

# The Configurations $3d^n4p$ in Doubly Ionized Atoms of the Iron Group\*

C. Roth

McGill University, Montreal, Canada

(June 18, 1968)

Experimental levels of the configurations  $3d^n4p$  in the third spectra of the iron group were compared with corresponding calculated values. Besides the electrostatic and spin-orbit interactions the  $\alpha L(L+1)$ ,  $\beta Q$  and  $T$  corrections were considered in the individual and general treatments. The insertion of the parameters  $\beta$  and  $T$  improved the results by about 25 percent. The root-mean-square (rms) error on fitting 581 experimental levels by means of 21 free interaction parameters was  $138 \text{ cm}^{-1}$ . Altogether 912 energy levels were predicted.

Key Words:  $\beta Q$  and  $T$  corrections; configurations  $3d^n4p$ ; energy levels; iron group; interaction parameters; third spectra.

## 1. Introduction

Individual and general treatments of the configurations  $3d^n + 3d^{n-1}4s$  in the third spectra of the iron group were considered by Y. Shadmi [1]. Preliminary investigations of some configurations  $3d^n4p$  in the third spectra of the iron group were performed by Shimoni, Hollander and Abraham [2–4].

Racah and Trees [5–7] have shown that second order effects caused by perturbations on the configuration  $ln$  by configurations differing from  $ln$  by two electrons can be described by a model interaction of the form

$$2\alpha(1_1 \cdot 1_2) + \beta q_{12},$$

where  $q_{12}$  is the seniority operator [8]. For the configuration  $d^n$  this becomes

$$\alpha[L(L+1) - 6n] + \beta Q,$$

where  $Q$  is the total seniority operator [8]. If the constant  $-6n\alpha$  is incorporated into the height of the configuration the above correction reduces to

$$\alpha L(L+1) + \beta Q.$$

The  $\alpha L(L+1)$  correction was first introduced by Trees [5]. The effect of the  $\beta Q$  correction was studied

by Racah and Shadmi [9] in the even configurations  $(3d+4s)^n$  of the second spectra of V, Cr, and Fe.

Trees and Jorgenson [10] have shown that the main perturbing configuration on  $3s^23p^63d^n$  is the configuration  $3s^23p^43d^{n+2}$ . Trees [11] also remarked that the configuration  $3s3p^63d^{n+1}$  should give a perturbation of the same magnitude as  $3s^23p^43d^{n+2}$ . This perturbation is not included in  $2\alpha(1_1 \cdot 1_2) + \beta q_{12}$ , since now the configurations differ by only one electron. By second-order perturbation theory this effect depends upon the ratio  $\frac{H^2}{\Delta E}$ , where  $H$  is the interaction parameter that appears in the nondiagonal term,

$$H = \frac{R^2(3d \ 3d, \ 3d \ 3s)}{35},$$

and  $\Delta E$  is the energy difference between the two configurations. The parameter  $\frac{H^2}{\Delta E}$  is denoted by  $T$ . When

calculating the model interaction one uses second-order perturbation theory of degenerate configurations which permits the introduction of these interactions before diagonalizing the energy matrices of the separate configurations. Hence the algebraic matrices of  $T$  are not diagonal. It should be noted that  $T$  represents a three-body interaction whereas  $\alpha$  and  $\beta$  represent two-body interactions.

Rajnak and Wybourne [12], by using second-order perturbation theory obtained expressions for the matrix elements of the electrostatic interaction between the  $\ell^n$  configuration and the different species

\*An invited paper. The major part of this paper is based on a chapter of the author's doctoral dissertation, the Hebrew University of Jerusalem, Israel.

of perturbing configurations differing from  $\ell^n$  by one or two electrons or electron-holes. Effective three-body interactions were considered to account for the perturbation due to one-electron excitations. Racah and Stein [13] developed an elegant method which considerably simplified the calculations of Rajnak and Wybourne.

The electrostatic and spin-orbit interaction matrices for the configurations  $d^n p$  were available from the matrix library at the Hebrew University. To these matrices the author added the algebraic matrices of the parameters  $\beta$  and  $T$  using the program ADDCONF of Racah.

In the first part (the individual treatment, ILS), the algebraic matrices multiplied by radial parameters are diagonalized using the program of Racah [14]. Besides the eigenvalues, the diagonalization routine also yields the derivatives of the eigenvalues with respect to the parameters, the squares of the eigenvectors (percentage compositions) and the calculated Lande  $g$  values. The appropriate experimental levels are then fitted to the eigenvalues and using the derivatives obtained in the diagonalization, a least squares optimization of the parameters is performed. In these calculations the improved values of the theoretical energy levels, the corrected values of the parameters including their statistical deviations and the sum of the squares of the differences between the observed and calculated levels are obtained.

Where the  $\Delta_i$  are the differences between the observed and calculated levels,  $n$  is the number of known levels, and  $m$  is the number of free parameters, the rms error  $\Delta$  defined as

$$\Delta = \sqrt{\frac{\sum_{i=1}^n \Delta_i^2}{n-m}}$$

is also given by the least squares routine. The same derivatives can be used for several variations in the least squares either imposing different conditions on the parameters or inserting the experimental levels with different assignments. These latter variations are particularly important since they help to determine whether certain experimental levels may be inserted with changed assignments, or in some cases even rejected. The parameters of that variation which yields the best results are used to perform a new diagonalization. This iterative process is continued until mathematical convergence is attained.

If the parameters obtained from the individual treatments can be expressed in terms of simple interpolation formulas a general diagonalization is performed. Then in the general least squares (GLS) all the configurations  $3d^n 4p$  are considered as one problem by forcing the interaction parameter to vary linearly, or perhaps linearly with small quadratic corrections.

## 2. Parameters

For the  $d-d$  interaction the Slater parameters  $F^2$  and  $F^4$  were replaced by

$$B = \frac{1}{441} [9F^2(dd) - 5F^4(dd)] = F_2(dd) - 5F_4(dd)$$

$$C = \frac{5}{63} F^4(dd) = 35F_4(dd).$$

For the  $d-p$  interaction the parameters  $F_2$ ,  $G_1$ , and  $G_3$  are given by

$$F_2 = \frac{1}{35} F^2(dp), \quad G_1 = \frac{1}{15} G^1(dp) \quad \text{and} \quad G_3 = \frac{3}{245} G^3(dp)$$

The parameters of the spin-orbit interactions for the electrons  $d$  and the electron  $p$  are denoted by  $\zeta_d$  and  $\zeta_p$ , respectively. The three correction parameters mentioned previously are denoted by  $\alpha$ ,  $\beta$ , and  $T$ . Finally, the additive parameter chosen to normalize to zero the lowest energy value for a particular configuration, is denoted by  $A$ .

## 3. Discussion and Results

By extrapolating and intrapolating the results of Shimoni, Hollander and Abraham [2-4], approximate initial values for the parameters of the individual treatment were obtained. Since the effects of the parameters  $\beta$  and  $T$  had not been considered previously for the third spectra, they were inserted initially here with a value of zero. However, since derivatives with respect to these two parameters were obtained it was possible to study the effects of  $\beta$  and  $T$  by letting them vary freely in the least-squares. After two iterations in the individual treatments of all the configurations mathematical convergence was attained for all the parameters. Then on the basis of the results from the individual treatments a general diagonalization was performed in which the parameters  $B$ ,  $C$ ,  $F_2$ ,  $G_1$ ,  $G_3$ ,  $\alpha$ , and  $\zeta_p$  varied linearly, whereas  $\zeta_d$  had in addition a small quadratic correction. The parameters  $\beta$  and  $T$  again had an initial value of zero.

The configurations  $d^n p$  consist of 372 theoretical terms splitting into 912 levels. In the general least-squares 225 experimental terms splitting into 581 levels were inserted. The rms error with  $\beta$  and  $T$  eliminated was  $180.3 \text{ cm}^{-1}$  (28 free parameters) whereas when  $\beta$  and  $T$  were allowed to vary linearly the rms error was reduced to  $138.4 \text{ cm}^{-1}$  (32 free parameters). The values of  $\beta$  and  $T$  in the latter variation were

$$\beta(d^n p) = -285 \pm 22 - (45 \pm 20)(n-5)$$

$$T(d^n p) = -3.2 \pm 0.2 - (0.6 \pm 0.2)(n-5)$$

the uncertainties in these parameters and those following in the text and tables are the rms deviations obtained in the least squares optimization of their values.

Since  $\alpha$  and  $\beta$  take into account second order effects by two-body interactions we would expect that if  $\beta$  be allowed to vary the value of  $\alpha$  should drop. That is indeed the case as in the variation with  $\beta$  and  $T$  eliminated  $\alpha$  had values (in units of  $\text{cm}^{-1}$ )

$$\alpha_1 = 82 \pm 1 + (1.2 \pm 0.9)(n-5),$$

whereas by letting  $\beta$  and  $T$  vary linearly in the GLS we obtained

$$\alpha_2 = 56 \pm 1.8 - (2.5 \pm 1.4)(n-5).$$

In addition  $C$  increases when  $\beta$  is inserted. With  $\beta$  and  $T$  eliminated the value of  $C$  in the GLS was

$$C(d^np) = 3920.8 \pm 6.3 + (287.1 \pm 5.5)(n-5)$$

whereas by letting  $\beta$  and  $T$  vary linearly in the GLS we had

$$C(d^np) = 4062.2 \pm 9.9 + (327.8 \pm 8.6)(n-5).$$

This result also is as expected since if we consider the basis configuration  $d^2$  the only term affected by  $\beta$  is  $^1S$ , which contains  $7C$ .

In figures (1-8) we give values of the parameters versus atomic number obtained from the individual least squares (the vertical lines indicate the rms errors in the values of the parameters). The straight lines (and the parabola for  $\zeta_d$ ) give the values of the parameters from the general least squares. From the graphs it is apparent that the assumption of linearity (with a small quadratic correction for  $\zeta_d$ ) is valid here.

Unless specified otherwise the source of the experimental data is "Atomic Energy Levels," Vols. I and II by C. E. Moore [15], henceforth referred to as AEL.

The numerical values of all levels and parameters are in  $\text{cm}^{-1}$ .

We now wish to discuss briefly the results for each configuration.

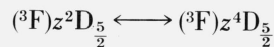
Sc III- $4p$ . This configuration consists of only 1 term splitting into 2 levels. It is useful in providing a value for the parameter  $\zeta_p$ .

Ti III- $3d4p$ . In the configuration  $dp$  there are 6 terms splitting into 12 levels, all of which are known experimentally for Ti III.

In the individual least squares we fitted the 12 experimental levels to the theoretical levels with the same assignments as in AEL. The 4 electrostatic parameters  $A$ ,  $F_2$ ,  $G_1$ , and  $G_3$  were used to determine the 6 terms. The rms error obtained was 162. Furthermore, all the 12 levels fitted very nicely in the GLS. This result is significant and indicates that the interaction with the configuration  $sp$  is not strong here.

V III- $3d^24p$ . In the configuration  $d^2p$ , there are 19 terms splitting into 45 levels. In the paper by Iglesias [16], 18 observed terms splitting into 43 levels are given—the only term missing is  $(^1S)^2P$ .

The only change in assignment was



Without the exchange, the deviations of these two levels were  $-680$  for  $z^2D_{\frac{5}{2}}$  and  $410$  for  $z^4D_{\frac{5}{2}}$ . With the exchange the deviations were reduced to  $-152$  and  $-128$  respectively. In addition, the eigenfunctions of the two levels are strongly mixed.

Since there are no levels based on the core  $d^2^1S$ , we can only have a maximum of 4 electrostatic parameters of  $d^2$  to satisfy the 4 terms  $^3P$ ,  $^1D$ ,  $^3F$ , and  $^1G$ . These 4 parameters are  $A$ ,  $B$ ,  $C$ , and  $\alpha$ . If we give either  $T$  or  $\beta$  freedom then the problem is overdefined. In the individual least squares the mean error in fitting 43 levels with  $\beta$  and  $T$  eliminated was 135.

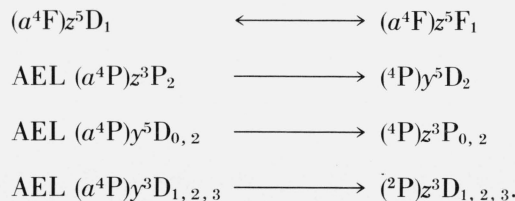
Cr III- $3d^34p$ . In the configuration  $d^3p$  there are 48 theoretical terms splitting into 110 levels. In AEL, there are 27 observed terms splitting into 74 levels. We found it necessary to reject 7 experimental levels.

The following is a list of the 7 levels neglected with their approximate deviations had they been inserted into the last GLS

Name	Value	Deviation
$(^4F)z^5D_0$	95779	-810
$(^2G)z^1G_4$	114355	1160
$(^2H)y^1G_4$	117099	-2090
$(^2G)z^1H_5$	117187	3840
$(^2F)v^3D_2$	138362	5740
$(^2F)v^3D_3$	138976	6710
$(b^2D)v^3F_3$	150972	1680

In the individual least squares, the deviation obtained for the level  $(^4F)z^5D_0$  was  $-625$ , whereas the other levels of  $z^5D$  fitted with deviations of less than 50. Thus we felt justified in neglecting the level  $z^5D_0$ . The levels  $(^2G)z^1G_4$ ,  $(^2H)y^1G_4$ ,  $(^2G)z^1H_5$  and  $(^2F)v^3D_2$  had deviations higher than 1000 in the individual least squares, and were thus rejected. In the individual least squares we considered the variation of assigning the level  $(b^2D)v^3F_3$  to  $(b^2D)^1F_3$ . However, this required that  $\beta$  have a value of  $-590$ , whereas the value of  $\beta$  from the GLS is  $-195$ . With the latter value of  $\beta$ , the deviation obtained on assigning  $v^3F_3$  to  $(b^2F)^1F$  is  $-1056$ , and thus too high to be considered.

The following changes in assignment were performed



In the first three cases the eigenfunctions of all the levels concerned are mixed considerably. The term  $(^4P)^3D$  is definitely higher than the term  $(^2P)^3D$ .

By neglecting the level  $(^2D)v^3F_3$  at 150972, it was found that  $\beta$  and  $T$  did not suffer any appreciable change. Thus, the best result in the individual least squares was obtained on fitting 22 terms splitting into 67 levels with 7 electrostatic and 2 spin-orbit parameters, to yield a mean error of 136.

Mn III— $3d^44p$ . The configuration  $d^4p$  comprises 68 terms splitting into 180 levels. In AEL there are only 6 observed terms, all based on  $d^4^5D$ , which split into 25 levels. No individual least squares were performed as then we would have to keep the parameters  $\alpha$ ,  $B$ , and  $C$  fixed. The 25 observed levels fit very well in the GLS with the same assignments as in AEL.

Fe III— $3d^54p$ . In the configuration  $d^5p$  there are 88 terms splitting into 214 levels, of which 75 terms splitting into 189 levels are known experimentally for Fe III. All the observed levels fit well with the following changes in assignment:

$$(^4P)z^5D_3 \longleftrightarrow (^4G)z^5F_3$$

$$(^2I)z^3I_{6,7} \longleftrightarrow (^2I)z^3K_{6,7}$$

$$(^4F)y^5G_5 \longleftrightarrow (^2F)y^3G_5$$

$$\text{AEL } (b^2F)t^3F_4 \longrightarrow (b^2F)w^1G_4$$

$$\text{AEL } (a^2H)x^1G_4 \longrightarrow (b^2F)t^3F_4$$

It should be emphasized that in each of the changed levels the composition is never pure, but contains a contribution of that level which has the same assignment as that given in AEL. In general the mixing in this configuration is very strong. Racah [17] has shown that for  $d^5$ , or equivalently for  $d^5p$ , all diagonal second-order effects are well represented by two-body interactions. Thus, the parameter  $T$  has little if any significance here. In the individual least squares the mean error was 186 with  $\beta$  eliminated, and 144 when  $\beta$  was allowed to vary freely. Then  $\beta$  assumed a value of  $-292 \pm 23$ .

Co III— $3d^64p$ . From 68 theoretical terms splitting into 180 levels there are 33 experimental terms splitting into 95 levels.

The two levels  $(^3P)y^4P_{\frac{5}{2}}$  and  $(^3P)z^2D_{\frac{5}{2}}$  are given with question marks in AEL. As they would yield deviations of around  $-800$  and  $-600$  respectively, if inserted into the GLS, they were neglected.

The following changes in assignment were performed:

$$(^3H)z^4H_{9, \frac{11}{2}, \frac{13}{2}} \longleftrightarrow (^3H)z^4I_{9, \frac{11}{2}, \frac{13}{2}}$$

$$(^3G)x^4G_{\frac{9}{2}} \longleftrightarrow (^3G)x^4F_{\frac{9}{2}}$$

$$(^1I)x^2H_{9, \frac{11}{2}} \longleftrightarrow (^1G)w^2H_{9, \frac{11}{2}}$$

$$\text{AEL } (^3P')z^4S_{\frac{3}{2}} \longrightarrow (B^3P)^4D_{\frac{3}{2}}$$

$$\text{AEL } (^3P')x^4P_{\frac{5}{2}} \longrightarrow (B^3P)^4D_{\frac{5}{2}}$$

In each of the first three exchanges there was considerable mixing of the eigenfunctions involved.

The calculated values of the levels  $(B^3P)^4S_{\frac{3}{2}}$  and  $(B^3P)^4P_{\frac{5}{2}}$  are 161611 and 164334, respectively. Thus, the two levels  $z^4S_{\frac{3}{2}}$  and  $x^4P_{\frac{5}{2}}$  cannot be fitted to the theoretical levels with the same assignments. The only possible assignment for the level  $(^3P')z^4S$  is the theoretical level consisting of a mixture of  $(B^3P)^4D_{\frac{3}{2}}$  and  $(B^3F)^4D_{\frac{3}{2}}$ . In the GLS the deviation for this level is  $-282$ . Similarly the level  $(^3P')x^4P_{\frac{5}{2}}$  was assigned to the same theoretical term as  $z^4S$  with  $J$  equal to  $\frac{5}{2}$  giving a deviation of 120 in the GLS.

In the individual least squares  $\beta$  and  $T$  have a marked effect. On fitting 93 levels using 7 electrostatic parameters and 2 spin-orbit parameters ( $\beta$  and  $T$  eliminated) the mean error was 176. When  $\beta$  and  $T$  were allowed to vary freely, the mean error was reduced to 130. The values of  $\beta$  and  $T$  in that variation were

$$\beta = -424 \pm 86$$

$$T = -4.8 \pm 0.6$$

Ni III— $3d^74p$ . From 48 predicted terms splitting into 110 levels, Shenstone [18] gives 43 experimental terms which split into 95 levels. The following 3 levels were rejected:

$$(^2P)^3P_2 \text{ at } 141112.5?$$

$$(b^2D)u^3D_2 \text{ at } 173062.0?$$

$$(b^2D)u^3D_3 \text{ at } 172916.9?$$

The calculated level  $(^2P)^3P_2$  is at 133902, and since for  $J$  equal to 2 all the theoretical levels in the vicinity of 141000 have corresponding experimental levels, the level  $(^2P)^3P_2$  was rejected. Similarly the calculated levels  $(b^2D)u^3D_{2,3}$  are at 183976 and 184740, respectively, and since there are no theoretical levels in the vicinity of 173000, the levels  $u^3D_{2,3}$  could not be inserted into the least-squares calculations.

Shenstone [18] mentions that two strong lines should be due to transitions between the odd levels  $z^3I_7$ ,  $z^3H_6$  and the even levels  $a^3H_6$ ,  $a^3G_5$ . Shenstone then attributes these two lines as being due to  $a^3G_5 - z^3H_6$  ( $56304.2 \text{ cm}^{-1}$ ) and  $a^3H_6 - z^3I_7$  ( $57044.7 \text{ cm}^{-1}$ ). Thus, he obtains the levels  $(^2G)z^3H_6$  at 131428 and  $(^2H)z^3I_7$  at 138731. However, from our initial diagonalization the level  $(^2H)z^3I_7$  was at 137842 and the level  $(^2G)z^3H_6$  was at 131901. This shows that the transitions to which Shenstone attributes these two lines should

be interchanged. Then one obtains the experimental levels  $(^2\text{H})z^3\text{I}_7$  at 137990.6 and  $(^2\text{G})z^3\text{H}_6$  at 132168.9. In the GLS these fitted with deviations of 154 and 263, respectively.

As suggested by Professor Racah the two strong lines given by Shenstone at  $147723\text{ cm}^{-1}$  and  $145094\text{ cm}^{-1}$  correspond to the transitions  $(^2\text{F})^1\text{F}_3 - a^1\text{D}_2$  and  $(^2\text{F})^1\text{F}_3 - a^3\text{P}_2$ , respectively. Then it follows that the experimental level  $(^2\text{F})^1\text{F}$  should have a value of 161755. In the GLS this level fitted with a deviation of only 20. The following changes in assignment were performed:

1.  $(^4\text{P})y^3\text{D}_{2,3} \longleftrightarrow (^4\text{P})z^5\text{P}_{2,3}$
2. Shen.  $(^4\text{P})z^3\text{P}_0 \longrightarrow (^2\text{P})^1\text{S}_0$
3. Shen.  $(^2\text{P})z^1\text{P}_1 \longrightarrow (^2\text{P})^3\text{S}_1$
4. Shen.  $(^2\text{P})y^3\text{P}_1 \longrightarrow (^2\text{P})^1\text{P}_1$
5.  $(^2\text{F})w^3\text{F}_2 \longleftrightarrow (^2\text{F})w^1\text{D}_2$
6.  $(^2\text{F})w^3\text{F}_3 \longleftrightarrow (^2\text{F})v^3\text{D}_3$
7. Shen.  $(^2\text{F})w^3\text{F}_4 \longrightarrow (^2\text{F})^3\text{G}_4$

In the first case there is considerable mixing between the eigenfunctions of  $(^4\text{P})y^3\text{D}$  and  $(^4\text{P})z^5\text{P}$ . The predicted level  $(^4\text{P})^3\text{P}_0$  is at  $135695\text{ cm}^{-1}$ , and thus the experimental level  $z^3\text{P}_0$  at  $138147\text{ cm}^{-1}$  cannot be assigned to the theoretical level with the same term designation. This level fits quite well to the theoretical level  $(^2\text{P})^1\text{S}$  as indicated by change 2. It should be noted that the eigenfunction of  $(^2\text{P})^1\text{S}$  contains 39 percent of  $(^4\text{P})^3\text{P}$ .

A variation was considered to fit the level  $(^2\text{P})z^1\text{P}$  to the theoretical level with the same term designation and perform the change  $(^2\text{P})y^3\text{P}_1 \rightarrow (^2\text{P})^3\text{S}_1$ . However, the deviations for both levels were much larger than the deviations with changes 3 and 4 ( $-167$  for the level  $(^2\text{P})^3\text{S}$  and  $22$  for the level  $(^2\text{P})z^1\text{P}$ ).

When the levels of the term  $(^2\text{F})w^3\text{F}$  were assigned to the theoretical levels of the same term designation, the deviations were almost 1000. Since such high deviations are completely incompatible with the other results obtained, we performed the changes 5, 6, and 7, thus completely splitting the term  $(^2\text{F})w^3\text{F}$ . It should be noted, however, that in all these changes the parent,  $^2\text{F}$ , remains the same.

In the individual least squares, on inserting 93 experimental levels with  $\beta$  and  $T$  eliminated, the mean error was 169. When  $\beta$  and  $T$  were allowed to vary freely the mean error was reduced to 136. In that variation the values of  $\beta$  and  $T$  were

$$\begin{aligned}\beta &= -413 \pm 63 \\ T &= -4.9 \pm 0.6.\end{aligned}$$

$\text{Cu III} - 3d^8 4p$ . Of the 19 predicted terms of  $d^8 p$ , the only experimental term missing in  $\text{Cu III}$  is  $(^1\text{S})^2\text{P}$ .

The only change in assignment was

$$(^3\text{P})x^2\text{D}_{\frac{3}{2}} \leftrightarrow (^3\text{P})y^2\text{P}_{\frac{3}{2}}.$$

The eigenfunctions of these two levels are strongly mixed.

As for  $d^2 p$ , since there are no levels based on the parent  $(d^2)^1\text{S}$ , it is not possible to let either  $\beta$  or  $T$  change freely.

In the individual least squares, the mean error on fitting 43 levels with  $\beta$  and  $T$  eliminated was 126. For the values of  $\beta$  and  $T$  fixed at  $-427$  and  $-4.9$  respectively (the values obtained for those parameters in the first GLS) the mean error dropped only to 125.

This result is as expected since the inclusion of  $\beta$  affects only the term  $d^8(^1\text{S})$ , which is not known experimentally, and  $T$  reduces in this case to a two-body interaction, the effect of which is absorbed by the other  $d^8$  parameters.

$\text{Zn III} - 3d^9 4p$ . In this configuration all 12 predicted levels are known. The following changes in assignment were performed:

1.  $^3\text{D}_2 \leftrightarrow ^1\text{D}_2$
2.  $^3\text{D}_3 \leftrightarrow ^1\text{F}_3$ .

In both cases there was mixing between the eigenfunctions of the levels involved.

In the individual least squares using the 4 electrostatic parameters  $A$ ,  $F_2$ ,  $G_1$ , and  $G_3$  as well as the 2 spin-orbit parameters  $\zeta_a$  and  $\zeta_p$ , the mean error was 105.

$\text{Ga III} - 3d^{10} 4p$ . Like  $\text{Sc III} - p$  this configuration consists of only 1 term splitting into 2 levels, and is useful in providing a value for  $\zeta_p$ .

#### 4. Table Entries

The numerical values of all levels and parameters given in the following tables are in units of  $\text{cm}^{-1}$

1. *Parameters*: Tables 1-10

In the general diagonalization all the parameters with the exception of  $\zeta_a$  had approximate expressions of the form

$$P(d^n p) = P + (n-5)\Delta P.$$

In the general least squares then only  $P$  and  $\Delta P$  were the independent parameters.

For  $\zeta_a$  we had

$$\zeta_a(d^n p) = \zeta_a + (n-5)\Delta_1\zeta_a + [(n-5)^2 - 10]\Delta_2\zeta_a.$$

Here  $\zeta_a$ ,  $\Delta_1\zeta_a$  and  $\Delta_2\zeta_a$  were the independent parameters in the general least squares.

The numerical values of the parameters for the initial general diagonalization are given in the column GDIAG 1.

The columns ILS1 and GLS1 give the values of

the parameters of the initial iteration with  $\beta$  and  $T$  eliminated, in the individual and general least squares, respectively. The columns ILS'1 and GLS'1 give the values of the parameters of the initial iteration with  $\beta$  and  $T$  free to change in the individual and general least squares respectively.

The parameters as given in GLS'1 were taken for the general diagonalization of the final iteration. The column GLS'2 gives the values of the parameters in the general least squares of the final iteration.

TABLE 1. Parameters of Ti III-3d4p

Parameter	GDIAG 1	ILS 1	GLS 1	GLS' 1	GLS' 2
A	79440	78917 ± 52	78938	79016	78999
F <sub>2</sub>	460	437 ± 10	443	442	441
G <sub>1</sub>	410	423 ± 13	409	408	407
G <sub>3</sub>	50	48 ± 4	48	49	50
α	84	Fix 84	78	66	68
β	115	154 ± 58	136	135	139
T	359	379 ± 206	334	336	328
Δ		162			

TABLE 2. Parameters of V III-3d<sup>3</sup>4p

Parameter	GDIAG 1	ILS 1	GLS 1	GLS' 1	GLS' 2
A	95958	95900 ± 43	95992	96387	96313
B	911	880 ± 4	903	918	915
C	3062	3183 ± 33	3060	3091	3078
F <sub>2</sub>	466	454 ± 4	452	451	450
G <sub>1</sub>	410	416 ± 5	408	407	405
G <sub>3</sub>	52	49 ± 2	51	51	51
α	84	72 ± 5	79	63	62
β	0	Fix 0	Fix 0	-220	-150
T	0	Fix 0	Fix 0	-1.7	-1.3
ζ <sub>d</sub>	177	220 ± 24	206	207	208
ζ <sub>p</sub>	442	371 ± 64	420	414	406
Δ		135			

TABLE 3. Parameters of Cr III-3d<sup>3</sup>4p

Parameter	GDIAG 1	ILS 1	GLS 1	GLS' 1	GLS' 2
A	113164	113160 ± 70	113142	113633	113559
B	966	962 ± 4	960	969	966
C	3350	3354 ± 21	3347	3417	3406
F <sub>2</sub>	472	458 ± 7	461	460	459
G <sub>1</sub>	410	403 ± 6	407	406	405
G <sub>3</sub>	54	57 ± 2	53	53	53
α	84	81 ± 3	80	61	63
β	0	Fix 0	Fix 0	-254	-195
T	0	Fix 0	Fix 0	-2.2	-1.9
ζ <sub>d</sub>	257	272 ± 28	290	292	291
ζ <sub>p</sub>	525	496 ± 58	496	492	486
Δ		136			

TABLE 4. Parameters of Mn III-3d<sup>4</sup>4p

Parameter	GDIAG 1	GLS 1	GLS' 1	GLS' 2
A	138047	137848	138256	138187
B	1021	1015	1019	1017
C	3638	3634	3743	3734
F <sub>2</sub>	478	470	469	468
G <sub>1</sub>	410	406	405	404
G <sub>3</sub>	56	54	54	54
α	84	81	58	60
β	0	Fix 0	-289	-240
T	0	Fix 0	-2.8	-2.5
ζ <sub>d</sub>	355	385	389	387
ζ <sub>p</sub>	608	572	570	562

TABLE 5. Parameters of Fe III-3d<sup>5</sup>4p

Parameter	GDIAG 1	ILS 1	ILS' 1	GLS 1	GLS' 1	GLS' 2
A	126350	125832 ± 91	125710 ± 74	125843	125781	125725
B	1076	1071 ± 2	1068 ± 2	1071	1070	1068
C	3926	3920 ± 9	4071 ± 9	3921	4069	4062
F <sub>2</sub>	484	477 ± 4	474 ± 3	479	478	477
G <sub>1</sub>	410	404 ± 4	397 ± 3	405	403	403
G <sub>3</sub>	58	55 ± 1	57 ± 1	56	56	56
α	84	82 ± 1	55 ± 1	82	56	57
β	0	Fix 0	-292 ± 23	Fix 0	-323	-285
T	0	Fix 0	Fix 0	Fix 0	-3.3	-3.2
ζ <sub>d</sub>	471	484 ± 30	521 ± 23	494	498	494
ζ <sub>p</sub>	691	730 ± 43	692 ± 34	648	648	640
Δ		186	144			

TABLE 6. Parameters of Co III-3d<sup>6</sup>4p

Parameter	GDIAG 1	ILS 1	ILS' 1	GLS 1	GLS' 1	GLS' 2
A	131330	131748 ± 131	131593 ± 106	131512	131544	131507
B	1131	1139 ± 6	1120 ± 5	1127	1121	1119
C	4214	4177 ± 15	4426 ± 32	4208	4395	4390
F <sub>2</sub>	490	506 ± 5	497 ± 4	488	486	486
G <sub>1</sub>	410	412 ± 6	403 ± 5	403	402	402
G <sub>3</sub>	60	55 ± 2	57 ± 1	57	58	58
α	84	88 ± 3	47 ± 6	83	53	55
β	0	Fix 0	-424 ± 86	Fix 0	-358	-330
T	0	Fix 0	-4.8 ± 0.6	Fix 0	-3.8	-3.8
ζ <sub>d</sub>	605	641 ± 30	672 ± 30	615	621	617
ζ <sub>p</sub>	774	662 ± 56	672 ± 43	724	727	718
Δ		176	130			

TABLE 7. Parameters of Ni III-3d<sup>7</sup>4p

Parameter	GDIAG 1	ILS 1	ILS' 1	GLS 1	GLS' 1	GLS' 2
A	129516	129509 ± 52	129715 ± 47	129556	129751	129733
B	1186	1176 ± 4	1166 ± 3	1182	1171	1170
C	4502	4530 ± 18	4762 ± 32	4495	4721	4718
F <sub>2</sub>	496	499 ± 5	499 ± 4	497	495	495
G <sub>1</sub>	410	395 ± 5	398 ± 4	403	401	401
G <sub>3</sub>	62	59 ± 2	58 ± 2	59	59	59
α	84	83 ± 3	49 ± 5	84	51	52
β	0	Fix 0	-413 ± 63	Fix 0	-393	-375
T	0	Fix 0	-4.9 ± 0.6	Fix 0	-4.4	-4.2
ζ <sub>d</sub>	757	703 ± 26	726 ± 18	750	755	751
ζ <sub>p</sub>	857	772 ± 54	755 ± 38	800	805	796
Δ		169	136			

TABLE 8. Parameters of Cu III-3d<sup>8</sup>4p

Parameter	GDIAG 1	ILS 1	GLS 1	GLS' 1	GLS' 2
A	131863	131864 ± 45	131847	132122	132123
B	1241	1247 ± 5	1238	1222	1221
C	4790	4764 ± 35	4782	5047	5046
F <sub>2</sub>	502	498 ± 4	507	504	503
G <sub>1</sub>	410	402 ± 5	402	400	401
G <sub>3</sub>	64	64 ± 3	60	61	61
α	84	84 ± 5	86	48	49
β	0	Fix 0	Fix 0	-427	-420
T	0	Fix 0	Fix 0	-4.9	-5.0
ζ <sub>d</sub>	927	890 ± 5	897	902	898
ζ <sub>p</sub>	940	862 ± 49	877	883	874
Δ		126			

TABLE 9. Parameters of Zn III-3d<sup>9</sup>4p

Parameter	GDIAG 1	ILS 1	GLS 1	GLS' 1	GLS' 2
A	142734	142277 ± 39	142285	142529	142531
F <sub>2</sub>	508	504 ± 6	516	513	512
G <sub>1</sub>	410	408 ± 6	401	398	399
G <sub>3</sub>	66	60 ± 6	62	63	62
α	84	Fix 84	87	46	46
β	1215	1095 ± 39	1056	1062	1059
T	1023	1013 ± 72	953	961	952
ζ <sub>d</sub>		105			
ζ <sub>p</sub>					
Δ					

TABLE 10. General parameters of the third spectra of the iron group

Parameter	GDIAC 1	GLS 1	GLS' 1	GLS' 2
B	1076	1071.4 ± 1.5	1070.0 ± 1.3	1068.5 ± 1.3
ΔB	55	55.8 ± 1.1	50.6 ± 0.9	50.9 ± 0.9
C	3926	3920.8 ± 6.3	4068.8 ± 10.0	4062.2 ± 9.9
ΔC	288	287.1 ± 5.5	326.0 ± 8.5	327.8 ± 8.6
F <sub>2</sub>	484	479.3 ± 2.2	477.5 ± 1.8	477.0 ± 1.8
ΔF <sub>2</sub>	6	9.3 ± 1.1	8.8 ± 0.9	8.9 ± 0.9
G <sub>1</sub>	410	404.8 ± 2.1	403.4 ± 1.7	402.7 ± 1.7
ΔG <sub>1</sub>	0	-0.9 ± 1.1	-1.3 ± 0.9	-1.0 ± 0.9
G <sub>3</sub>	58	55.6 ± 0.7	56.0 ± 0.6	56.0 ± 0.6
ΔG <sub>3</sub>	2	1.5 ± 0.5	1.6 ± 0.4	1.6 ± 0.4
α	84	82.2 ± 1.1	55.9 ± 1.8	57.4 ± 1.7
Δα	0	1.2 ± 0.9	-2.5 ± 1.4	-2.9 ± 1.4
β	0	Fix 0	-323.5 ± 23.6	-285.0 ± 21.7
Δβ	0	Fix 0	-34.5 ± 20.2	-45.1 ± 20.5
T	0	Fix 0	-3.3 ± 0.2	-3.2 ± 0.2
ΔT	0	Fix 0	-0.5 ± 0.2	-0.6 ± 0.2
ξ <sub>d</sub>	561	558.0 ± 17.5	560.9 ± 13.8	560.3 ± 13.5
Δξ <sub>d</sub>	125	115.2 ± 5.1	115.9 ± 4.1	115.4 ± 4.0
Δξ <sub>d</sub>	9	6.4 ± 2.5	6.3 ± 2.0	6.5 ± 2.0
ξ <sub>p</sub>	691	648.2 ± 22.6	648.4 ± 17.9	639.5 ± 17.7
Δξ <sub>p</sub>	83	76.3 ± 11.0	78.1 ± 8.7	78.1 ± 8.6
Δ		180.3	140.1	138.4

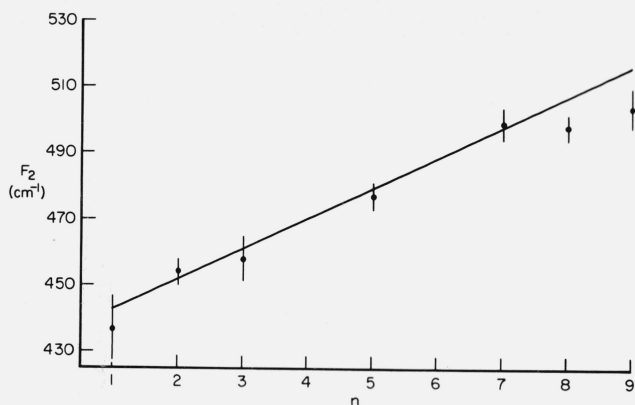


FIGURE 3. Parameter F<sub>2</sub>(dp) versus n for 3d<sup>n</sup>4p configurations (Ti III to Zn III).

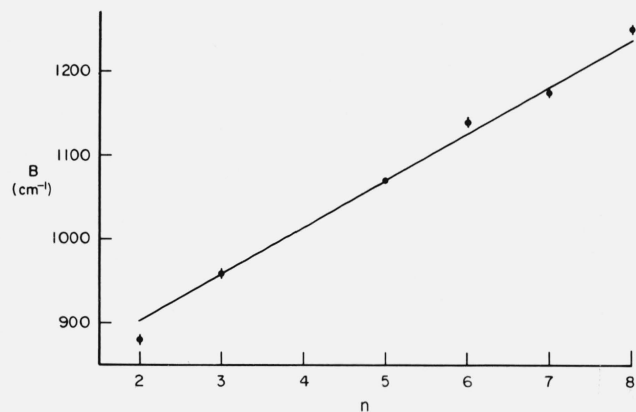


FIGURE 1. Parameter B(dd) versus n for 3d<sup>n</sup>4p configurations (V III to Cu III).

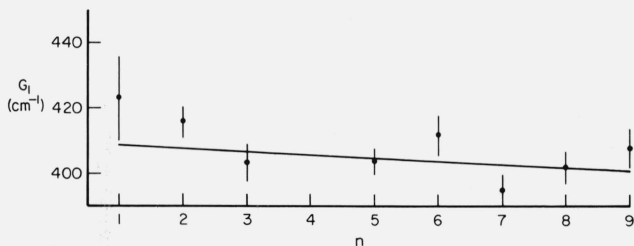


FIGURE 4. Parameter G<sub>1</sub>(dp) versus n for 3d<sup>n</sup>4p configurations (Ti III to Zn III).

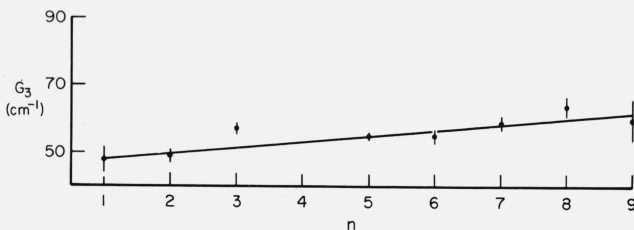


FIGURE 5. Parameter G<sub>3</sub>(dp) versus n for 3d<sup>n</sup>4p configurations (Ti III to Zn III).

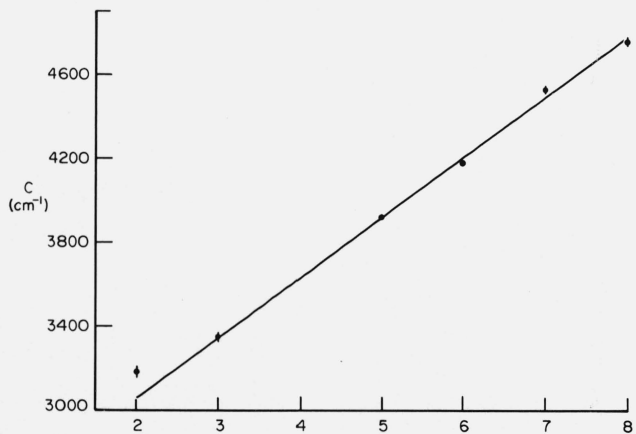


FIGURE 2. Parameter C(dd) versus n for 3d<sup>n</sup>4p configurations (V III to Cu III).

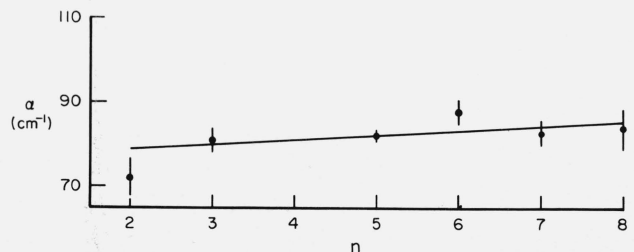


FIGURE 6. Parameter α versus n for 3d<sup>n</sup>4p configurations (V III to Cu III).

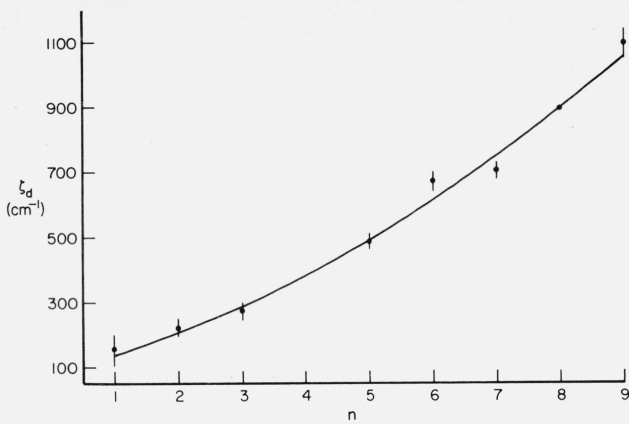


FIGURE 7. Parameter  $\zeta_d$  versus  $n$  for  $3d^n4p$  configurations (Ti III to Zn III).

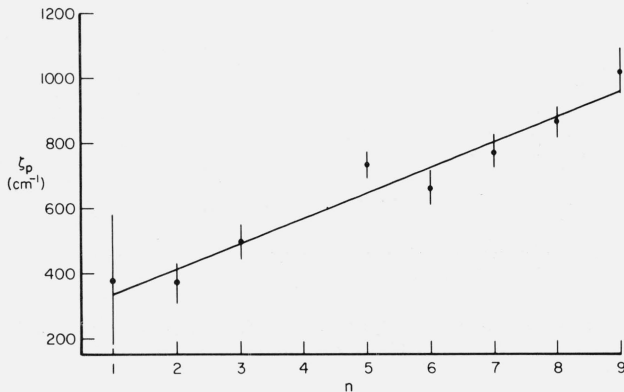


FIGURE 8. Parameter  $\zeta_p$  versus  $n$  for  $3d^n4p$  configurations (Ti III to Zn III).

## 2. Levels: Tables 11-21

In the column "NAME" the calculated designation of the term is given. Whenever terms of the parent  $d^n$  have different seniorities these are denoted by the letters A and B (for  $d^5\ ^2D$  by A, B, and C), the higher calculated term being designated by A. Whenever a calculated term has a corresponding experimental term, the small letters  $z, y, x \dots$  are used as in AEL [13].

The entries in the columns "J", "OBSERVED", and "CALCULATED" are self-evident. In the column "PERCENTAGE", for each calculated level either the three highest contributions or all those contributions exceeding 7 percent are given.

TABLE 11. Observed and calculated levels of SC III 4p

Name	J	Percentage	AEL	Observed	Calculated	O-C	Lande C.
4p	1/2	100		62102	62152	-50	0.667
	3/2	100		62576	62526	50	1.333

TABLE 12. Observed and calculated levels of Ti III 3d4p

Name	J	Percentage	AEL	Observed	Calculated	O-C	Lande C.
$(^2D)z^2D$	2	98		75197	75413	-216	0.997
$(^2D)z^2D$	1	100		77000	76926	74	0.501
	2	95 + 4 $(^2D)z^2F$		77167	77096	71	1.144
	3	93 + 6 $(^2D)z^2F$		77424	77334	90	1.317
$(^2D)z^2F$	2	94 + 5 $(^2D)z^2D$		77421	77444	-23	0.693
	3	94 + 6 $(^2D)z^2D$		77746	77728	18	1.100
	4	100		78159	78107	52	1.250
$(^2D)z^3P$	0	100		80944	81010	-66	
	1	99		80938	81011	-73	1.496
	2	100		81024	81086	-62	1.499
$(^2D)z^1F$	3	100		83117	82791	326	1.000
$(^2D)z^1P$	1	99		83796	83987	-191	1.003

TABLE 13. Observed and calculated levels of V III 3d<sup>3</sup>4p

Name	J	Percentage	AEL	Observed	Calculated	O-C	Lande C.
$(^3F)z^1G$	5/2	98		85524	85539	-15	0.579
	7/2	99		85876	85871	5	0.986
	9/2	100		86306	86279	27	1.172
	11/2	100		86809	86753	56	1.273
$(^3F)z^1F$	3/2	98		86717	86651	66	0.407
	5/2	99		86938	86866	72	1.028
	7/2	99		87219	87147	72	1.236
	9/2	99		87544	87490	54	1.332
$(^3F)z^2F$	5/2	85 + 6 $(^3D)z^2F$ + 4 $(^3F)z^2D$		87881	87952	-71	0.878
	7/2	88 + 5 $(^3D)z^2F$ + 5 $(^3F)z^2D$		88328	88424	-96	1.156
$(^3F)z^2D$	3/2	59 + 29 $(^3F)z^2D$ + 9 $(^3P)z^2D$	$(^3F)z^2D$	88559	88720	-161	0.913
	5/2	52 + 35 $(^3F)z^2D$ + 9 $(^3P)z^2D$		89458	89610	-152	1.260
$(^3F)z^1D$	1/2	96 + 4 $(^3F)z^1D$		89006	89026	-20	0.001
	3/2	67 + 25 $(^3F)z^1D$ + 4 $(^3P)z^1D$		89193	89264	-71	1.080
	5/2	59 + 28 $(^3F)z^1D$ + 5 $(^3F)z^1F$	$(^3F)z^1D$	88944	89072	-128	1.285
	7/2	91 + 4 $(^3F)z^1F$ + 4 $(^3F)z^1D$		89418	89520	-102	1.414
$(^3F)z^2G$	7/2	96		91710	91483	227	0.890
	9/2	96		92053	91871	182	1.112
$(^3P)z^2S$	1/2	99		94714	94906	-192	1.992
$(^3P)z^1S$	3/2	74 + 25 $(^1D)z^1P$		97512	97509	3	1.826
$(^1D)z^2P$	1/2	97		98399	98300	99	0.674
	3/2	70 + 26 $(^3P)z^1S$		98062	98063	-1	1.490
$(^1D)z^2F$	5/2	88 + 7 $(^3F)z^2F$		98384	98240	144	0.872
	7/2	86 + 6 $(^3F)z^2F$ + 5 $(^3P)z^2D$		98825	98598	227	1.157
$(^3P)z^1D$	1/2	95 + 4 $(^3F)z^1D$		99073	99044	29	0.004
	3/2	91 + 4 $(^3F)z^1D$ + 4 $(^1D)z^2D$		99182	99170	12	1.184
	5/2	88 + 5 $(^1D)z^2D$		99440	99421	19	1.349
	7/2	91 + 5 $(^1D)z^2F$		99941	99846	95	1.413
$(^1D)z^2D$	3/2	81 + 6 $(^3P)z^2D$ + 6 $(^3F)z^2D$		99508	99765	-257	0.836
	5/2	80 + 7 $(^3P)z^2D$ + 6 $(^3F)z^2D$		99805	100046	-241	1.217
$(^3P)z^1P$	1/2	99		101646	101618	28	2.662
	3/2	99		101786	101757	29	1.729
	5/2	98		102075	102040	35	1.590
$(^1G)z^2G$	7/2	96 + 4 $(^3F)z^2G$		102961	102970	-9	0.890
	9/2	96 + 4 $(^3F)z^2G$		103035	103032	3	1.110
$(^3P)z^1D$	3/2	80 + 10 $(^1D)z^2D$ + 9 $(^3F)z^1D$		105320	105269	51	0.807
	5/2	82 + 10 $(^3F)z^1D$ + 8 $(^1D)z^2D$		105283	105267	16	1.200
$(^1G)z^2H$	9/2	99		106441	106288	153	0.910
	11/2	100		106903	106682	221	1.091
$(^3P)z^1P$	1/2	99		107060	107049	11	0.667
	3/2	97		107166	107184	-18	1.327
$(^1G)z^1F$	5/2	97		110181	110364	-183	0.857
	7/2	97		109855	110075	-220	1.143
$(^1S)z^1P$	1/2	98			129512		0.667
	3/2	98			130003		1.333

















- [4] Abraham, B. Z., M.Sc. Thesis, The Hebrew University of Jerusalem (1961).
- [5] Trees, R. E., Phys. Rev. **83**, 756 (1951); *ibid.*, **84**, 1089 (1951).
- [6] Racah, G., Phys. Rev. **85**, 381 (1952).
- [7] Racah, G., Rydberg Centennial Conference, Lunds Univ. Arsskr. **50**, 31 (1955).
- [8] Racah, G., Phys. Rev. **63**, 367 (1943).
- [9] Racah, G., and Shadmi, Y., Phys. Rev. **119**, 156 (1960).
- [10] Trees, R. E., and Jorgensen, C. K., Phys. Rev. **123**, 1278 (1961).
- [11] Trees, R. E., Phys. Rev. **129**, 1220 (1963).
- [12] Rajnak, K., and Wybourne, B. G., Phys. Rev. **132**, 280 (1963).
- [13] Racah, G., and Stein, J., Phys. Rev. **156**, 58 (1967).
- [14] Racah, G., Bull. Res. Council. of Israel **8F**, No. 1, 1 (1959).
- [15] Moore, C. E., "Atomic Energy Levels", NBS Circular 467, Vol. I (1949), *ibid.*, Vol. II (1952).
- [16] Iglesias, L., An. Real. Soc. Espan. Fis. Quim. (Spain), **58** (A), No. 7-8, 191 (1962).
- [17] Racah, G., J. Quant. Spectrosc. Radiat. Transfer **4**, 617 (1964). Pergamon Press Ltd.
- [18] Shenstone, A. G., J. Opt. Soc. Am. **44**, 749 (1954).

(Paper 72A5-518)