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Theoretical Interpretation of the Third Spectrum of Gold (Au III)*

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The levels belonging to the configurations $5d^9+5d^86s$ and $5d^86p$ of Au III were calculated and compared with experiment with an rms error of about 260 cm^{-1}. By using semiempirical methods and theoretical calculations it is shown that these configurations are best described by use of the *j–j* coupling scheme.

Key Words: Analysis, atomic energy levels, atomic spectra, doubly ionized gold, *j–j* coupling, theoretical

1. Introduction

In a paper by L. Iglesias [1][2] an analysis of the spectrum of Au III is reported. Seventeen even levels are reported, belonging to the configurations $5d^9$ and $5d^86s$. The baricenter of the configuration d^8s is about 40000 cm^{-1} higher than the baricenter of d^9. Only the highest level of d^8s was not observed. Forty-three odd levels reported in reference [1] belong to the configuration $5d^86p$. Two of these levels are doubtful. For the d^8p configuration, the theory predicts 45 levels. In reference [1] the even levels are grouped into terms. The assignments given to the odd levels are tentative. Only their total J is really known.

The use of $L–S$ coupling assignments for the even levels of Au III seemed to us rather problematical for the following reasons: (1) The spread of some terms is of the order of magnitude of 10000 cm^{-1}, (2) many terms overlap, (3) from the distance between the two levels of d^9, which are practically unperturbed, one sees that the spin-orbit interaction parameter ζ_d is larger than 5000 cm^{-1}. This is much larger than the approximate values of the electrostatic parameters as estimated from previous calculations [2] on Pt II, while the necessary presumption for $L–S$ coupling is that the electrostatic interaction is considerably stronger than the spin-orbit interaction.

Because of this situation we thought it worthwhile to try to interpret the levels of Au III by use of the *j–j* coupling scheme. In this scheme it is assumed that the spin-orbit interaction is much stronger than the electrostatic interaction. Thus for every electron its orbital angular momentum is first coupled with its spin. We designate by small j the total angular momentum of an individual electron, which is a good quantum number in this scheme.

In d^9 only two states occur, which differ by their total J. Hence all the coupling schemes are equivalent. In d^8s and d^8p we first have to specify the "parent state" generated by the d electrons. Then we add the angular momentum of the outer electron to the total angular momentum J_d of all the d electrons and obtain the total angular momentum J of the state. For d electrons, j may be either 3/2 or 5/2. Thus the configuration d^8 splits into three fundamental groups:

$$(1)\quad d^4_{3/2}d^4_{5/2},\qquad (2)\quad d^3_{3/2}d^5_{5/2},\qquad (3)\quad d^2_{3/2}d^6_{5/2}.$$

The superscript gives the number of d electrons having the given j. Since we are dealing with an almost closed shell of d electrons, it is more convenient to characterize the parent states by counting the number of d-electron "holes" in the two subshells with $j=3/2$ and $j=5/2$. From now on "$d_{3/2}$" and "$d_{5/2}$" will not symbolize electrons but electron holes. The three fundamental groups will be designated:

$$(1)\quad d^2_{5/2},\qquad (2)\quad d_{3/2}d_{5/2},\qquad (3)\quad d^2_{3/2}.$$

Since we are dealing with holes, the spin-orbit interaction is negative. Hence the first group is the lowest one, the second group is the intermediate one and the third group is the highest group.

In groups (1) and (3) we have two equivalent holes. Thus, in order to get antisymmetric states J_d can assume only even values. For group (2), J_d can assume any value which is consistent with the triangular condition. Now we have the full list of the parent states. The different states belonging to the same group are distinguished by their values of J_d. The degeneracy of these states is removed by introducing a weak electrostatic interaction. We shall write J_d as a subscript. We get the list of 9 parent states, as follows:

$$\text{(I)}\quad (d^2_{5/2})_0,\qquad (d^2_{5/2})_2,\qquad (d^2_{5/2})_4$$

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[2] Figures in brackets indicate the literature references at the end of this paper.

(II) $(d_{3/2}d_{5/2})_1$, $(d_{3/2}d_{5/2})_2$, $(d_{3/2}d_{5/2})_3$, $(d_{3/2}d_{5/2})_4$

(III) $(d^2_{3/2})_0$, $(d^2_{3/2})_2$.

In order to get the states of d^8s, we have to add to J_d the j of the s electron which has the magnitude 1/2. For d^8p, one has to add to J_d the j of the p electron, 1/2 or 3/2.

We shall describe separately the treatment of these two configurations.

The Qualitative Treatment of the Configuration $5d^86s$. First we shall write down the list of j–j states for d^8s. It is sufficient to check which parent-states of d^8 appear for each total J. They are:

$J=1/2$	$J=3/2$	$J=5/2$	$J=7/2$	$J=9/2$
$(d^2_{5/2})_0$ $(d_{3/2}\ d_{5/2})_1$ $(d^2_{3/2})_0$	$(d^2_{5/2})_2$ $(d_{3/2}\ d_{5/2})_1$ $(d_{3/2}\ d_{5/2})_2$ $(d^2_{3/2})_2$	$(d^2_{5/2})_2$ $(d_{3/2}\ d_{5/2})_2$ $(d_{3/2}\ d_{5/2})_3$ $(d^2_{3/2})_2$	$(d^2_{5/2})_4$ $(d_{3/2}\ d_{5/2})_3$ $(d_{3/2}\ d_{5/2})_4$	$(d^2_{5/2})_4$ $(d_{3/2}\ d_{5/2})_4$

In this list we have 7 parents with $J_d \neq 0$ occurring twice and 2 terms belonging to the parents $(d^2_{5/2})_0$ and $(d^2_{3/2})_0$ occurring once.

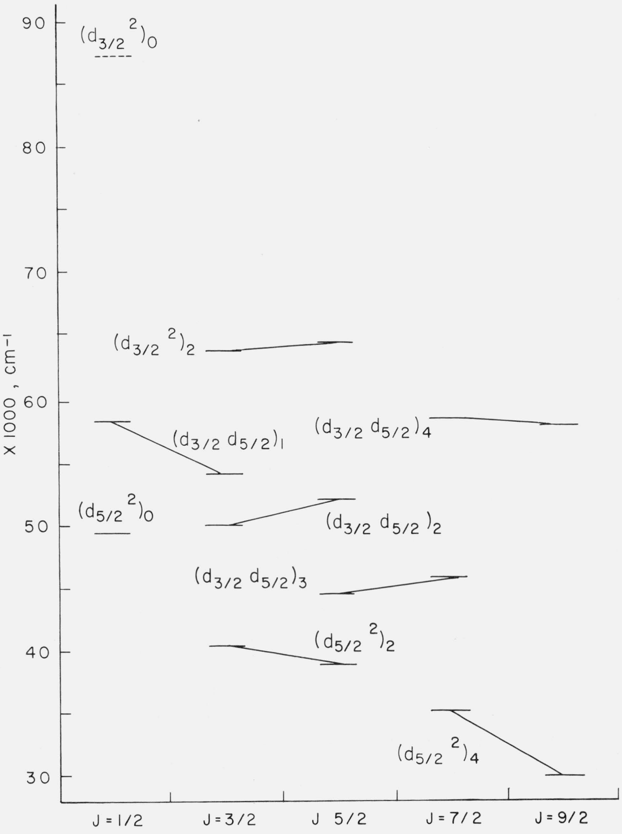

FIGURE 1. *The levels of the configuration* $5d^86s$.

Now we can compare this list with figure 1, where the observed levels of d^8s are represented. For $J=1/2$, 9/2 the situation is very simple, since only one representative (at most) of each of the three fundamental groups of parents (defined earlier) appears in them. Hence, for $J=9/2$ it is obvious that the low-lying level belongs to $(d^2_{5/2})_4$ and the high one to $(d_{3/2}\ d_{5/2})_4$. For $J=1/2$ it is clear that the low lying level is the singlet belonging to $(d^2_{5/2})_0$. The second level having $J=1/2$ belongs to $(d_{3/2}\ d_{5/2})_1$. The level belonging to $(d^2_{3/2})_0$ is the highest level of the configuration and was not observed.

For $J=3/2$, 5/2, 7/2 we always have 2 levels belonging to 2 parent terms which are both members of group II. For example, for $J=5/2$ we know that the lowest level belongs to $(d^2_{5/2})_2$ and the highest one belongs to $(d^2_{3/2})_2$, but we do not know which of the remaining levels belongs to $(d_{3/2}\ d_{5/2})_2$ and which one belongs to $(d_{3/2}\ d_{5/2})_3$. But this difficulty can be easily overcome if we start from the two levels with $J=9/2$ and connect each of them with the nearest level having $J=7/2$. The only remaining level with $J=7/2$ obviously belongs to the parent $(d_{3/2}\ d_{5/2})_3$, which is not represented in $J=9/2$. Now we can proceed from $J=7/2$ to $J=5/2$, and so on. By this way the j–j coupling classification can be very easily and uniquely completed. Only on the passage from $J=5/2$ to $J=3/2$ are there two levels with $J=3/2$ which apparently could be connected with the level belonging to $(d_{3/2}\ d_{5/2})_2$. However, only the highest of these two levels can be connected to the level with $J=1/2$ belonging to $(d_{3/2}\ d_{5/2})_1$. Thus, the uniqueness of the classification is preserved.

The classification could also be done by calculating the diagonal elements of a weak electrostatic interaction as a function of J_d, but in this section we wanted to show that such a classification can be performed without any theoretical calculation.

Several problems remain open. First of all, we did not *prove* the assumption that the actual states of Au III are j–j states, but we showed that this assumption leads to a reasonable interpretation. Next, even if the j–j coupling scheme is the best one, one can hardly expect pure states, so that it is interesting to have information on mixtures of states. It is also very interesting to check whether the empirical grouping of levels (in reference [1] and in the present section as well) is consistent with the theoretical assignments which one can get by diagonalization of the complete Hamiltonian including the spin orbit interaction and the electrostatic interaction as well.

To answer all these questions a quantitative treatment of the spectrum of Au III is necessary.

2. Notations and Definitions

Before we start to describe the quantitative treatment we shall give short definitions of the parameters used in the calculations.

The parameter A is an additive constant common to all the levels of a configuration.

The parameters B and C are linear combinations of Slater integrals: $B=F_2(d^2)-5F_4(d^2)$, and $C=35F_4(d^2)$. The parameter $G=G_2(ds)$ measures the exchange interaction between d and s electrons. The quantity $H=(1/35)R^2(dd, ds)$ is the parameter of the interaction of the configuration d^8s with the configuration d^9. The term α is the parameter of the $L(L+1)$ correction. The term ζ_d is the parameter of the spin-orbit interaction of a d electron-hole. The configurations d^9+d^8s were calculated together and their parameters are given in table 1. In order to distinguish between parameters which appear in both configurations we use the symbols A and ζ_d for d^9 and the symbols A′ and ζ_d' for d^8s.

For the configuration d^8p we use also the electrostatic parameters A, B, C. In addition we need three parameters to describe the interaction between d and p electrons: $F_2=F_2(dp)$ describes the direct interaction between them, while $G_1=G_1(dp)$ and $G_3=G_3(dp)$ describe their exchange interaction. In addition to ζ_d we use also ζ_p, which is the parameter of spin-orbit interaction of the p electron.

"Diag." is an abbreviation for "diagonalization" and "L.S." is an abbreviation for "least-squares calculation."

The quantitative treatment of the configurations (d^9+d^8s). We estimated starting values for the parameters in the first diagonalization in the following way. From a preliminary calculation on the isoelectronic spectrum of Pt II [2] we took the values of B, C and G. Vaules for H and α were taken from a general treatment of the first spectra of the Pt group [3], which was then in progress. ζ_d, A and A′ were estimated from the experimental levels of Au III, and ζ_d' was set equal to ζ_d. All these parameters are given in table 1 under the column "Diag. 1." In the following least-squares calculation (L.S. 1) we got an rms error of ±276 cm^{-1}. The parameters C and G changed rather strongly. For α we got the value -1 ± 33; also the uncertainty of H is bigger than its value.

In the following diagonalization (Diag. 2) we used for the parameters the values obtained in L.S. 1. The parameter α was given the value zero. Diag. 2 was followed by two least-squares calculations. In L.S. 2a all the parameters are free and we got an rms error of ±298. For H and α we got the values -120 ± 907 and -10 ± 47, respectively. Both are meaningless and equal to zero within their statistical errors. In L.S. 2b, α was forced to be equal to zero. The rms error reduced to ±281 cm^{-1}, but H remained meaningless and equal to zero within its uncertainty. This means that the interaction between the configurations d^9 and d^8s is very weak.

In the third diagonalization (Diag. 3) the parameters of L.S. 2b were used; both H and α were given the value zero. In the following least-squares (L.S. 3) α and H were forced to remain equal to zero and we got an rms error of ±266 cm^{-1}. The values of all the parameters of L.S. 3 are equal to their values in Diag. 3. This indicates that convergence of the mathematical process was reached. Thus, the calculated levels of L.S. 3 are the best theoretical predictions, within the approximation we use. The parameters of the various stages of the calculation are given in table 1.

The elements of the energy matrices are usually calculated in the L–S coupling scheme. Thus the process of diagonalization gives us directly the eigenvectors in this scheme. They are simply the rows of the diagonalizing orthogonal matrix. The j–j coupling eigenvectors are calculated in the following way. Let us denote by H_1 the energy matrix in the L–S coupling scheme and by H_2 the energy matrix in the j–j coupling scheme. E is the diagonalized energy matrix. We define three orthogonal matrixes Ω_1, Ω_2 and T by the following equations:

$$\Omega_1 H_1 \tilde{\Omega}_1 = E, \tag{1a}$$

$$\Omega_2 H_2 \tilde{\Omega}_2 = E, \tag{1b}$$

$$T H_1 \tilde{T} = H_2. \tag{1c}$$

Of course, the rows of Ω_1 are the L–S coupling eigenvectors, the rows of Ω_2 are the j–j coupling eigenvectors, and T is the transformation matrix from the L–S scheme to the j–j scheme. It is not necessary to calculate H_2 and diagonalize it in order to obtain Ω_2.

TABLE 1. *Parameters of the configurations* d^9+d^8s *in the various stages of the calculation*

	Daig. 1	L.S. 1	Diag. 2	L.S. 2a	L.S. 2b	Diag. 3	L.S. 3
A	6000	5063 ± 460	5063	4917 ± 594	5002 ± 411	5000	5002 ± 380
A′ − A	44000	44762 ± 602	44762	45039 ± 824	44900 ± 458	44900	44899 ± 407
B	540	596 ± 35	596	597 ± 42	605 ± 16	605	605 ± 13
C	2700	3782 ± 309	3782	3794 ± 423	3711 ± 138	3710	3711 ± 106
G	3200	2802 ± 112	2800	2815 ± 119	2812 ± 111	2810	2812 ± 105
H	500	253 ± 322	270	−120 ± 907	46 ± 415	0	....
α	30	−1 ± 33	0	−10 ± 47	....	0	....
ζ_d	5300	5068 ± 176	5068	5050 ± 196	5068 ± 166	5070	5068 ± 157
ζ_d'	5300	5426 ± 62	5426	5395 ± 72	5402 ± 62	5400	5401 ± 59
Δ	....	± 276	....	± 298	± 281	....	± 266

Δ designates the rms error in the calculated levels.

Instead, we use the relation

$$\Omega_2 = \Omega_1 \cdot \tilde{T}. \tag{2}$$

The matrix T is calculated by performing diagonalization with fictitious parameters in which ζ_d is given a very large value, B is given a very small value and all other parameters are equal to zero. In this case the diagonalized energy matrix is in the j–j scheme, so that the diagonalizing matrix is equal to T. It is necessary to give B a nonzero value in order to remove the degeneracy between states which differ only by their values of J_d.

The computer program which we use for the above-mentioned calculations is described in a paper by G. Racah [4].

The results of our calculations on the configurations $5d^9+5d^86s$ are given in table 2. The levels are grouped according to their j–j classification. This arrangement practically avoids overlapping. In addition to the j–j percentage composition the square of the largest component of the L–S eigenvector is also given. For d^9 both couplings are equivalent.

TABLE 2. *Observed and calculated levels of the configurations* $5d^9+5d^86s$

Conf.	j–j Coupling Assignment	J	L–S coupling largest component	Observed	Calculated	O–C
d^9	100% $d_{5/2}$	5/2	100% ^2D	0.0	0	0
d^9	100% $d_{3/2}$	3/2	100% ^2D	12694.0	12694	0
d^8s	93% $(d^2_{5/2})_4s_{1/2}$	9/2	96% $(^3F)^4F$	29753.6	30240	−486
	83% $(d^2_{5/2})_4s_{1/2}$	7/2	58% $(^3F)^4F$	35076.7	34906	171
d^8s	93% $(d^2_{5/2})_2s_{1/2}$	5/2	45% $(^3P)^4P$	38822.2	38781	41
	85% $(d^2_{5/2})_2s_{1/2}$	3/2	45% $(^1D)^2D$	40345.6	40307	39
d^8s	76% $(d_{3/2}d_{5/2})_3s_{1/2}$	5/2	72% $(^3F)^4F$	44425.9	44461	−35
	87% $(d_{3/2}d_{5/2})_3s_{1/2}$	7/2	56% $(^3F)^2F$	45740.5	45524	217
d^8s	63% $(d^2_{5/2})_0s_{1/2}$	1/2	87% $(^3P)^4P$	49438.9	49233	205
d^8s	[47% $(d_{3/2}d_{5/2})_2$ + 39% $(d_{3/2}d_{5/2})_1$]$s_{1/2}$	3/2	64% $(^3P)^4P$	49969.4	49779	190
	81% $(d_{3/2}d_{5/2})_2s_{1/2}$	5/2	50% $(^3F)^2F$	52059.6	51723	336
d^8s	[57% $(d_{3/2}d_{5/2})_1$ + 18% $(d_{3/2}d_{5/2})_2$]$s_{1/2}$	3/2	49% $(^3P)^2P$	54133.2	54388	−254
	81% $(d_{3/2}d_{5/2})_1s_{1/2}$	1/2	81% $(^3P)^2P$	58327.1	58523	−196
d^8s	93% $(d_{3/2}d_{5/2})_4s_{1/2}$	9/2	96% $(^1G)^2G$	57818.6	58026	−207
	96% $(d_{3/2}d_{5/2})_4s_{1/2}$	7/2	93% $(^1G)^2G$	58584.6	58407	178
d^8s	72% $(d^2_{3/2})_2s_{1/2}$	3/2	50% $(^1D)^2D$	63670.9	63837	−166
	93% $(d^2_{3/2})_2s_{1/2}$	5/2	45% $(^1D)^2D$	64244.0	64286	−42
d^8s	79% $(d^2_{3/2})_0s_{1/2}$	1/2	84% $(^1S)^2S$		87357	

For the 16 levels of d^8s the situation is as follows: In the j–j scheme 15 levels have a definite assignment, while only 10 have an assignment in L–S scheme. Also, the j–j purities generally are much better.

In table 3 we arrange the observed levels of d^8s in L–S terms. First we give the arrangement deduced in reference [1]. Then in the two columns under theory, we arrange the observed levels according to the largest of the calculated L–S components. Comparison with table 2 clearly shows the superiority of the j–j coupling arrangement. We can conclude that the theoretical calculations on the configuration $5d^86s$ justify the qualitative treatment, by showing that the j–j coupling scheme has more physical significance.

The Quantitative treatment of the configuration 5d⁸6p. This configuration is more complicated than the even configurations. Hence we preferred the theoretical treatment from the beginning. Starting values for B, C, α, and ζ_d were taken from the treatment of d^8s. Values for $F_2=F_2(dp)$, $G_1=G_1(dp)$, $G_3=G_3(dp)$ and ζ_p were estimated from the configuration $5d^96p$ of Hg III. The first diagonalization was followed by three least-squares calculations which we call "L.S. 1a," "L.S. 1b," and "L.S. 1c." In these three calculations the parameters B, C, α, ζ_d, which we believed to be known rather well, were "fixed" i.e., forced not to change their values. In L.S. 1a, 40 observed levels were fitted with the calculated levels. This was done by grouping together all the levels with the same total J, and then by arranging them according to increasing value and finally by fitting them with the calculated levels according to this arrangement. No attention was given to the assignments of the observed levels. In L.S. 1a we did not include 3 levels. For $J=1/2$ there are two levels with values 113749.9 cm^{-1} and 113764.9 cm^{-1}. They are designated in reference [1] as $18^{\circ}_{1/2}$ and $19^{\circ}_{1/2}$, respectively. We could fit only one of them, and arbitrarily chose the first one. Also we did not include the two levels designated as $33^{\circ}_{1/2}$ and $36^{\circ}_{1/2}$ which are reported in reference [1] as doubtful. The rms error of L.S. 1a is ±2592 cm^{-1}. This is a very bad result, and we tried to improve it in L.S. 1b. For this purpose three more levels were excluded from the calculation and some assignments were changed. However, the rms error was only reduced to ±1723 cm^{-1}, which is still very bad. The additional levels discarded in L.S. 1b are $23^{\circ}_{7/2}$, $42^{\circ}_{5/2}$, and $43^{\circ}_{5/2}$. In L.S. 1c we also discarded the levels $5^{\circ}_{1/2}$ and $34^{\circ}_{3/2}$. On the other hand it was possible to add the level $43^{\circ}_{5/2}$. Thirty-six observed levels were included in L.S. 1c which gave an rms error of ±568 cm^{-1}.

TABLE 3. L–S *coupling arrangement of the levels of* 5d⁸6s

Term	J	Published analysis ref. [1]	Theory	
			Purity	Level (observed)
			%	
$(^3F)^4F$	9/2	29753.6	96	29753.6
	7/2	35076.7	58	35076.7
	5/2	38822.2	72	44425.9
	3/2	40345.6	33	*40345.6
$(^3P)^4P$	5/2	44425.9	45	38822.2
	3/2	49969.4	64	49969.4
	1/2	49438.9	87	49438.9
$(^3F)^2F$	7/2	45740.5	56	45740.5
	5/2	52059.6	50	52059.6
$(^3P)^2P$	3/2	63670.9	49	54133.2
	1/2	58327.1	81	58327.1
$(^1G)^2G$	9/2	57818.6	96	57818.6
	7/2	58584.6	93	58584.6
$(^1D)^2D$	3/2	54133.2	50	63670.9
	5/2	64244.0	45	64244.0
$(^1S)^2S$	1/2	………	84	………

*45 percent of the state belonging to this level is $^2D_{3/2}$.

For further improvement of the calculation better derivatives are necessary. Thus, we performed a second diagonalization (Diag. 2) with the parameters of L.S. 1c. The derivatives of Diag. 2 were used for 2 least-squares calculations: L.S. 2a, and L.S. 2b. In both calculations all the 36 levels of L.S. 1c were

TABLE 4. *Parameters of the various stages of calculation of the configuration* 5d^{8}6p

	Diag. 1	L.S. 1a	L.S. 1b	L.S. 1c	Diag. 2	L.S. 2a	L.S. 2b	Diag. 3	L.S. 3a	L.S. 3b
A	114000	111236±825	111338±552	112155±195	112000	112113±197	111786±211	111786	111819±200	111703±149
B	620	Fixed	Fixed	Fixed	620	539±21	597±28	600	596±28	587±20
C	3850	Fixed	Fixed	Fixed	3850	3673±162	3225±215	3225	3247±203	3373±146
α	0	Fixed	Fixed	Fixed	0	Fixed	68±24	68	62±25	60±17
F_2	550	503±105	624±70	518±24	520	521±20	514±18	514	509±18	509±14
G_1	600	637±110	631±74	549±25	550	563±21	565±18	565	561±17	551±12
G_3	50	81±100	114±68	83±22	100	84±19	88±17	88	91±16	99±12
ζ_d	5500	Fixed	Fixed	Fixed	5500	5457±71	5440±64	5440	5430±63	5497±48
ζ_p	7000	8736±923	8519±626	8605±205	8600	8849±170	8789±154	8790	8815±155	8744±126
Δ	–	±2592	±1723	±568	–	±426	±381	–	±373	±257

Δ designates the rms error in the calculated levels.

included. In L.S. 2a α was forced to remain zero (as it was in d^8s) and the rms error reduced to ±426 cm^{-1}. In L.S. 2b all the parameters were allowed to change freely and we got an rms error of ±381 cm^{-1}. A third diagonalization (Diag. 3) was performed with the parameters of L.S. 2b. It was also followed by 2 least-squares calculations: L.S. 3a, and L.S. 3b. In L.S. 3a all the 36 observed levels used in the previous iteration were included. We obtained an rms error of ±373 cm^{-1}. In L.S. 3b we excluded also the levels $24^{\circ}_{3/2}$ and $8^{\circ}_{11/2}$. The level $20^{\circ}_{7/2}$ was replaced by the level $23^{\circ}_{7/2}$. Theoretically there is room for only one of these levels, and the second one gives a much better fit.

The parameters of the various stages of the calculation are given in table 4. The observed levels and the calculated levels of L.S. 3b are given in table 5. Observed levels enclosed in parentheses were not included in the calculation. In table 6 we summarize the situation of the problem levels. Eleven levels were discarded in various stages of the calculation, but two of them were reintroduced later. Under the column "present situation" we designate by "+" two levels which turned out to be good ones. We designate by "—" six levels which are discarded by theory without any doubt. One of them is also doubtful in reference [1]. Three levels are assigned as doubtful. Two of them (8° and 24°) have large deviations from the corresponding theoretical levels, while the third one (36°) was excluded mainly because the experimental evidence was doubtful.

The components of the eigenvectors in the j–j coupling scheme were calculated by the method described in the previous section. In the diagonalization with fictitious parameters which calculates the transformation matrix T from L–S coupling to j–j coupling scheme we chose $\zeta_d = 100000$, $\zeta_p = 100$, $B = 0.1$ and all other parameters were equal to zero. In table 5, for each level both the j–j coupling assignment and the largest L–S component are given. The levels are grouped according to j–j assignments.

Now we can compare the validity of the two coupling schemes for the configuration $5d^86p$. Out of 45 levels, 39 levels have a j–j component which is at least 50 percent. Only 14 levels have an L–S component which is at least 50 percent. For 41 levels the main j–j component is larger than the main L–S component, for two levels the L–S component is larger, and for two levels both components are equal. Thus, for this configuration the superiority of the j–j coupling scheme is clearly demonstrated. Actually, for most levels the L–S assignments are meaningless.

In table 5 we see that several states are mixed, showing a tendency towards intermediate coupling. Most mixtures are one of the two following types:

$$\text{(a)}\ (d^2_{5/2})\ \mathrm{J}_d p_{3/2} + (d_{5/2}d_{3/2})\ \mathrm{J}'_d p_{1/2},$$

$$\text{(b)}\ (d_{3/2}d_{5/2})\ \mathrm{J}_d p_{3/2} + (d^2_{3/2})\ \mathrm{J}'_d p_{1/2}.$$

TABLE 5. *Observed and calculated levels of the configuration* 5d^{8}6p

j–j coupling assignment	J	L–S coupling largest component	Observed	Calculated	O–C
91% $(d^2_{5/2})_4p_{1/2}$	7/2	63% $(^3F)^4D$	88788.5	89052	−263
94% $(d^2_{5/2})_4p_{1/2}$	9/2	36% $(^3F)^2G$	91409.4	91115	295
97% $(d^2_{5/2})_2p_{1/2}$	3/2	26% $(^1D)^2D$	95740.0	96012	−272
87% $(d^2_{5/2})_2p_{1/2}$	5/2	26% $(^1D)^2F$	96094.5	96152	−58
69% $(d_{3/2}d_{5/2})_3p_{1/2}$	5/2	45% $(^3F)^4D$	101728.2	101645	84
78% $(d_{3/2}d_{5/2})_3p_{1/2}$	7/2	59% $(^3F)^4G$	102320.2	102033	287
95% $(d^2_{5/2})_4p_{3/2}$	11/2	95% $(^3F)^4G$	(102993.7)	102069	
94% $(d^2_{5/2})_4p_{3/2}$	9/2	66% $(^3F)^4F$	104564.6	104491	74
57% $(d^2_{5/2})_4p_{3/2}$ + 20% $(d_{3/2}d_{5/2})_3p_{1/2}$	7/2	61% $(^3F)^2F$	105809.1	106088	−279
52% $(d^2_{5/2})_4p_{3/2}$ + 27% $(d_{3/2}d_{5/2})_2p_{1/2}$	5/2	44% $(^3F)^2D$	108221.2	108481	−260
57% $(d^2_{5/2})_0p_{1/2}$ + 26% $(d^2_{5/2})_2p_{3/2}$	1/2	26% $(^3P)^4D$	104348.3	104637	−289
61% $(d_{3/2}d_{5/2})_2p_{1/2}$	3/2	31% $(^3P)^4D$	106263.1	106508	−244
50% $(d^2_{5/2})_2p_{3/2}$ + 32% $(d_{3/2}d_{5/2})_2p_{1/2}$	5/2	29% $(^3P)^4P$	107554.2	107116	437
45% $(d^2_{3/2})_2p_{1/2}$ + 20% $(d_{3/2}d_{5/2})_2p_{3/2}$	5/2	35% $(^3F)^2F$	122530.3	122423	107
57% $(d^2_{3/2})_2p_{1/2}$ + 21% $(d_{3/2}d_{5/2})_2p_{3/2}$	3/2	47% $(^3F)^2D$	128250.9	128154	97
58% $(d^2_{5/2})_0p_{3/2}$ + 12% $(d^2_{3/2})_0p_{3/2}$	3/2	30% $(^3P)^2D$	123179.0	122639	540
67% $(d_{3/2}d_{5/2})_1p_{3/2}$	5/2	42% $(^3P)^4D$		125580	
82% $(d_{3/2}d_{5/2})_1p_{3/2}$	3/2	40% $(^3P)^4S$	127467.6	127490	−23
75% $(d_{3/2}d_{5/2})_1p_{3/2}$	1/2	48% $(^3P)^2S$	125846.2	125930	−84
95% $(d_{3/2}d_{5/2})_4p_{3/2}$	11/2	95% $(^1G)^2H$	(127467.0?)	127104	
92% $(d_{3/2}d_{5/2})_4p_{3/2}$	9/2	82% $(^1G)^2G$	132353.0	132346	7
85% $(d_{3/2}d_{5/2})_4p_{3/2}$	7/2	74% $(^1G)^2G$	130978.2	131145	−167
74% $(d_{3/2}d_{5/2})_4p_{3/2}$	5/2	70% $(^1G)^2F$	128512.7	128390	122
88% $(d^2_{3/2})_2p_{3/2}$	7/2	48% $(^1D)^2F$		135014	
77% $(d^2_{3/2})_2p_{3/2}$	5/2	28% $(^1D)^2D$	134953.0	135392	−439
86% $(d^2_{3/2})_2p_{3/2}$	3/2	26% $(^1D)^2P$		133181	
63% $(d^2_{3/2})_2p_{3/2}$	1/2	45% $(^1D)^2P$		137443	
76% $(d^2_{3/2})_0p_{1/2}$	1/2	74% $(^1S)^2P$		144606	
79% $(d^2_{3/2})_0p_{3/2}$	3/2	80% $(^1S)^2P$		156369	
89% $(d_{3/2}d_{5/2})_1p_{1/2}$	1/2	61% $(^3P)^4P$		108293	
53% $(d_{3/2}d_{5/2})_1p_{1/2}$ + 23% $(d^2_{5/2})_2p_{3/2}$	3/2	35% $(^3P)^2P$	(116892.1)	115987	
88% $(d^2_{5/2})_2p_{3/2}$	7/2	44% $(^1D)^2F$	110984.1	111042	−58
42% $(d^2_{5/2})_2p_{3/2}$ + 20% $(d_{3/2}d_{5/2})_2p_{1/2}$	5/2	30% $(^3F)^2D$	112879.6	113102	−223
38% $(d^2_{5/2})_2p_{3/2}$ + 22% $(d_{3/2}d_{5/2})_1p_{1/2}$	3/2	20% $(^3P)^4P$	109387.6	109071	316
67% $(d^2_{5/2})_2p_{3/2}$	1/2	34% $(^1D)^2P$	113749.9	113664	86
74% $(d_{3/2}d_{5/2})_4p_{1/2}$	9/2	68% $(^1G)^2H$		115091	
50% $(d_{3/2}d_{5/2})_4p_{1/2}$ + 32% $(d_{3/2}d_{5/2})_3p_{3/2}$	7/2	42% $(^1G)^2F$	118324.6	118125	200
81% $(d_{3/2}d_{5/2})_3p_{3/2}$	9/2	43% $(^3F)^4G$	115724.2	115595	129
60% $(d_{3/2}d_{5/2})_3p_{3/2}$	7/2	47% $(^3F)^4F$	116293.8	116220	73
77% $(d_{3/2}d_{5/2})_3p_{3/2}$	5/2	29% $(^3F)^4D$	115374.2	115414	−40
42% $(d_{3/2}d_{5/2})_3p_{3/2}$ + 22% $(d^2_{5/2})_2p_{3/2}$	3/2	29% $(^1D)^2P$	118561.7	118601	−39
83% $(d_{3/2}d_{5/2})_2p_{3/2}$	7/2	44% $(^3P)^4D$	121826.4	121838	−11
44% $(d_{3/2}d_{5/2})_2p_{3/2}$ + 31% $(d^2_{3/2})_2p_{1/2}$	5/2	26% $(^3P)^4P$	120027.3	119922	105
38% $(d_{3/2}d_{5/2})_2p_{3/2}$ + 15% $(d^2_{3/2})_2p_{1/2}$	3/2	27% $(^3P)^2P$	121943.5	122156	−213
50% $(d_{3/2}d_{5/2})_2p_{3/2}$ + 28% $(d^2_{3/2})_2p_{3/2}$	1/2	55% $(^3F)^4D$	122407.0	122333	74

TABLE 6. *The dubious levels in the configuration* 5d^{8}6p

Assignment	*J*	Level	Excluded	Retained	Present situation
5°	1/2	98559.1	L.S. 1c	....	–
8°	11/2	102993.7	L.S. 3b	....	?
19°	1/2	113764.9	L.S. 1a	....	–
20°	7/2	115339.9	L.S. 3b	....	–
23°	7/2	116293.8	L.S. 1b	L.S. 3b	+
24°	3/2	116892.1	L.S. 3b	....	?
33°	9/2	123508.8?	L.S. 1a	....	–
34°	3/2	125767.9	L.S. 1c	....	–
36°	11/2	127467.0?	L.S. 1a	....	?
42°	5/2	133058.9	L.S. 1b	....	–
43°	5/2	134953.0	L.S. 1b	L.S. 1c	+

In both types the difference between the first component and the second one is that a $d_{5/2}$ is replaced by a $d_{3/2}$ and the $p_{3/2}$ is replaced by a $p_{1/2}$. Now let us compare the energies:

$$E\,(p_{3/2}) - E\,(p_{1/2}) = 1.5\ \zeta_p = 13100\ \mathrm{cm}^{-1},$$
$$E\,(d_{5/2}) - E\,(d_{3/2}) = 2.5\ \zeta_d = -13750\ \mathrm{cm}^{-1}.$$

We see that energetically both changes cancel each other. In the *j–j* scheme the diagonal elements corresponding to the two states represented in the mixture are rather close, and the nondiagonal elements which are of the order of magnitude of the electrostatic parameters can strongly mix them. This is an interesting example that for configurations containing nonequivalent electrons (in nonclosed shells) the requirement that all spin-orbit interactions be much larger than the electrostatic interactions is not a sufficient condition for pure *j–j* coupling. A similar situation was found by Mrs. Z. Goldschmidt [5] for the configuration 4$f^2$6p in the isoelectronic spectra of Ce II and Pr III.

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3. References

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