JJ	$[J_1, J_2]_J$	2	JJ	(5)
3	$J_1 L_2 (\to K)$	K, S_2	$^{2S_2+1}[K]$	JK	$J_1 [K]_J$	2	JK	(6)
4	$LS_1 (\to K)$	K, S_2	$^{2S_2+1}[K]$	LK	$L[K]_J$	2	LK	(7)

momentum of a level (indicated by the J value). For configurations of more than one unfilled subshell, the angular momenta involved in the final coupling derive from two groups of electrons (either group may consist of only one electron). These are often an inner group of coupled electrons and an outer group of coupled electrons, respectively. In any case the quantum numbers for the two groups can be distinguished by subscripts 1 and 2, so that quantum numbers represented by capital letters without subscripts are total quantum numbers for both groups. Thus, the quantum numbers for the two vectors that couple to give the final J are related to the term symbol as presented in the Table 1. Parity is indicated by degree symbols appended to odd-parity terms. All four main different coupling schemes listed in the Table 1, respectively, are created in the following way:

$$\vec{L}_1 + \vec{L}_2 = \vec{L}, \quad \vec{S}_1 + \vec{S}_2 = \vec{S}, \quad \vec{L} + \vec{S} = \vec{J} \qquad \text{(first scheme)} \qquad (4)$$

$$\vec{L}_1 + \vec{S}_1 = \vec{J}_1, \quad \vec{L}_2 + \vec{S}_2 = \vec{J}_2, \quad \vec{J}_1 + \vec{J}_2 = \vec{J} \qquad \text{(second scheme)} \quad (5)$$

$$\vec{L}_1 + \vec{S}_1 = \vec{J}_1, \quad \vec{J}_1 + \vec{L}_2 = \vec{K}, \quad \vec{K} + \vec{S}_2 = \vec{J} \qquad \text{(third scheme)} \qquad (6)$$

$$\vec{L}_1 + \vec{L}_2 = \vec{L}, \quad \vec{L} + \vec{S}_1 = \vec{K}, \quad \vec{K} + \vec{S}_2 = \vec{J} \qquad \text{(fourth scheme)} \quad (7)$$

Martin and Wiese [3] determined the main different coupling schemes for complex configurations in atomic theory. They are based on the four momentum

Table 2

Connection between the notations of coupling classification from [3] and the program COUPLING. The number of coupled shells (third column) means the number of shells in LS representation.

No.	Coupling classification from [3]	Identification in the program COUPLING		
		Number of coupled shells	Labels	Expression of coupling scheme
	• LS Coupling (Russell-Saunders Coupling)			
1	$3d^7\,{}^4F_{7/2}$	1	LSJ	(8)
2	$3d^7\left({}^4F\right)4s4p\left({}^3P^o\right)\,{}^6F^\circ_{9/2}$	3	LS3	(17)
3	$4f^7\left({}^8S^\circ\right)6s6p^2\left({}^4P\right)\,{}^{11}P^\circ_5$	3	LS3	(17)
4	$3p^5\left({}^2P^\circ\right)3d^2\left({}^1G\right)\,{}^2F^\circ_{7/2}$	2	LSJ	(10)
5	$4f^{10}\left({}^3K2\right)6s6p\left({}^1P^\circ\right)\,{}^3L^\circ_6$	3	LS3	(17)
6	$4f^7\left({}^8S^\circ\right)5d\,\left({}^7D^\circ\right)6p\,{}^8F^e_{13/2}$	3	LSJ	(16)
7	$4f^7\left({}^8S^\circ\right)5d^2\left({}^1G\right)\left({}^8G^\circ\right)6p\,{}^7F_0$	3	LSJ	(16)
8	$4f\left({}^2F^\circ\right)5d^2\left({}^1G\right)6s\,\left({}^2G\right)\,{}^1P^\circ_1$	3	LSJ	(16)
	• jj Coupling			
9	$\left(6p^2_{1/2}\right)_0$	1	jj	(9)
10	$\left(6p^2_{1/2}6p_{3/2}\right)^\circ_{3/2}$	1	jj	(15)
11	$\left(6p^2_{1/2}6p^2_{3/2}\right)_2$	1	jj	(15)
12	$4d^3_{5/2}4d^2_{3/2}\,(9/2,\,2)_{11/2}$	1	jj	(15)
	• J_1j or J_1J_2 Coupling			
13	$3d^9\left({}^2D_{5/2}\right)4p_{3/2}\,(5/2,\,3/2)^\circ_3$	2	LScjj	(14)
14	$4f^{11}\left({}^2H2^\circ_{9/2}\right)6s6p\left({}^3P^\circ_1\right)(9/2,\,1)_{7/2}$	3	LSJ3	(18)
15	$5f^4_{7/2}5f^5_{5/2}\,(8,\,5/2)^\circ_{21/2}\,7p_{3/2}\,(21/2,\,3/2)_{10}$	2	jj	(15)
16	$5f^3_{7/2}5f^3_{5/2}\,(9/2,\,9/2)_9\,7s7p\left({}^3P^\circ_2\right)(9,\,2)^\circ_7$	3	cLSJ3	(21)
	• J_1l or J_1L_2 Coupling (J_1K Coupling)			
17	$3p^5\left({}^2P^\circ_{1/2}\right)5g^2\,[9/2]^\circ_5$	2	JK	(12)
18	$4f^2\left({}^3H_4\right)5g^2\,[3]_{5/2}$	2	JK	(12)
19	$4f^{13}\left({}^2F^\circ_{7/2}\right)5d^2\left({}^1D\right)\,{}^1\,[7/2]^\circ_{7/2}$	2	JK	(12)
20	$4f^{13}\left({}^2F^\circ_{5/2}\right)5d6s\left({}^3D\right)\,{}^3\,[9/2]^\circ_{11/2}$	3	JK3	(19)
	• LS_1 Coupling (LK Coupling)			
21	$3s^23p\left({}^2P^\circ\right)4f\,G\,{}^2\,[7/2]_3$	2	LK	(13)
22	$3d^7\left({}^4P\right)4s4p\left({}^3P^\circ\right)D^\circ\,{}^3\,[5/2]^\circ_{7/2}$	3	LK3	(20)

coupling schemes (4), (5), (6), and (7). These coupling schemes for one, two, and three coupled shells (in LS coupling) are listed in Table 2. The classification of these schemes is used according to [3].

LS Coupling (Russell-Saunders Coupling) [3]

In the second example $(3d^7\,(^4F)\,4s4p\,(^3P^\circ)\;^6F^\circ_{9/2})$ from Table 2, the seven $3d$ electrons couple to give a ^4F term, and the $4s$ and $4p$ electrons couple to form the $^3P^\circ$ term; the final $^6F^\circ$ term is one of the nine possible terms obtained by coupling the ^4F grandparent and $^3P^\circ$ parent terms. The next three examples are similar to the second one. The meaning of the index 2 following the ^3K symbol in the fifth example is explained in [3].

The coupling in example 6 $(4f^7(^8S^\circ)5d\,(^7D^\circ)6p\,^8F^e_{13/2})$ is appropriate if the interaction of the $5d$ and $4f$ electrons is stronger than the $5d$-$6p$ interaction. The $^7D^\circ$ parent term results from coupling the $5d$ electron to the $^8S^\circ$ grandparent, and the $6p$ electron is then coupled to the $^7D^\circ$ parent to form the final ^8F term. A space is inserted between the $5d$ electron and the $^7D^\circ$ parent to emphasize that the latter is formed by coupling a term $(^8S^\circ)$ listed to the left of the space.

Example 7 shows an $^8G^\circ$ parent term formed by coupling the $^8S^\circ$ and ^1G grandparent terms. A space is again used to emphasize that the following $(^8G^\circ)$ term is formed by the coupling of the terms listed before the space.

A different order of coupling is indicated in the example 8, the $5d^2\,^1G$ term being coupled first to the external $6s$ electron instead of directly to the $4f$ core electron. The $4f(^2F^\circ)$ core term is isolated by a space to denote that it is coupled (to the $5d^2(^1G)6s\,^2G$ term) only after the other electrons have been coupled. The notation in this particular case (with a single $4f$ electron) could be simplified by writing the $4f$ electron after the ^2G term to which it is coupled. It appears more important, however, to retain the convention of giving the core portion of the configuration first.

jj Coupling [3]

This scheme is used, for example, in relativistic calculations. The lower-case j indicates the angular momentum of one electron ($j = l \pm 1/2$) or of each electron in an l^N_j group. Various ways of indicating which of the two possible j values applies to such a group without writing the j-value subscript have been used by different authors; we give the j values as shown in Table 2. We use the symbols J and j to represent total angular momenta.

The relatively large spin-orbit interaction of the $6p$ electrons produces jj-coupling structures for the $6p^2$, $6p^3$, and $6p^4$ ground configurations of neutral Pb, Bi, and Po, respectively; the notations for the ground levels of these atoms are given as the examples 9-12 in the Table 2. The configuration in the example

5

9 shows the notation for equivalent electrons having the same j value l_j^N, in this case two $6p$ electrons each having $j = 1/2$. A convenient notation for a particular level ($J = 0$) of such a group is also indicated. The example 10 extends this notation to the case of a $6p^3$ configuration divided into two groups according to the two possible j values. A similar notation is shown for the $6p^4$ level in the example 11; this level might also be designated $(6p_{3/2}^{-2})_2$, the negative superscript indicating the two $6p$ holes. The $(J_1, J_2)_J$ term and level notation shown on the right in the example 12 is convenient because each of the two electron groups $4d^3{}_{5/2}$ and $4d^2{}_{3/2}$ has more than one allowed total J_i value. The assumed convention is that J_1 applies to the group on the left ($J_1 = 9/2$ for the $4d^3{}_{5/2}$ group) and J_2 to that on the right.

J_1j or J_1J_2 Coupling [3]

The coupling schemes 13 and 14 in Table 2 have core electrons in LS coupling, whereas the coupling schemes 15 and 16 in the same Table indicate jj coupling for the $5f$ core electrons. Since the J_1 and J_2 values in the final (J_1, J_2) term have already been given as subscripts in the configuration, the (J_1, J_2) term notations are redundant in all these examples. Unless separation of the configuration and final term designations is desired, as in some data tables, one may obtain a more concise notation by simply enclosing the entire configuration in brackets and adding the final J value as a subscript. Thus, the level in the example 13 can be designated as $[3d^9(^2D_{5/2})4p_{3/2}]_3^\circ$. If the configuration and coupling order are assumed to be known, still shorter designations may be used.

J_1l or J_1L_2 Coupling (J_1K Coupling) [3]

The final terms in the examples 17 and 18 result from coupling a parent-level J_1 to the orbital angular momentum of a $5g$ electron to obtain a resultant K, the K value being enclosed in brackets. The spin of the external electron is then coupled with the K angular momentum to obtain a pair of J values, $J = K \pm 1/2$ (for $K \neq 0$). The multiplicity (2) of such pair terms is usually omitted from the term symbol, but other multiplicities occur in the more general J_1L_2 coupling (examples 19 and 20). The examples 19 and 20 are straightforward extensions of J_1l coupling, with the L_2 and S_2 momenta of the "external" term (^1D and ^3D in examples 19 and 20, respectively) replacing the l and s momenta of a single external electron.

LS_1 Coupling (LK Coupling) [3]

In the examples 21 and 22, the orbital angular momentum of the core is coupled with the orbital angular momentum of the external electron(s) to give the total orbital angular momentum L. The letter symbol for the final L value is listed with the configuration because this angular momentum is then coupled with the spin of the core (S_1) to obtain the resultant K angular momentum of the final term (in brackets). The multiplicity of the $[K]$ term arises from the spin of the external electron(s).

$$*\quad*\quad*$$

The transformation from LSJ-coupling to all coupling schemes listed in Table 1 and Table 2 is performed by the program COUPLING. The program is designed in such a way that it can perform transformation for given classes in general cases such as LSJ, LS3, LSJ3, cLSJ3, and etc. for s, p, d, f shells with any occupation number and for $l > 3$ with the occupation number n=1,2. The number and types of coupling schemes depend on the number of coupled shells in LS-coupling. Below in subsections 2.1, 2.2, and 2.3 there are listed all coupling schemes supported by the program COUPLING for a particular number of coupled shells.

2.1   The one shell coupling

The coupling schemes LSJ and jj for one coupled shell are presented in this section.

LSJ-coupling scheme

$$nl^N \, \alpha \, LSJ \tag{8}$$

jj-coupling scheme

$$\left(nl_-^{N_-} J_- \cdot nl_+^{N_+} J_+\right) J \tag{9}$$

where $j = l - 1/2$ for l_-, $j = l + 1/2$ for l_+, $N = N_- + N_+$, $\vec{J} = \vec{J}_- + \vec{J}_+$.

2.2 The two shells coupling

The coupling schemes LSJ, JJ, JK, LK, $LScjj$, and jj for two coupled shells are presented in this section.

LSJ-coupling scheme

$$\left(n_1 l_1^{N_1}\,\alpha_1\,L_1 S_1 \cdot n_2 l_2^{N_2}\,\alpha_2\,L_2 S_2\right) LSJ \tag{10}$$

JJ-coupling scheme

$$\left(\left(n_1 l_1^{N_1}\,\alpha_1\,L_1 S_1\right) J_1 \cdot \left(n_2 l_2^{N_2}\,\alpha_2\,L_2 S_2\right) J_2\right) J \tag{11}$$

JK-coupling scheme

$$\left(\left(n_1 l_1^{N_1}\,\alpha_1\,L_1 S_1\right) J_1 \cdot \left(n_2 l_2^{N_2}\,\alpha_2\,L_2 S_2\right) K\right) J \tag{12}$$

where $\vec{K} = \vec{J_1} + \vec{L_2}$, $\vec{J} = \vec{K} + \vec{S_2}$.

LK-coupling scheme

$$\left(\left(n_1 l_1^{N_1}\,\alpha_1\,L_1 S_1 \cdot \left(n_2 l_2^{N_2}\,\alpha_2\,L_2 S_2\right) L\right) K\right) J \tag{13}$$

where $\vec{L} = \vec{L_1} + \vec{L_2}$, $\vec{K} = \vec{L} + \vec{S_1}$, $\vec{J} = \vec{K} + \vec{S_2}$.

LScjj-coupling scheme

$$\left(\left(n_1 l_1^{N_1}\,\alpha_1\,L_1 S_1\right) J_1 \cdot \left(n_2 l_{2-}^{N_{2-}} J_{2-} \cdot n_2 l_{2+}^{N_{2+}} J_{2+}\right) J_2\right) J \tag{14}$$

where $j = l_2 - 1/2$ for l_{2-}, $j = l_2 + 1/2$ for l_{2+}, $N_1 = N_{2-} + N_{2+}$, $\vec{J} = \vec{J_1} + \vec{J_2}$.

jj-coupling scheme

$$\left(\left(\left(n_1 l_{1-}^{N_{1-}} J_{1-} \cdot n_1 l_{1+}^{N_{1+}} J_{1+}\right) J_{12}\ n_2 l_{2-}^{N_{2-}} J_{2-}\right) J_{123}\ n_2 l_{2+}^{N_{2+}} J_{2+}\right) J \tag{15}$$

where $j = l_1 - 1/2$ for l_{1-}, $j = l_1 + 1/2$ for l_{1+}, $N_1 = N_{1-} + N_{1+}$, $\vec{J}_{12} = \vec{J}_{1-} + \vec{J}_{1+}$,

$j = l_2 - 1/2$ for l_{2-}, $j = l_2 + 1/2$ for l_{2+}, $N_2 = N_{2-} + N_{2+}$, $\vec{J}_{123} = \vec{J}_{12} + \vec{J}_{2-}$,
$\vec{J} = \vec{J}_{1123} + \vec{J}_{2+}$.

2.3   The three shells coupling

The coupling schemes LSJ, $LS3$, $LSJ3$, $JK3$, $LK3$, $cLSJ3$, and jj for three coupled shells are presented in this section.

LSJ-coupling scheme

$$\left(\left(\left(n_1 l_1^{N_1} \, \alpha_1 \, L_1 S_1 \cdot n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \right) L_{12} S_{12} \right) \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3 \right) LSJ \tag{16}$$

LS3-coupling scheme

$$\left(n_1 l_1^{N_1} \, \alpha_1 \, L_1 S_1 \cdot \left(\left(n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3 \right) L_{23} S_{23} \right) \right) LSJ \tag{17}$$

LSJ3-coupling scheme

$$\left(n_1 l_1^{N_1} \, \alpha_1 \, L_1 S_1 J_1 \cdot \left(\left(n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3 \right) L_{23} S_{23} J_{23} \right) \right) J \tag{18}$$

2.3.1   JK3-coupling scheme

$$\left(n_1 l_1^{N_1} \, \alpha_1 \, L_1 S_1 J_1 \cdot \left(\left(n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3 \right) L_{23} S_{23} \right) \right) KJ \tag{19}$$

where $\vec{K} = \vec{J}_1 + \vec{L}_{23}$, $\vec{J} = \vec{K} + \vec{S}_{23}$.

LK3-coupling scheme

$$\left(n_1 l_1^{N_1} \, \alpha_1 \, L_1 S_1 \cdot \left(\left(n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3 \right) L_{23} S_{23} \right) \right) LKJ \tag{20}$$

where $\vec{L} = \vec{L}_1 + \vec{L}_{23}$, $\vec{K} = \vec{L} + \vec{S}_1$, $\vec{J} = \vec{K} + \vec{S}_{23}$.

cLSJ3-coupling scheme

$$\Big(\big(((n_1 l_{1-}^{N_{1-}} J_{1-} \cdot n_1 l_{1+}^{N_{1+}} J_{1+}) J_1) \cdot$$

$$\cdot \big((n_2 l_2^{N_2} \, \alpha_2 \, L_2 S_2 \cdot n_3 l_3^{N_3} \, \alpha_3 \, L_3 S_3) \, L_{23} S_{23} J_{23} \big) \Big) \, J \qquad (21)$$

where $j = l_1 - 1/2$ for l_{1-}, $j = l_1 + 1/2$ for l_{1+}, $N_1 = N_{1-} + N_{1+}$, $\vec{J} = \vec{J}_1 + \vec{J}_{23}$.

jj-coupling scheme

$$\Bigg(\Bigg(\Bigg(\Bigg(\Big(n_1 l_{1-}^{N_{1-}} J_{1-} \cdot n_1 l_{1+}^{N_{1+}} J_{1+} \Big) \, J_{12} \ \ n_2 l_{2-}^{N_{2-}} J_{2-} \Big) \, J_{123} \ \cdot$$

$$\cdot \ n_2 l_{2+}^{N_{2+}} J_{2+} \Big) \, J_{1234} \ \ n_3 l_{3-}^{N_{3-}} J_{3-} \Big) \, J_{12345} \ \ n_3 l_{3+}^{N_{3+}} J_{3+} \Bigg) \, J \qquad (22)$$

where $j = l_1 - 1/2$ for l_{1-}, $j = l_1 + 1/2$ for l_{1+}, $N_1 = N_{1-} + N_{1+}$, $\vec{J}_{12} = \vec{J}_{1-} + \vec{J}_{1+}$,

$j = l_2 - 1/2$ for l_{2-}, $j = l_2 + 1/2$ for l_{2+}, $N_2 = N_{2-} + N_{2+}$, $\vec{J}_{123} = \vec{J}_{12} + \vec{J}_{2-}$, $\vec{J}_{1234} = \vec{J}_{123} + \vec{J}_{2+}$,

$j = l_3 - 1/2$ for l_{3-}, $j = l_3 + 1/2$ for l_{3+}, $N_3 = N_{3-} + N_{3+}$, $\vec{J}_{1235} = \vec{J}_{1234} + \vec{J}_{3-}$, $\vec{J} = \vec{J}_{112345} + \vec{J}_{3+}$.

3 Example calculation: P II $3p4f$

Here we present an analysis of different coupling schemes for the energy structure of P II $3p4f$. As an example, we will use three different approximations: a single reference case, an approximation that includes valence-valence correlations, and an approximation that includes valence-valence and core-valence correlations. This is just an illustration of the COUPLING program use to obtain identification of energy levels in an optimal coupling scheme in different situations. However, these examples do not show how to obtain accurate results for the energy structure itself.

The general scheme for performing these calculations with the GRASP2018 package is shown in Figure 1. At the beginning we need to generate the nuclear data as shown in Figure 2. The file `isodata` is needed for calculation of P II in any approximation.

```
rnucleus          Generation of nuclear data

    ↓

rcsfgenerate      Generation of list of CSFs based on rules
                  for excitations

    ↓

rcsfinteract      Reduction of a list to CSFs interacting with
                  the multireference

    ↓

rangular          Angular integration

    ↓

rwfnestimate      Initial estimates of radial orbitals

    ↓

rmcdhf            Self-consistent field procedure

    ↓

rci               Relativistic RCI with optional transverse photon
                  (Breit) interaction and vacuum polarization and
    ↓             self-energy (QED) corrections

jj2lsj            Transform representation from $jj$-
                  to $LSJ$-coupling

    ↓

Coupling          Present atomic state functions in different
                  coupling schemes
```

rbiotransform   Biorthonormal transf.   rhfs or rhfsd, ris Eval. of expect. values

    ↓

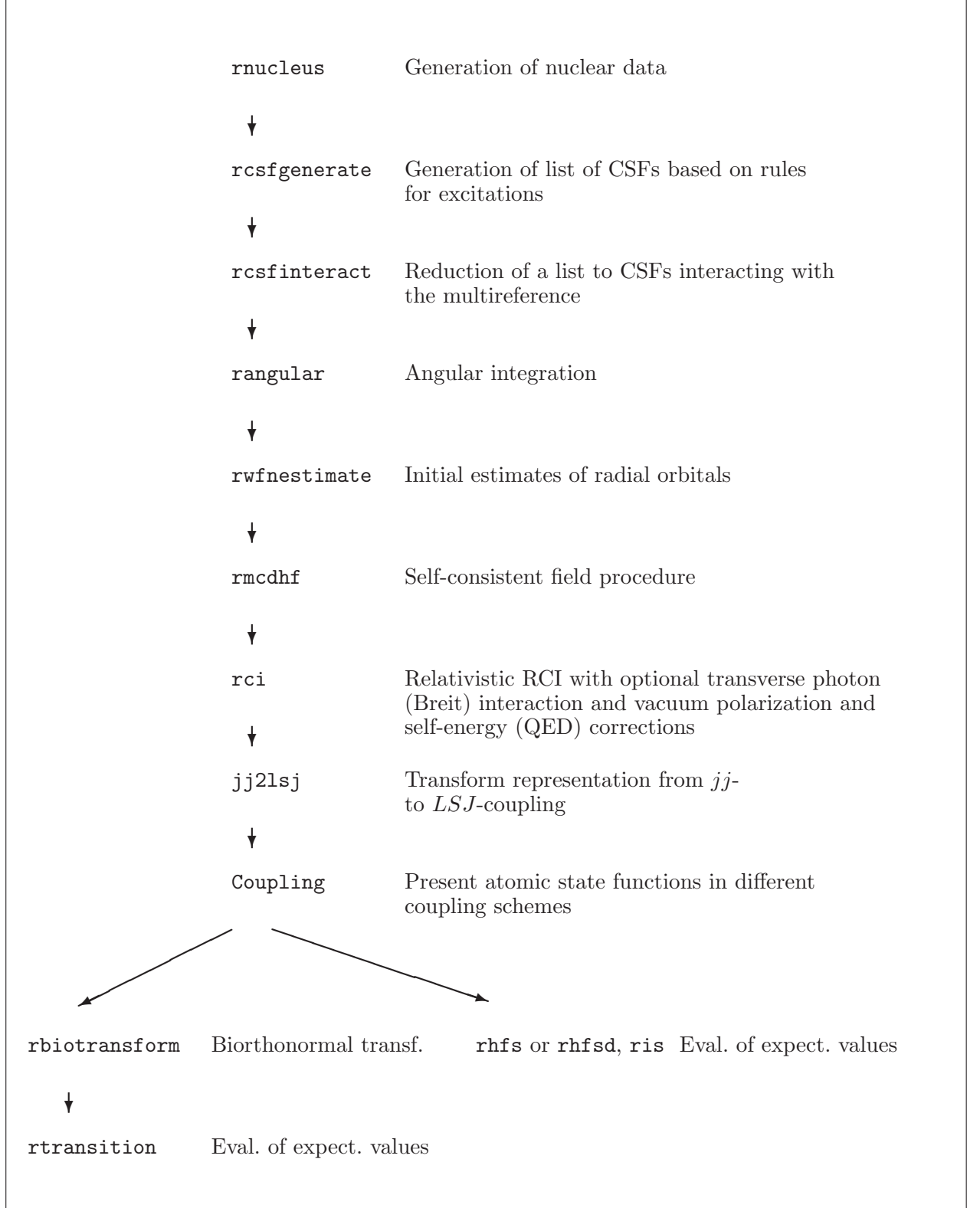rtransition   Eval. of expect. values

Fig. 1. Typical sequence of program calls to compute different expectation values in different coupling schemes.

11

```
>>rnucleus
 Enter the atomic number:
>>15
 Enter the mass number (0 if the nucleus is to be modelled as a point source:
>>10
 The default root mean squared radius is    2.37110740086665        fm;
  the default nuclear skin thickness is    2.30000000000000        fm;
 Revise these values?
>>n
 Enter the mass of the neutral atom (in amu) (0 if the nucleus is to be static):
>>10.4867
 Enter the nuclear spin quantum number (I) (in units of h / 2 pi):
>>1
 Enter the nuclear dipole moment (in nuclear magnetons):
>>1
 Enter the nuclear quadrupole moment (in barns):
>>1
```

Fig. 2. Description of an **rnucleus** session where nuclear parameters are defined for the chemical element P.

3.1   Single reference calculation

The simplest approximation of this investigation is the single reference case in which the list of configuration state functions is generated with the program **rcsfgenerate** as shown in Figure 3. The next step for calculating the energy structure of P II is to obtain the radial functions in the self-consistent field approximation. For this we need to generate initial estimates for radial orbitals with the program **rwfnestimate**, to perform spin-angular integration with the program **rangular**, and to perform the self-consistent field calculation with the program **rmcdhf** (see Figure 4). The next step is to obtain the final results of energy structure. For this we need to perform a relativistic interaction calculation in which the transverse photon interaction (Breit), vacuum polarization, and self-energy (QED) corrections are included (see Figure 5).

Now it is time to determine the optimal coupling scheme for P II. For this, we need to run the programs **jj2lsj** and COUPLING, as shown in Figure 7. Below we will discuss output files of programs which will help us to find the optimal coupling scheme for identification of energy structure.

The **<name>.lsj.lbl** *output file*

The **jj2lsj** program transforms from jj- to LSJ-coupling (10) and gives the LSJ-composition of the states. Below is the output file **SR.lsj.lbl** from the **jj2lsj** run of the RCI wave functions given in the **SR.c**, **SR.w**, **SR.cm** files. For each case, the first line gives the position (number) of the eigenstate in the interaction matrix, parity, total energy and the percentage of the atomic state function (ASF) that has been transformed.

```
 Pos   J   Parity      Energy Total      Comp. of ASF
```

```
>>rcsfgenerate
 RCSFGENERATE
 This program generates a list of CSFs

 Configurations should be entered in spectroscopic notation
 with occupation numbers and indications if orbitals are
 closed (c), inactive (i), active (*) or has a minimal
 occupation e.g. 1s(2,1)2s(2,*)
 Outputfiles: rcsf.out, rcsfgenerate.log

 Default, reverse, symmetry or user specified ordering? (*/r/s/u)
>>*
 Select core
        0: No core
        1: He (       1s(2)                  =  2 electrons)
        2: Ne ([He] + 2s(2)2p(6)             = 10 electrons)
        3: Ar ([Ne] + 3s(2)3p(6)             = 18 electrons)
        4: Kr ([Ar] + 3d(10)4s(2)4p(6)       = 36 electrons)
        5: Xe ([Kr] + 4d(10)5s(2)5p(6)       = 54 electrons)
        6: Rn ([Xe] + 4f(14)5d(10)6s(2)6p(6) = 86 electrons)
>>2
 Enter list of (maximum 100) configurations. End list with a blank line or an as
 terisk (*)

 Give configuration           1
>>3s(2,i)3p(1,i)4f(1,i)
 Give configuration           2
>>
 Give set of active orbitals, as defined by the highest principal quantum number
 per l-symmetry, in a comma delimited list in s,p,d etc order, e.g. 5s,4p,3d
>>3s,3p,4f
 Resulting 2*J-number? lower, higher (J=1 -> 2*J=2 etc.)
>>2,10
 Number of excitations (if negative number e.g. -2, correlation
 orbitals will always be doubly occupied)
>>0
 Generate more lists ? (y/n)
>>n
  Excitation data file opened


........


 12 configuration states have been generated.
 12 configuration states in the final list.
 Generate another list? (y/*)

 Group CSFs into symmetry blocks

 5 blocks were created

         block   J/P           NCSF
             1    1+              1
             2    2+              3
             3    3+              4
             4    4+              3
             5    5+              1
```

Fig. 3. A `rcsfgenerate` session in which the list of CSF is generated.

```
RMCDHF
This program determines the radial orbitals
and the expansion coefficients of the CSFs
in a self-onsistent field proceedure
Input file:  isodata, rcsf.inp, rwfn.inp, mcp.30, ...
Outputfiles: rwfn.out, rmix.out, rmcdhf.sum, rmcdhf.log

 Loading CSF file ... Header only
 There are/is           9  relativistic subshells;
 Loading CSF File for ALL blocks
 There are          12  relativistic CSFs... load complete;
 Loading Radial WaveFunction File ...
 Default settings?  (y/n)  There are           5  blocks
>>y
 (block   J/Parity   NCF):
  1   1+        1    2   2+        3    3   3+        4    4   4+        3
  5   5+        1

 Enter ASF serial numbers for each block
 Block            1   ncf =           1  id =    1+
>>1
 Block            2   ncf =           3  id =    2+
>>1-3
 Block            3   ncf =           4  id =    3+
>>1-4
 Block            4   ncf =           3  id =    4+
>>1-3
 Block            5   ncf =           1  id =    5+
>>1
 level weights (1 equal;  5 standard;  9 user)
>>1
 Radial functions
 1s 2s 2p- 2p 3s 3p- 3p 4f- 4f
 Enter orbitals to be varied (Updating order)
>>*
 Which of these are spectroscopic orbitals?
>>*
 Enter the maximum number of SCF cycles:
>>999

 Average energy =  -3.4001530036D+02 Hartrees
 Average energy =  -3.4001742077D+02 Hartrees
 Average energy =  -3.4001989369D+02 Hartrees
 Average energy =  -3.4001863578D+02 Hartrees
 Average energy =  -3.4001770882D+02 Hartrees

.....

Weighted average energy of these levels =  -3.4061719642D+02

Generalised occupation numbers:

   2.0000D+00  2.0000D+00  2.0000D+00  4.0000D+00  2.0000D+00  3.3333D-01
   6.6667D-01  5.0000D-01  5.0000D-01

 Wall time:
        0 seconds

 Finish Date and Time:
   Date (Yr/Mon/Day): 2019/01/21
   Time (Hr/Min/Sec): 12/56/40.250
   Zone: +0200

 RMCDHF: Execution complete.
```

Fig. 4. A `rmcdhf` session in which the radial wave functions are calculated for P II.

```
 RCI
 This is the configuration interaction program
 Input file:  isodata, name.c, name.w
 Outputfiles: name.cm, name.csum, name.clog
              rci.res (can be used for restart)

Default settings?
>>y
Name of state:
>>SR
 Block              1 ,  ncf =               1
 Block              2 ,  ncf =               3
 Block              3 ,  ncf =               4
 Block              4 ,  ncf =               3
 Block              5 ,  ncf =               1
 Loading CSF file ... Header only
 There are/is              9  relativistic subshells;
 Include contribution of H (Transverse)?
>>y
 Modify all transverse photon frequencies?
>>n
 Include H (Vacuum Polarisation)?
>>y
 Include H (Normal Mass Shift)?
>>n
 Include H (Specific Mass Shift)?
>>n
 Estimate self-energy?
>>y
 Largest n quantum number for including self-energy for orbital
 n should be less or equal 8
>>3
 Loading Radial WaveFunction File ...
 There are          5  blocks  (block   J/Parity   NCF):
   1   1+      1      2   2+      3      3   3+      4      4   4+      3
   5   5+      1

 Enter ASF serial numbers for each block
 Block              1   ncf =              1  id =    1+
>>1
 Block              2   ncf =              3  id =    2+
>>1-3
 Block              3   ncf =              4  id =    3+
>>1-4
 Block              4   ncf =              3  id =    4+
>>1-3
 Block              5   ncf =              1  id =    5+
>>1
 Calling STRSUM...
 Calling FACTT...
 Calling GENINTRK...
 Allocating space for          664  Rk integrals
 Calling GENINTBREIT1...
 Computing         4282  Breit integrals of type 1
 Calling GENINTBREIT2...
 Computing         2130  Breit integrals of type 2

...

 Wall time:
        0 seconds

 Finish Date and Time:
   Date (Yr/Mon/Day): 2019/01/21
   Time (Hr/Min/Sec): 12/56/41.255
   Zone: +0200

 RCI: Execution complete.
```

Fig. 5. A `rci` session in which the energy structure is calculated for P II.

```
  1     1      +             -340.499397452      100.000%
        -1.00000000    1.00000000    3s(2).3p_2P.4f_3D


  1     2      +             -340.505325391      100.000%
         0.96663641    0.93438595    3s(2).3p_2P.4f_3F
         0.19033942    0.03622909    3s(2).3p_2P.4f_1D
         0.17142040    0.02938495    3s(2).3p_2P.4f_3D
  ...
```

There is a one state per energy value. For each state the file gives the LSJ-expansion. The $J = 1$ state (pos 1) with even parity and energy -340.499397452 a.u. has the LSJ-expansion

```
        -1.00000000    1.00000000    3s(2).3p_2P.4f_3D
```

We see that the state is close to pure LSJ-coupling and the file provides meaningful labels that match labels given, for example, in the data tables of the National Institute of Standards and Technology (NIST). The first column of the output gives expansion coefficients (signed amplitudes), while the second column gives the LSJ-composition, i.e. the squared expansion coefficients.

Finally, a few words about how to interpret the notation in the composition of the ASF. Each shell in the configuration is given with occupation, LS term designation and Nielson-Koster indexes [5]. When the shell is singly or fully occupied, the term designation and Nielson-Koster indexes are not written out. The LS term for each shell is coupled from left to right. Intermediate couplings are given after the underscore symbol _.

There is a list of all possible terms and their Nielson-Koster indexes for commonly occurring shells in [5].

Consider the following example of how to interpret the notation:

```
    3s(2).3p_2P.4f_3D
```

The first shell 3s(2) is fully occupied and has only one LS term ^1S that is not written out explicitly. The second shell 3s is singly occupied and has one LS term ^1P that is not written out explicitly. Coupling ^1S and ^2P from of shells one and two leads to the intermediate LS term 2P. The third shell has only one LS term ^2F that is not written out explicitly. Coupling 2P and ^2F leads to the final LS term 3D.

The programs rtablevels and rtabtransE1 from GRASP2018 package [6] implement a LaTeX translation of the ASCII notation. In the LaTeX translation the LS term and seniority of a shell are given in parentheses just after the shell. For the intermediate terms the underscore of the ASCII notation

has been replaced by a space. In the LaTeX translation the user also has a choice to omit the closed core. Translating the above example to LaTeX and omitting the `3s(2)` we get

$$3p(^2P)\ 4f\ ^3D.$$

The `<name>.coup2.LS.lbl` *output file*

The COUPLING program presents the LSJ-composition (10) of the states. Below is the output file `SR.coup2.LS.lbl` from the COUPLING run of the RCI wave functions given in the `SR.lsj.c`, `SR.j` files which was created by the program `jj2lsj` in not default mode.

```
Pos   J   Parity        Energy Total       Comp. of ASF
 1    1                  -340.499397452      100.000%
        -1.00000000    1.00000000   3p_4f_ 3D<1>


 1    2                  -340.505325391      100.000%
         0.96663641    0.93438595   3p_4f_ 3F<2>
         0.19033942    0.03622909   3p_4f_ 1D<2>
         0.17142040    0.02938495   3p_4f_ 3D<2>
 ...
```

The content of the file is the same as for `SR.lsj.lbl` but notation of ASF is sligthly modified according to the notations of NIST's Atomic Spectra database. Consider the following example of how to interpret the notation of ASF:

```
    3p_4f_ 3D<1>
```

The first shell `3p` is singly occupied and has only one LS term ^2P that is not written out explicitly. The second shell `4f` is singly occupied and has only one LS term ^2F that is not written out explicitly. Coupling ^2P and ^2F from of shells one and two leads to the final LS term `3D`. The total value `J=1` is presented in angular brackets.

The `<name>.coup2.jj.lbl` *output file*

The COUPLING program transforms from LSJ- to jj-coupling (15) and gives the jj-composition of the states. Below is the output file `SR.coup2.jj.lbl` from the COUPLING run of the RCI wave functions given in the `SR.c`, `SR.lsj.j` files, which were created by the program `jj2lsj` in a non-default mode.

```
Pos   J   Parity        Energy Total       Comp. of ASF
```

```
-------------------------------------------------------------------------
Subshell TERMS (J, seniority)

 s(1)    (1/2 1)
 s(2)    (0   0)

 p-(1)   (1/2 1)
 p-(2)   (0   0)

 p+(1)   (3/2 1)
 p+(2)   (0   0) (2   2)

 d-(1)   (3/2 1)
 d-(2)   (0   0) (2   2)

 d+(1)   (5/2 1)
 d+(2)   (0   0) (2   2) (4   2)
 d+(3)   (5/2 1) (3/2 3) (9/2 3)

 f-(1)   (5/2 1)
 f-(2)   (0   0) (2   2) (4   2)
 f-(3)   (5/2 1) (3/2 3) (9/2 3)

 f+(1)   (7/2 1)
 f+(2)   (0   0) (2   2) (4   2) (6   2)
 f+(3)   (7/2 1) (3/2 3) (5/2 3) (9/2 3) (11/2 3) (15/2 3)
 f+(4)   (0   0) (2   2) (4   2) (6   2) (2   4) (4   4) (5   4) (8   4)
-------------------------------------------------------------------------
```

Fig. 6. List of possible terms and their seniority for commonly occurring subshells in jj-coupling.

```
    1    1                   -340.499397452      100.000%
            1.00000000    1.00000000   3p+_4f-_ <1>


    1    2                   -340.505325391      100.000%
            0.83512514    0.69743400   3p-_4f-_ <2>
           -0.52219380    0.27268637   3p+_4f-_ <2>
           -0.17285725    0.02987963   3p+_4f+_ <2>
...
```

There is a list of possible terms and their seniority for commonly occurring subshells in Figure 6.

The content of the file is the same as for `SR.lsj.lbl` but notation of ASF is in jj-coupling. Consider the following example of how to interpret the notation of ASF:

        3p+_4f-_ <1>

The first and second subshells, 3p+ and 4f-, each have only one possible jj term, J=3/2 and J=5/2, respectively, which are not written out explicitly. The second subshell 4f- is singly occupied and has only one jj term J=5/2 that is not written out explicitly. Coupling J=3/2 and J=5/2 from these two subshells leads to the final J=1.

18

The `<name>.coup2.JJ.lbl` *output file*

The COUPLING program transforms from LSJ- to JJ-coupling (11) and gives the JJ-composition of the states. Below is the output file `SR.coup2.JJ.lbl` from the COUPLING run of the RCI wave functions given in the `SR.lsj.c`, `SR.lsj.j` files, which were created by the program `jj2lsj` in a non-default mode.

```
Pos   J   Parity        Energy Total        Comp. of ASF
  1   1                  -340.499397452       100.000%
        1.00000000    1.00000000   3p<3/2>.4f<5/2> (3/2,5/2)<1>
  1   2                  -340.505325391       100.000%
        0.83512514    0.69743400   3p<1/2>.4f<5/2> (1/2,5/2)<2>
       -0.52219380    0.27268637   3p<3/2>.4f<5/2> (3/2,5/2)<2>
       -0.17285725    0.02987963   3p<3/2>.4f<7/2> (3/2,7/2)<2>
 ...
```

The content of the file is the same as for `SR.lsj.lbl` but notation of ASF is in JJ-coupling. Consider the following example of how to interpret the notation of ASF:

```
 3p<3/2>.4f<5/2> (3/2,5/2)<1>
```

The first and second subshells, `3p` and `4f`, each have only one possible LS term (^2P and ^2F, respectively), which are not written out explicitly, with J=3/2 and J=5/2, respectively, which are written in angular brackets. Coupling J=3/2 and J=5/2 from these two subshells (written in parentheses) leads to the final J=1 that is written in angular brackets. Duplication of the J values of the subshells in the final term is due to the fact that the final term designations are often used without the configuration labels in contexts limited to one non-relativistic configuration.

The `<name>.coup2.JK.lbl` *output file*

The COUPLING program transforms from LSJ- to JK-coupling (12) and gives the JK-composition of the states. Below is the output file `SR.coup2.JK.lbl` from the COUPLING run of the RCI wave functions given in the `SR.c`, `SR.lsj.j` files, which were created by the program `jj2lsj` in a non-default mode.

```
Pos   J   Parity        Energy Total        Comp. of ASF
  1   1                  -340.499397452       100.000%
        1.00000000    1.00000000   3p<3/2>.4f_ 2[3/2]<1>
  1   2                  -340.505325391       100.000%
        0.83512514    0.69743400   3p<1/2>.4f_ 2[5/2]<2>
       -0.54992020    0.30241223   3p<3/2>.4f_ 2[5/2]<2>
```

```
    ...
```

The content of the file is the same as for `SR.lsj.lbl`, but the notation of ASF is in JK-coupling. Consider the following example of how to interpret the notation of ASF:

```
 3p<3/2>.4f_ 2[3/2]<1>
```

The first subshell `3p` is singly occupied and has only one LS term ^2P that is not written out explicitly. The orbital angular momentum `L`$_1$`=1` of the first shell is coupled with the spin `S`$_1$`=1/2` of the term of the first shell and gives the total angular momentum `J`$_1$`=3/2` of the first shell that is written in angular brackets. The second subshell `4f` is singly occupied and has only one LS term ^2F that is not written out explicitly. The total angular momentum `J`$_1$`=3/2` of the first shell is coupled with the orbital angular momentum `L`$_2$`=3` of the second shell to obtain the resultant `K`$=$`3/2` angular momentum of the final term that is written in square brackets. The multiplicity (`"2"`) of the K term arises from the spin `S`$_2$`=1/2` of the term of the second shell that is written before the square brackets. Coupling `K`$=$`3/2` with the spin of the second shell `S`$_2$`=1/2` leads to the final `J`$=$`1` that is written in angular brackets.

The `<name>.coup2.LK.lbl` *output file*

The COUPLING program transforms from LSJ- to LK-coupling (13) and gives the LK-composition of the states. Below is the output file `SR.LK.lbl` from the COUPLING run of the RCI wave functions given in the `SR.lsj.c`, `SR.j` files, which were created by the program `jj2lsj` in a non-default mode.

```
 Pos   J   Parity      Energy Total      Comp. of ASF
  1    1                 -340.499397452     101.000%
       -1.00000000     1.00000000   3p_ 4f_ D_2[3/2]<1>
  1    2                 -340.505325391     101.000%
        0.96663641     0.93438595   3p_ 4f_ F_2[5/2]<2>
        0.25585206     0.06546028   3p_ 4f_ D_2[5/2]<2>
  ...
```

The content of the file is the same as for `SR.lsj.lbl`, but the ASF notation is in LK-coupling. Consider the following example of how to interpret the notation of ASF:

```
    3p_ 4f_ D_2[3/2]<1>
```

The first and second subshells `3p` and `4f` each have only one possible LS term (^2P and ^2F, respectively), which are not written out explicitly. The second

subshell 4f is singly occupied and has only one LS term ^2F that is not written out explicitly.

The orbital angular momentum L_1=1 of the first shell is coupled with the orbital angular momentum L_2=3 of the second shell to give the total orbital angular momentum L=2 that is written as D. After this, the total orbital angular momentum L=2 is coupled with the spin S_1=1/2 from the term of the first shell to obtain the resultant K=3/2 angular momentum of the final term that is written in square brackets. The multiplicity ("2") of the K term arises from the spin S_2=1/2 of the term of the second shell and is written before the square brackets. Coupling K=3/2 with the spin of the second shell S_2=1/2 leads to the final J term J=1 that is written in angular brackets.

The <name>.coup2.LScjj.lbl *output file*

The COUPLING program transforms from LSJ- to $LScjj$-coupling (14) and gives the $LScjj$-composition of the states. Below is the output file SR.coup2.LScjj.lbl from the COUPLING run of the RCI wave functions given in the SR.lsj.c, SR.lsj.j files, which were created by the program jj2lsj in a non-default mode.

```
Pos   J   Parity        Energy Total       Comp. of ASF
 1    1                   -340.499397452      100.000%
        1.00000000    1.00000000   3p_<3/2> 4f-_(5/2,0)<5/2> (3/2,5/2)<1>
 1    2                   -340.505325391      100.000%
        0.83512514    0.69743400   3p_<1/2> 4f-_(5/2,0)<5/2> (1/2,5/2)<2>
       -0.52219380    0.27268637   3p_<3/2> 4f-_(5/2,0)<5/2> (3/2,5/2)<2>
       -0.17285725    0.02987963   3p_<3/2> 4f+_(0,7/2)<7/2> (3/2,7/2)<2>
 ...
```

The content of the file is the same as for SR.lsj.lbl, but the ASF notation is in $LScjj$-coupling. Consider the following example of how to interpret the notation of ASF:

```
3p_<3/2> 4f-_(5/2,0)<5/2> (3/2,5/2)<1>
```

The first shell 3p presented in LS-coupling is singly occupied and has only one LS term ^2P that is not written out explicitly, but its J_1=3/2 value is written in angular brackets. The second subshell 4f- that is presented in jj-coupling is singly occupied and has a total J value J_-=5/2. Meanwhile, the subshell 4f+ is empty, and its total J value is J_+=0. The subshell J values J_-=5/2 and J_+=0 are written in parentheses as "(5/2,0)". The total orbital momentum J_2=5/2 of the subshells 4f- and 4f+ is written in angular brackets. The J values J_1=3/2 and J_2=5/2 are written in parentheses in the designation of the final term. The total J value J=1 of the ASF is written in angular brackets.

The `<name>.coup2.sum` *output file*

The Coupling program creates the `SR.coup2.sum` file in which all the necessary information about the problem is listed. At the beginning of the file the input to the program is printed. After this, the summary of output is printed.

```
        -------------------------------
        Summry file of program COUPLING
        -------------------------------


 The CSF input file:                SR.lsj.c
 The mixing coefficient input file: SR.lsj.j
 There are            2 (in LS-coupling) coupled shells case.
 Specification of couplings:  yyyynnnnnynyn
 (LS JJ LK JK LS3 LSJ3 LK3 JK3 cLSJ3 LScjj jj1 jj2 jj3)
   y  y  y  y  n   n   n   n    n    y    n   y   n


 The value below which an eigenvector composition
 is to be neglected for printing:   1.0000000000000000E-002


 List of the shells included in the recoupling:
 3p 4f



 Symmetry block:     1
 Total number of CSF in the input file =        1  (number of csf in expansion)
 -----------------------------------------------------------------
 List of configurations which are eliminated from the calculation

    No.           Configurations
 -----------------------------------------------------------------
 -----------------------------------------------------------------
 Number of states =     1
 ------------------------------------------------------------------------
 List of maximum values of expansion coefficients and  Summation rules
 ------------------------------------------------------------------------
 State   Maximum value   Maximum value   Expansion    Summation
 No.     included in     removed from    size         rules
         calculations    calculations
 ------------------------------------------------------------------------
    1                                       1    1.00000000000000000
 ------------------------------------------------------------------------


JJ coupling:
     end count_nr_of_csfs_JJ
```

```
State number    Expansion size    Summation rules
         1             1         0.99999999999999778


LK coupling:
State number    Expansion size    Summation rules
         1             1         1.0000000000000000


JK coupling:
State number    Expansion size    Summation rules
         1             1         0.99999999999999778


LScjj coupling:
State number    Expansion size    Summation rules
         1             1         0.99999999999999911


jj2 coupling:
State number    Expansion size    Summation rules
         1             1         1.0000000000000004
 -------------------------------------------------------
 -------------------------------------------------------
 There is one-to-one coupling
...
...
...
 --------------------------------------------------
 List of  P  values in different coupling schemes:
 (The bigger P the better is coupling)
    LS  coupling             0.799
    JJ  coupling             0.727
    LK  coupling             0.880
    JK  coupling             0.759
    LScjj coupling           0.727
    jj2 coupling             0.727
 --------------------------------------------------
```

The program cannot transform all configuration state functions in one run and, depending on the input, omits some configuration state functions from the calculations. These configuration state functions are listed in the file as

```
 ----------------------------------------------------------------
 List of configurations which are eliminated from the calculation

    No.           Configurations
 ------  --------------------------------------------------------
 ----------------------------------------------------------------
```

In this example all configurations in the transformation were included, therefore, no configurations are printed.

In the printout below

```
---------------------------------------------------------------------
List of maximum values of expansion coefficients and  Summation rules
---------------------------------------------------------------------
State   Maximum value   Maximum value   Expansion   Summation
No.     included in     removed from    size        rules
        calculations    calculations
---------------------------------------------------------------------
   1                                        1     1.00000000000000000
---------------------------------------------------------------------
```

there are listed the value of the largest expansion coefficient included in the calculation and the value of the largest expansion coefficient omitted from the calculations. In this example all configurations were transformed, therefore no information about these coefficients appears in this case. Also the summation rules (1) (in this case `1.00000000000000000`) indicating the accuracy of the results are printed. The results will be correct (with good accuracy) if they meet the following criteria:

- the value of the largest expansion coefficient omitted from the calculations is a small number;
- the value of the largest expansion coefficient omitted from the calculations is much smaller than the largest expansion coefficient included in the calculations;
- the value of the summation rule is close to one.

The program also presents the summation rules (1) for all coupling schemes for which the program performs the transformation. In this case the value of the summation rule

for JJ-coupling (11) is `0.99999999999999778`,

for LK-coupling (12) is `1.0000000000000000`,

for JK-coupling (13) is `0.9999999999999778`,

for $LScjj$-coupling (14) is `0.99999999999999911`,

and for jj-coupling (15) is `1.0000000000000004`.

All these values must be very close to the value in the LS-coupling. Otherwise, it indicates that transformation was performed insufficiently accurately and/or

24

not completely.

At the end of the output file `SR.coup2.sum` the value of the parameter P_s (2) for the different coupling schemes is listed. These values indicate how much the particular coupling scheme is useful for identification. The line in the output

```
There is one-to-one coupling
```

informs the user that there are the coupling scheme(s) with one-to-one identification of the states between the investigated coupling schemes.

<div align="center">*   *   *</div>

Identifiers of the most suitable coupling are specified in the files `SR.coup2.sum` and/or `SR.coup2.<coupling_name>.lbl`.

From all these files we learn that the LK coupling is optimal in our case. We prepare a correct format of the file `SR.lsj.lbl` as

```
cp SR.coup2.LK.lbl SR.lsj.lbl
```

for optimal classification. This file is later used for printing out the energy structure in the selected set of coupling schemes in the file `energy_levels_SR`

```
rlevels SR.cm  > energy_levels_SR .
```

Figure 8 presents the energy structure of P II. All energy levels are in LK coupling. The files `SR.c`, `SR.w`, `SR.cm`, and `SR.lsj.lbl` can be used for further calculations, such as transitions (the programs `rtansition` or `rtansition_mpi` from the Grasp2018 package) or hyperfine structure (the program `rhfs_lsj` from the Grasp2018 package). The determined combination of coupling schemes will be maintained in these calculations, as well as in the final output.

```
jj2lsj << S1
SR
y
n
n
y
0
0.01
S1

Coupling << S2
SR
y
2
0.01
3p 4f
S2

cp SR.coup2.LK.lbl SR.lsj.lbl

rlevels SR.cm > energy_levels_SR
```

Fig. 7. A `jj2lsj` and COUPLING script for calculation of eigenvectors in different coupling schemes for P II.

```
 Splitting is the energy difference with the lower neighbor
----------------------------------------------------------------------------------------
 No Pos  J Parity Energy Total   Levels    Splitting    Configuration
                    (a.u.)      (cm^-1)     (cm^-1)
----------------------------------------------------------------------------------------
  1  1   3   +    -340.5054773     0.00        0.00    3p_ 4f_ F_2[5/2]<3>
  2  1   2   +    -340.5053254    33.34       33.34    3p_ 4f_ F_2[5/2]<2>
  3  2   3   +    -340.5051295    76.34       43.00    3p_ 4f_ F_2[7/2]<3>
  4  1   4   +    -340.5049739   110.48       34.14    3p_ 4f_ F_2[7/2]<4>
  5  3   3   +    -340.5023171   693.59      583.10    3p_ 4f_ G_2[7/2]<3>
  6  2   4   +    -340.5020299   756.61       63.03    3p_ 4f_ G_2[7/2]<4>
  7  1   5   +    -340.5009213   999.92      243.31    3p_ 4f_ G_2[9/2]<5>
  8  4   3   +    -340.5004784  1097.13       97.21    3p_ 4f_ D_2[5/2]<3>
  9  2   2   +    -340.5002083  1156.42       59.29    3p_ 4f_ D_2[5/2]<2>
 10  3   4   +    -340.5001265  1174.37       17.95    3p_ 4f_ G_2[9/2]<4>
 11  1   1   +    -340.4993975  1334.37      160.00    3p_ 4f_ D_2[3/2]<1>
 12  3   2   +    -340.4990694  1406.36       71.99    3p_ 4f_ D_2[3/2]<2>
----------------------------------------------------------------------------------------
```

Fig. 8. The final results of the single reference calculations. The energy structure of P II labeled by optimal coupling schemes.

In this example we demonstrate the use of the Coupling program to search for an optimal coupling scheme for P II in valance-valence calculations. For this, we generate a configuration state list containing single and double excitations from $3p4f$ to $4s, 4p, 3d, 4f$ orbitals (see Figure 9).

The procedures for calculation of the radial functions in the self-consistent field approximation and calculation of the energy structure are similar to those described in Subsection 3.1.

Figure 10 shows how to search for an optimal coupling scheme in this case. We are searching for it separately in each symmetry block.

We obtain the name of the most suitable coupling scheme from the files `VV.coup2.sum` and `VV.coup2.<coupling_name>.lbl`. The LK coupling is optimal in this example, too.

We prepare a correct format of the file `VV.lsj.lbl` as

```
cp VV.coup2.LK.lbl VV.lsj.lbl .
```

This file is later used for printing out the energy structure in the selected set of coupling schemes

```
rlevels VV.cm > energy_levels_VV .
```

Figure 11 presents energy structure of P II. All energy levels are in LK coupling.

```
>>rcsfgenerate
 RCSFGENERATE
 This program generates a list of CSFs

 Configurations should be entered in spectroscopic notation
 with occupation numbers and indications if orbitals are
 closed (c), inactive (i), active (*) or has a minimal
 occupation e.g. 1s(2,1)2s(2,*)
 Outputfiles: rcsf.out, rcsfgenerate.log

 Default, reverse, symmetry or user specified ordering? (*/r/s/u)
>>*
 Select core
        0: No core
        1: He (       1s(2)                    =  2 electrons)
        2: Ne ([He] + 2s(2)2p(6)               = 10 electrons)
        3: Ar ([Ne] + 3s(2)3p(6)               = 18 electrons)
        4: Kr ([Ar] + 3d(10)4s(2)4p(6)         = 36 electrons)
        5: Xe ([Kr] + 4d(10)5s(2)5p(6)         = 54 electrons)
        6: Rn ([Xe] + 4f(14)5d(10)6s(2)6p(6)   = 86 electrons)
>>2
 Enter list of (maximum 100) configurations. End list with a blank line or an as
 terisk (*)

 Give configuration           1
>>3s(2,i)3p(1,*)4f(1,*)
 Give configuration           2
>>
 Give set of active orbitals, as defined by the highest principal quantum number
 per l-symmetry, in a comma delimited list in s,p,d etc order, e.g. 5s,4p,3d
>>4s,4p,3d,4f
 Resulting 2*J-number? lower, higher (J=1 -> 2*J=2 etc.)
>>2,10
 Number of excitations (if negative number e.g. -2, correlation
 orbitals will always be doubly occupied)
>>2
 Generate more lists ? (y/n)
>>n
  Excitation data file opened


........


 58 configuration states have been generated.
 58 configuration states in the final list.
 Generate another list? (y/*)

 Group CSFs into symmetry blocks

 5 blocks were created

        block   J/P          NCSF
            1    1+            11
            2    2+            21
            3    3+            12
            4    4+            11
            5    5+             3
```

Fig. 9. A `rcsfgenerate` session for valence-valence calculation in which the list of CSF is generated.

```
jj2lsj << S1
VV
y
n
n
y
0
0.01
S1


Coupling << S2
VV
y
2
0.01
3p 4f 3d 4p 5f
S2

cp VV.coup2.LK.lbl VV.lsj.lbl

rlevels VV.cm > energy_levels_VV
```

Fig. 10. A `jj2lsj` and Coupling script for calculation of the energy structure in the valence-valence approximation in different coupling schemes for P II.

```
 Splitting is the energy difference with the lower neighbor
----------------------------------------------------------------------------------
 No Pos  J Parity Energy Total    Levels    Splitting    Configuration
                     (a.u.)      (cm^-1)     (cm^-1)
----------------------------------------------------------------------------------
  1  3   2   +   -340.5056803      0.00        0.00   3p_ 4f_ F_2[5/2]<2>
  2  1   3   +   -340.5056554      5.47        5.47   3p_ 4f_ F_2[5/2]<3>
  3  1   4   +   -340.5053766     66.65       61.18   3p_ 4f_ F_2[7/2]<4>
  4  2   3   +   -340.5052728     89.45       22.80   3p_ 4f_ F_2[7/2]<3>
  5  2   4   +   -340.5025243    692.68      603.23   3p_ 4f_ G_2[7/2]<4>
  6  3   3   +   -340.5023360    734.01       41.33   3p_ 4f_ G_2[7/2]<3>
  7  3   4   +   -340.5010218   1022.42      288.42   3p_ 4f_ G_2[9/2]<4>
  8  1   5   +   -340.5009213   1044.48       22.06   3p_ 4f_ G_2[9/2]<5>
  9  4   3   +   -340.5005826   1118.83       74.35   3p_ 4f_ D_2[5/2]<3>
 10  4   2   +   -340.5004440   1149.24       30.41   3p_ 4f_ D_2[5/2]<2>
 11  2   1   +   -340.4994776   1361.34      212.10   3p_ 4f_ D_2[3/2]<1>
 12  5   2   +   -340.4994036   1377.59       16.25   3p_ 4f_ D_2[3/2]<2>
----------------------------------------------------------------------------------
```

Fig. 11. The final results for the valence-valence calculation. The energy structure of P II in the optimal coupling schemes.

3.3 Calculations including both valence-valence and core-valence excitations

Finally, we demonstrate the use of the Coupling program for finding an optimal coupling scheme for P II in calculations that include both valence-valence and core-valence excitations (hereafter, denoted as VV+CV). For this, we generate a configuration state list containing single and double excitations from $3p4f$ to the $4s, 4p, 3d, 4f$ orbitals and at the same time single excitations from core orbital $3s$ to the $4s, 4p, 3d, 4f$ orbitals (see Figure 12). In this case we have some configurations with an open core orbital $3s$ in the configuration state list (the file `CV.c`). Therefore, the optimal coupling scheme should be found by recoupling three shells $3s$, $3p$, and $4f$. It can be done by using the script presented in Figure 13.

29

We can define several sets of optimal coupling schemes from the files `CV.coup3.sum` and/or `CV.coup3.<coupling_name>.lbl`. One of them is the jj coupling. The reason for the change in the "optimal" coupling (from LK to jj) is probably related with the fact that for three open shells only two coupling schemes LS and jj were used to couple shells from left to right. For other couplings (i.e. $LS3$, $LSJ3$, $LK3$, $LK3$, and $cLSJ3$) the last two shells were coupled firstly, and the left side shell was coupled subsequently (see subsection 2.3). Meanwhile, the coupling in two shells case, as presented in Subsections 3.1 and 3.2, is always done from the left shell to the right shell (see subsection 2.2). This variation of coupling schemes, used for coupling of two and three shells, is based on [3].

Figure 14 presents the energy structure of P II labeled in the jj coupling scheme. We can also use a similar coupling scheme described in subsections 3.1 and 3.2. Figure 15 presents the energy structure of P II labeled in the set of $LK3$ coupling.

```
>>rcsfgenerate
 RCSFGENERATE
 This program generates a list of CSFs

 Configurations should be entered in spectroscopic notation
 with occupation numbers and indications if orbitals are
 closed (c), inactive (i), active (*) or has a minimal
 occupation e.g. 1s(2,1)2s(2,*)
 Outputfiles: rcsf.out, rcsfgenerate.log

 Default, reverse, symmetry or user specified ordering? (*/r/s/u)
>>*
 Select core
        0: No core
        1: He (       1s(2)                  =  2 electrons)
        2: Ne ([He] + 2s(2)2p(6)             = 10 electrons)
        3: Ar ([Ne] + 3s(2)3p(6)             = 18 electrons)
        4: Kr ([Ar] + 3d(10)4s(2)4p(6)       = 36 electrons)
        5: Xe ([Kr] + 4d(10)5s(2)5p(6)       = 54 electrons)
        6: Rn ([Xe] + 4f(14)5d(10)6s(2)6p(6) = 86 electrons)
>>2
 Enter list of (maximum 100) configurations. End list with a blank line or an as
 terisk (*)

 Give configuration            1
>>3s(2,1)3p(1,*)4f(1,*)
 Give configuration            2
>>
 Give set of active orbitals, as defined by the highest principal quantum number
 per l-symmetry, in a comma delimited list in s,p,d etc order, e.g. 5s,4p,3d
>>4s,4p,3d,4f
 Resulting 2*J-number? lower, higher (J=1 -> 2*J=2 etc.)
>>2,10
 Number of excitations (if negative number e.g. -2, correlation
 orbitals will always be doubly occupied)
>>2
 Generate more lists ? (y/n)
>>n
  Excitation data file opened


........


 943 configuration states have been generated.
 943 configuration states in the final list.
 Generate another list? (y/*)

 Group CSFs into symmetry blocks

 5 blocks were created

        block  J/P          NCSF
            1    1+           172
            2    2+           237
            3    3+           228
            4    4+           186
            5    5+           120
```

Fig. 12. A `rcsfgenerate` session for VV+CV calculation in which the list of CSF
is generated.

31

```
jj2lsj << S1
CV
y
n
n
y
0
0.01
S1

Coupling << S2
CV
y
3
0.01
3s 3p 4f 3d 4p 5f
S2

cp CV.coup3.jj.lbl CV.lsj.lbl
rlevels CV.cm > energy_levels_CV_jj

cp CV.coup3.LK3.lbl CV.lsj.lbl

rlevels CV.cm > energy_levels_CV_LK3
```

Fig. 13. A `jj2lsj` and COUPLING script for calculation of the energy structure in the VV+CV approximation in different coupling schemes for P II.

```
 Splitting is the energy difference with the lower neighbor
------------------------------------------------------------------------------------------
 No Pos  J Parity Energy Total    Levels    Splitting     Configuration
                     (a.u.)       (cm^-1)    (cm^-1)
------------------------------------------------------------------------------------------
  1  1   3   +    -340.5205445      0.00       0.00    3s+2_3p-_<1/2>.4f+_(7/2) <3>
  2  3   2   +    -340.5202373     67.42      67.42    3s+2_3p-_<1/2>.4f-_(5/2) <2>
  3  2   3   +    -340.5201443     87.82      20.41    3s+2_3p-_<1/2>.4f-_(5/2) <3>
  4  1   4   +    -340.5199618    127.88      40.05    3s+2_3p-_<1/2>.4f+_(7/2) <4>
  5  3   3   +    -340.5163207    927.01     799.14    3s+2_3p+_<3/2>.4f-_ <3>
  6  2   4   +    -340.5160606    984.09      57.08    3s+2_3p+_<3/2>.4f+_(7/2) <4>
  7  1   5   +    -340.5145396   1317.92     333.83    3s+2_3p+_<3/2>.4f+_(7/2) <5>
  8  4   3   +    -340.5143603   1357.28      39.36    3s+2_3p+_<3/2>.4f+_(7/2) <3>
  9  4   2   +    -340.5139563   1445.93      88.66    3s+2_3p+_<3/2>.4f-_ <2>
 10  3   4   +    -340.5136051   1523.03      77.09    3s+2_3p+_<3/2>.4f-_ <4>
 11  2   1   +    -340.5127713   1706.01     182.98    3s+2_3p+_<3/2>.4f-_(5/2) <1>
 12  5   2   +    -340.5125074   1763.93      57.91    3s+2_3p+_<3/2>.4f+_ <2>
------------------------------------------------------------------------------------------
```

Fig. 14. The final results for the VV+CV calculation. The energy structure of P II labeled in the optimal coupling schemes suggested by the COUPLING program.

```
Splitting is the energy difference with the lower neighbor
-----------------------------------------------------------------------------------
No Pos  J Parity Energy Total    Levels    Splitting     Configuration
                     (a.u.)      (cm^-1)    (cm^-1)
-----------------------------------------------------------------------------------
  1  1  3  +    -340.5205445       0.00       0.00   3s2_ 3p_4f_(1F) F_1[3]<3>
  2  3  2  +    -340.5202373      67.42      67.42   3s2_ 3p_4f_(3F) F_3[3]<2>
  3  2  3  +    -340.5201443      87.82      20.41   3s2_ 3p_4f_(3F) F_3[3]<3>
  4  1  4  +    -340.5199618     127.88      40.05   3s2_ 3p_4f_(3F) F_3[3]<4>
  5  3  3  +    -340.5163207     927.01     799.14   3s2_ 3p_4f_(3G) G_3[4]<3>
  6  2  4  +    -340.5160606     984.09      57.08   3s2_ 3p_4f_(3G) G_3[4]<4>
  7  1  5  +    -340.5145396    1317.92     333.83   3s2_ 3p_4f_(3G) G_3[4]<5>
  8  4  3  +    -340.5143603    1357.28      39.36   3s2_ 3p_4f_(3D) D_3[2]<3>
  9  4  2  +    -340.5139563    1445.93      88.66   3s2_ 3p_4f_(3D) D_3[2]<2>
 10  3  4  +    -340.5136051    1523.03      77.09   3s2_ 3p_4f_(1G) G_1[4]<4>
 11  2  1  +    -340.5127713    1706.01     182.98   3s2_ 3p_4f_(3D) D_3[2]<1>
 12  5  2  +    -340.5125074    1763.93      57.91   3s2_ 3p_4f_(1D) D_1[2]<2>
-----------------------------------------------------------------------------------
```

Fig. 15. The final results for the VV+CV calculation. The energy structure of P II labeled in the optimal coupling schemes found in the valence-valence calculation.

4 Acknowledgments

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online at `http://www.nist.gov/pml/pubs/atspec/index.cfm`.

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