

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

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

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

$$P_s = \frac{\sum_J P_J}{\sum_J m_J}, \quad (2)$$

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

$$P_J = \sum_{k=1}^{m_J} a_{max\ k}^2 \quad (3)$$

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

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 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	$J_1 L_2 (\rightarrow K)$	K, S_2	$^{2S_2+1}[K]$	JK	$J_1 [K]_J$	2	JK	(6)
4	$LS_1 (\rightarrow K)$	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:

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

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

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

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

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	$3d^7(^4F) \ 4s4p(^3P^\circ) \ ^6F_{9/2}^\circ$	3	LS3	(17)
3	$4f^7(^8S^\circ) \ 6s6p(^4P) \ ^{11}P_5^\circ$	3	LS3	(17)
4	$3p^5(^2P^\circ) \ 3d^2(^1G) \ ^2F_{7/2}^\circ$	2	LSJ	(10)
5	$4f^{10}(^3K2) \ 6s6p(^1P^\circ) \ ^3L_6^\circ$	3	LS3	(17)
6	$4f^7(^8S^\circ) \ 5d \ (^7D^\circ) \ 6p \ ^8F_{13/2}^e$	3	LSJ	(16)
7	$4f^7(^8S^\circ) \ 5d^2(^1G) \ (^8G^\circ) \ 6p \ ^7F_0$	3	LSJ	(16)
8	$4f(^2F^\circ) \ 5d^2(^1G) \ 6s \ (^2G) \ ^1P_1^\circ$	3	LSJ	(16)
• jj Coupling				
9	$\left(6p_{1/2}^2\right)_0$	1	jj	(9)
10	$\left(6p_{1/2}^2 6p_{3/2}\right)_{3/2}^\circ$	1	jj	(15)
11	$\left(6p_{1/2}^2 6p_{3/2}^2\right)_2$	1	jj	(15)
12	$4d_{5/2}^3 4d_{3/2}^2 (9/2, 2)_{11/2}$	1	jj	(15)
• J_1j or J_1J_2 Coupling				
13	$3d^9 \ (^2D_{5/2}) \ 4p_{3/2} \ (5/2, 3/2)_3^\circ$	2	LScj j	(14)
14	$4f^{11} \ (^2H_{9/2}^\circ) \ 6s6p \ (^3P_1^\circ) \ (9/2, 1)_{7/2}$	3	LSJ3	(18)
15	$5f_{7/2}^4 5f_{5/2}^5 (8, 5/2)_{21/2}^\circ 7p_{3/2} \ (21/2, 3/2)_{10}$	2	jj	(15)
16	$5f_{7/2}^3 5f_{5/2}^3 (9/2, 9/2)_9 7s7p \ (^3P_2^\circ) \ (9, 2)_7^\circ$	3	cLSJ3	(21)
• J_1l or J_1L_2 Coupling (J_1K Coupling)				
17	$3p^5 \ (^2P_{1/2}^\circ) \ 5g^2 \ [9/2]_5^\circ$	2	JK	(12)
18	$4f^2 \ (^3H_4) \ 5g^2 \ [3]_{5/2}$	2	JK	(12)
19	$4f^{13} \ (^2F_{7/2}^\circ) \ 5d^2 \ (^1D) \ ^1[7/2]_{7/2}^\circ$	2	JK	(12)
20	$4f^{13} \ (^2F_{5/2}^\circ) \ 5d6s \ (^3D) \ ^3[9/2]_{11/2}^\circ$	3	JK3	(19)
• LS_1 Coupling (LK Coupling)				
21	$3s^2 3p \ (^2P^\circ) \ 4f \ G \ ^2[7/2]_3$	2	LK	(13)
22	$3d^7 \ (^4P) \ 4s4p \ (^3P^\circ) \ D^\circ \ ^3[5/2]_{7/2}^\circ$	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 $(3d^7 (^4F) 4s4p (^3P^\circ) ^6F_{9/2}^\circ)$ 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 $(4f^7(^8S^\circ)5d (^7D^\circ)6p ^8F_{13/2}^\circ)$ 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_j^N 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

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 $4d_{5/2}^3$ and $4d_{3/2}^2$ 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 $4d_{5/2}^3$ 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.

LS₁ 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).

* * *

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 , LS_{cjj} , and jj for two coupled shells are presented in this section.

LSJ-coupling scheme

$$\left(n_1 l_1^{N_1} \alpha$$

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+} , $N_2 = N_{2-} + N_{2+}$, $\vec{J}_{123} = \vec{J}_{12} + \vec{J}_{2-}$,
 $\vec{J} = \vec{J}_{123} + \vec{J}_{2+}$.

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

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

LS3-coupling scheme

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

LSJ3-coupling scheme

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

2.3.1 *JK3-coupling scheme*

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

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

LK3-coupling scheme

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

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

$$\begin{aligned} & \left((n_1 l_{1-}^{N_{1-}} J_{1-} \cdot n_1 l_{1+}^{N_{1+}} J_{1+}) J_1 \right) \cdot \\ & \cdot \left((n_2 l_{2-}^{N_{2-}} \alpha_2 L_2 S_2 \cdot n_3 l_{3-}^{N_{3-}} \alpha_3 L_3 S_3) L_{23} S_{23} J_{23} \right) J \end{aligned} \quad (21)$$

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

$$\begin{aligned} & \left(\left(\left(\left(n_1 l_{1-}^{N_{1-}} J_{1-} \cdot n_1 l_{1+}^{N_{1+}} J_{1+} \right) J_{12} \ n_2 l_{2-}^{N_{2-}} J_{2-} \right) J_{123} \cdot \right. \right. \\ & \left. \left. \cdot n_2 l_{2+}^{N_{2+}} J_{2+} \right) J_{1234} \ n_3 l_{3-}^{N_{3-}} J_{3-} \right) J_{12345} \ n_3 l_{3+}^{N_{3+}} J_{3+} \right) J \end{aligned} \quad (22)$$

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

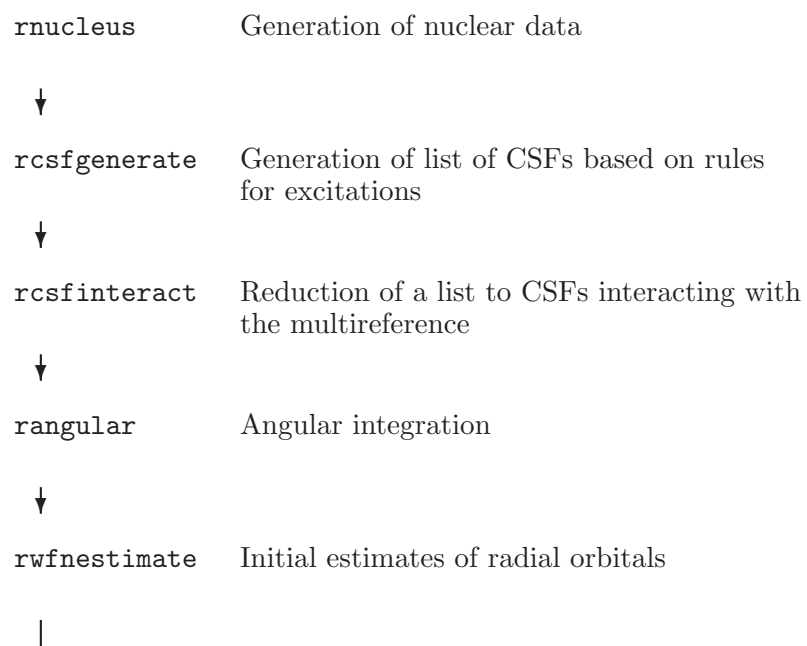
$j = l_2 - 1/2$ for l_{2-} , $j = l_2 + 1/2$ for l_{2+} , $N_2 = N_{2-} + N_{2+}$, $\vec{J}_{123} = \vec{J}_{12} + \vec{J}_{2-}$,
 $\vec{J}_{1234} = \vec{J}_{123} + \vec{J}_{2+}$,

$j = l_3 - 1/2$ for l_{3-} , $j = l_3 + 1/2$ for l_{3+} , $N_3 = N_{3-} + N_{3+}$, $\vec{J}_{1235} = \vec{J}_{1234} + \vec{J}_{3-}$,
 $\vec{J} = \vec{J}_{12345} + \vec{J}_{3+}$.

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 schemtsd2739(o)-0.328784(r)-327.629(s)-52845(1.77.126613(v)26.675088(e)-325.739(o)



```

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      2.300000000000000      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( a ) or has a minimal
occupation e.g. 1s 2, i 2s 2, a
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/n )

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-consistent field procedure
Input file  isodata, rcsf.inp, rwn.inp, mcp.30, ...
Outputfiles rwn.out, rmix.out, rmcdf.sum, rmcdf.log

Loading CSF file ... Header only
There are/is      0  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,  0 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
000

Average energy ~ -3.4001530036D+02 Hartrees
Average energy ~ -3.4001742077D+02 Hartrees
Average energy ~ -3.400174364D+02 Hartrees
Average energy ~ -3.4001863578D+02 Hartrees
Average energy ~ -3.4001770882D+02 Hartrees

.....

Weighted average energy of these levels ~ -3.406171642D+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, 2012/01/21
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      0 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)  2012/01/21
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%
			-1.000000000	1.000000000
				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

-1.000000000	1.000000000	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]

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.1b1 output file

The COUPLING program presents the LSJ -composition (10) of the states. Below is the output file `SR.coup2.LS.1b1` from the COUPLING run of the RCI wave functions given in the `SR.1sj.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%
		-1.000000000	1.000000000	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.1sj.1b1` but notation of ASF is slightly 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.1b1 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.1b1` from the COUPLING run of the RCI wave functions given in the `SR.c`, `SR.1sj.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 2 (7/2 2	
f	1	(5/2 1	
f	2	(0 0 (2 2 (4 2	
f	3	(5/2 1 (3/2 2 (7/2 2	
f	1	(7/2 1	
f	2	(0 0 (2 2 (4 2 (6 2	
f	3	(7/2 1 (3/2 2 (5/2 2 (7/2 2 (9/2 2 (11/2 2 (13/2 2	
f	4	(0 0 (2 2 (4 2 (6 2 (8 2 (10 2 (12 2 (14 2 (16 2	

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

1	1	-340.499397452	100.000%
	1.000000000	1.000000000	3p+_4f-_ <1>
1	2	-340.505325391	100.000%
	0.83512514	0.69743400	3p-_4f-_ <2>
	-0.52219380	0.297000.000%	
	0.83512514	0.<..005J	4353p38.000%
	0.83514		

The <name>.coup2.JJ.1b1 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.1b1 from the COUPLING run of the RCI wave functions given in the SR.1sj.c, SR.1sj.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.1sj.1b1 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.1b1 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.1b1 from the COUPLING run of the RCI wave functions given in the SR.c, SR.1sj.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.1b1`, 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.1b1 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.1b1` 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%
		-1.000000000	1.000000000	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.1b1`, 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

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.

Summary 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 No.	Maximum value included in calculations	Maximum value removed from calculations	Expansion size	Summation rules

1			1	1.0000000000000000

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	1.00000000000000000

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	1.00000000000000004

 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 No.	Maximum value included in calculations	Maximum value removed from calculations	Expansion size	Summation rules

1			1	1.000000000000000000

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 1.0000000000000000) 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 0.9999999999999778,

for LK -coupling (12) is 1.0000000000000000,

for JK -coupling (13) is 0.9999999999999778,

for $LScjj$ -coupling (14) is 0.9999999999999911,

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

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.

* * *

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.10.26640% 1 0.-0.1.2 0.-0.0.0% 1 0.-0.1.2 0.26640% 1 0.-0.1.2 0.53040% 1 0.-0.1.2 0.-0.1.2 1.988 0 Td

```

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 (a.u.)	Levels (cm ⁻¹)	Splitting (cm ⁻¹)	Configuration
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	+	-340.5051245	76.34	43.00	3p_ 4f_ F_2[7/2] 3
4	1	4	+	-340.504739	110.48	34.14	3p_ 4f_ F_2[7/2] 4
5	3	3	+	-340.5023171	63.5	583.10	3p_ 4f_ G_2[7/2] 3
6	2	4	+	-340.502029	756.61	63.03	3p_ 4f_ G_2[7/2] 4
7	1	5	+	-340.500213	999.92	243.31	3p_ 4f_ G_2[9/2] 5
8	4	3	+	-340.5004784	107.13	97.21	3p_ 4f_ D_2[5/2] 3
9	2	2	+	-340.5002083	1156.42	5.2	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	+	-340.499375	1334.37	160.00	3p_ 4f_ D_2[3/2] 1
12	3	2	+	-340.499064	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.

3.2 Valence-valence calculations

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( 0 , inactive( 1 , active( 2 or has a minimal
occupation e.g. 1s 2, 1p 2s 2, 2p
Outputfiles rcsf.out, rcsfgenerate.log

Default, reverse, symmetry or user specified ordering( */r/s/1
*
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, 1p 3p 1, 2f 4f 1, 2
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/n

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 (a.u.)	Levels (cm ⁻¹)	Splitting (cm ⁻¹)	Configuration
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	82.45	22.80	3p_ 4f_ F_2[7/2] 3
5	2	4	+	-340.5025243	62.68	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	+	-340.500213	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	1142.24	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	1377.52	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.

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( 0 , inactive( 1 , active( 2 or has a minimal
occupation e.g. 1s 2, 1p 2s 2, 2p
Outputfiles rcsf.out, rcsfgenerate.log

Default, reverse, symmetry or user specified ordering( */r/s/1
*
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, 1p 3p 1, 2f 1, 2
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

.....

43 configuration states have been generated.
43 configuration states in the final list.
Generate another list? ( y/n

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.

```

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 (a.u.)	Levels (cm ⁻¹)	Splitting (cm ⁻¹)	Configuration
1	1	3	+	-340.5205445	0.00	0.00	3s+2_3p- $\frac{1}{2}$.4f+ $\frac{7}{2}$ \leftarrow 3
2	3	2	+	-340.5202373	67.42	67.42	3s+2_3p- $\frac{1}{2}$.4f- $\frac{5}{2}$ \leftarrow 2
3	2	3	+	-340.5201443	87.82	20.41	3s+2_3p- $\frac{1}{2}$.4f- $\frac{5}{2}$ \leftarrow 3
4	1	4	+	-340.5199618	127.88	40.05	3s+2_3p- $\frac{1}{2}$.4f+ $\frac{7}{2}$ \leftarrow 4
5	3	3	+	-340.5163207	927.01	799.14	3s+2_3p+ $\frac{3}{2}$.4f- $\frac{3}{2}$ \leftarrow 3
6	2	4	+	-340.5160606	984.09	57.08	3s+2_3p+ $\frac{3}{2}$.4f+ $\frac{7}{2}$ \leftarrow 4
7	1	5	+	-340.5145396	1317.92	333.83	3s+2_3p+ $\frac{3}{2}$.4f+ $\frac{7}{2}$ \leftarrow 5
8	4	3	+	-340.5143603	1357.28	39.36	3s+2_3p+ $\frac{3}{2}$.4f+ $\frac{7}{2}$ \leftarrow 3
9	4	2	+	-340.5139563	1445.93	88.66	3s+2_3p+ $\frac{3}{2}$.4f- $\frac{3}{2}$ \leftarrow 2
10	3	4	+	-340.5136051	1523.03	77.09	3s+2_3p+ $\frac{3}{2}$.4f- $\frac{3}{2}$ \leftarrow 4
11	2	1	+	-340.5127713	1706.01	182.98	3s+2_3p+ $\frac{3}{2}$.4f- $\frac{5}{2}$ \leftarrow 1
12	5	2	+	-340.5125074	1763.93	57.91	3s+2_3p+ $\frac{3}{2}$.4f+ $\frac{3}{2}$ \leftarrow 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 (a.u.)	Levels (cm ⁻¹)	Splitting (cm ⁻¹)	Configuration
1	1	3	+	-340.5205445	0.00	0.00	3s2_ 3p_4f(1F ₃ F_1[3] 3
2	3	2	+	-340.5202373	67.42	67.42	3s2_ 3p_4f(3F ₃ F_3[3] 2
3	2	3	+	-340.5201443	87.82	20.41	3s2_ 3p_4f(3F ₃ F_3[3] 3
4	1	4	+	-340.5199618	127.88	40.05	3s2_ 3p_4f(3F ₃ F_3[3] 4
5	3	3	+	-340.5163207	227.01	79.14	3s2_ 3p_4f(3G ₃ G_3[4] 3
6	2	4	+	-340.5160606	284.02	57.08	3s2_ 3p_4f(3G ₃ G_3[4] 4
7	1	5	+	-340.5145336	1317.22	333.83	3s2_ 3p_4f(3G ₃ G_3[4] 5
8	4	3	+	-340.5143603	1357.28	33.36	3s2_ 3p_4f(3D ₃ D_3[2] 3
9	4	2	+	-340.5139563	1445.23	88.66	3s2_ 3p_4f(3D ₃ D_3[2] 2
10	3	4	+	-340.5136051	1523.03	77.02	3s2_ 3p_4f(1G ₃ G_1[4] 4
11	2	1	+	-340.5127713	1706.01	182.98	3s2_ 3p_4f(3D ₃ D_3[2] 1
12	5	2	+	-340.5125074	1763.23	57.21	3s2_ 3p_4f(1D ₃ 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.

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