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Interaction between 3*d* and 3*s* Electrons in the Second Spectra of the Iron Group*

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Six hundred and fifty levels of the low even configurations of the second spectra of the iron group are calculated. The values of the parameters appearing in the theoretical formulas are determined by comparison with 408 experimental levels. The use of interpolation formulas for the parameters reduces their number to 46, which makes the results very reliable. The introduction of the interaction between 3*d* and 3*s* electrons, and the Q correction reduces the mean error from 230 cm^{-1} to 115 cm^{-1}, which is 0.12% of the experimental range. The special role of the interaction between configurations having the same set of principal quantum numbers is discussed.

INTRODUCTION

SINCE the fundamental paper of Slater,[1] several corrections to his first-order formulas for the electrostatic interaction have been introduced and successfully used.[2–6]

By using an old idea of Bacher and Goudsmit,[7] Racah has been able to interpret the $\alpha L(L+1)$ and βQ corrections [Q is the "seniority operator"; see, for example, Ref. 9] as two-body "model interactions" which can represent the effect on the configuration d^n of the interactions with all the configurations differing from it by two electrons and lying far from it.[8,9]

The present author performed a systematic treatment of many spectra of the iron group in which the above-mentioned corrections, as well as the interaction between the neighboring configurations, $3d^n$, $3d^{n-1}4s$, $3d^{n-2}4s^2$, and the spin-orbit interaction were included.[4,5] Similar treatments were also performed in the Pd group[6,10] and in the Pt group.[10] In general, very good results were obtained. It was found possible to treat all the spectra belonging to the same period and with the same degree of ionization (a "sequence") as one problem by introducing simple interpolation formulas for the interaction parameters, and to calculate many hundreds of experimentally known levels belonging to eleven different spectra by use of 31 to 36 adjustable parameters only. Thus, we could get a very reliable check of the various corrections. It turned out that the $\alpha L(L+1)$ correction is very important in the iron group, while in the palladium group, its role is less important. The interaction between the three neighboring configurations is probably the most important correction in the Pd group. Its effect is still remarkable in the second spectra of the Fe group; but it is negligible in the third spectra of the Fe group. In the second spectra of the Fe group it was possible also to evaluate the importance of the βQ correction.[9]

In 1961, Trees and Jørgensen[11] tried to explain the observed values of α and β by considering the interaction of $3p^63d^n$ with $3p^43d^{n+2}$. But when they introduced the exchange integrals evaluated from observed data of Ca III, they got for α a value which was smaller than what was considered the experimental value.

The above-mentioned treatment of the third spectra of the iron group[5] was generally rather satisfactory. (Four hundred eighty-three levels, 307 of which are experimentally known, were calculated by the use of 31 parameters only; the mean error is ±160 cm^{-1}—about 0.13% of the range of the observed levels.) Only the configuration $3d^6$ of Fe III remained problematic. The deviations in this spectrum are much bigger than in the other spectra of the sequence; especially the level $3d^6\ a^1S$ deviates by more than 1000 cm^{-1} from its observed value. It should be noted that the same deviation appears for the level $3d^6(^1S)4s\ a^2S$ of Fe II, so that we have here a systematic discrepancy between theory and experiment.

In 1962, Trees[12] tried to improve our calculations on the configuration $3d^6$ of Fe III by including the interaction of $3s^23p^63d^6$ with $3s3p^63d^7$, and got excellent results (a mean error of ±65 cm^{-1}).

We therefore thought it worthwhile to perform a new systematic treatment of a whole sequence of the Fe group including the new interaction. Such a treatment is necessary in order to get more reliable information on the relative importance and interconnections of semiempirical interaction parameters, independently of accidental features of a too limited amount of experimental material.

For this renewed treatment we chose the second spectra of the Fe group, in which all the interactions except the new one already had proved significant. In this sequence we also have maximum experimental material: Out of 650 theoretically predicted levels, 408 were actually observed.

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THE INTRODUCTION OF THE INTERACTION OF $3s^23d^n$ WITH $3s3d^{n+1}$ AS A "MODEL INTERACTION"

Let us designate states belonging to $3s^23d^n$ by Latin suffixes, and states belonging to $3s3d^{n+1}$ by Greek ones. An element $E_{k\alpha}$ of the energy matrix connecting such states can always be written in the form

$$E_{k\alpha}=h_{k\alpha}H'\,, \tag{1}$$

where $h_{k\alpha}$ is a numerical factor depending only on the angular part of the matrix element; its value was calculated long ago by well-known algebraic methods.[13] H' is essentially a Slater integral.

$$H'=(1/35)R^2(3d3d;3d3s)\,. \tag{2}$$

Now, one could calculate the effect of this interaction by direct diagonalization of the energy matrix of both configurations. The configuration $3s3d^{n+1}$ is completely unknown, but the distance between $3s^23d^n$ and $3s3d^{n+1}$ is much bigger than their internal spread, so that it is permissible to assume an arbitrary large value for $(3s3d^{n+1}-3s^23d^n)$, and determine H' by least squares.[12]

This direct method is, in the general case, very cumbersome. One should remember that we are already treating three configurations together: $3s^23d^n$, $3s^23d^{n-1}4s$, $3s^23d^{n-2}4s^2$. Thus, we have to add three interacting configurations, respectively, $3s3d^{n+1}$, $3s3d^n4s$, $3s3d^{n-1}4s^2$. This would result in energy matrices of gigantic size. Therefore, we replace the direct method by second-order perturbation theory.

In this case, obviously,

$$\begin{aligned} |E_{kk}-E_{11}| &\ll E_{\alpha\alpha}-E_{kk}\,, \\ |E_{\alpha\alpha}-E_{\beta\beta}| &\ll E_{\alpha\alpha}-E_{kk}\,. \end{aligned} \tag{3}$$

Hence, one has to use perturbation theory for degenerate cases, and we may assume

$$E_{\alpha\alpha}-E_{kk}=W=\text{const}\,. \tag{4}$$

Adding the perturbation-theory correction terms to the energy matrix E_{k1} of $3s^23d^n$, we get a modified matrix E_{k1}':

$$E_{k1}'=E_{k1}+\Delta E_{k1}\,, \tag{5}$$

where

$$\Delta E_{k1}=-\textstyle\sum_\alpha (E_{k\alpha}E_{\alpha 1}/W)\,;$$

using relation (1), we get

$$\Delta E_{k1}=(\textstyle\sum_\alpha h_{k\alpha}h_{\alpha 1})(-H'^2/W)\,. \tag{6}$$

Now, we define

$$t_{k1}=\textstyle\sum_\alpha h_{k\alpha}h_{\alpha 1}\,;\quad T=-H'^2/W\,. \tag{7}$$

Thus, we finally have

$$E_{k1}'=E_{k1}+t_{k1}T\,. \tag{8}$$

In (8) the t_{k1} are numerical factors. T is treated as an additional parameter of the energy matrix; its numerical value is to be calculated by the least-squares method as usual. In (8), only that part of the energy matrix which belongs to $3s^23d^n$ is involved; hence the effect of the perturbing configuration is represented by an internal "model-interaction" of $3s^23d^n$ alone. It has been shown that this "model interaction" is a three-body interaction.[7,14,15] The reason for this situation is that three different electrons (at the most) can participate in the definition of the matrix elements t_{k1}.[15]

NOTATIONS AND DEFINITIONS

First we shall define the parameters which refer to the configuration $3d^n$; they are A, B, C, α, β, T, ζ. A is an additive parameter common to all the levels of the configuration. B and C are linear combinations of Slater integrals: $B=F_2(3d^2)-5F_4(3d^2)$, $C=35F_4(3d^2)$. The quantities α and β are the parameters of the $L(L+1)$ and Q corrections, respectively. T is the new parameter representing the interaction of $3s^23d^n$ with $3s3d^{n+1}$ as a model interaction of the $3d$ electrons only within the configuration $3d^n$. The exact definition of T is given in Eq. (7). $\zeta=\zeta_d$ is the parameter of the spin-orbit interaction.

A', B', C', α', β', T', ζ' are the analogous parameters for the configuration $3d^{n-1}4s$, and A'', B'', C'', α'', β'', T'', ζ'' are the analogous parameters for the configuration $3d^{n-2}4s^2$.

In the least-squares calculations, A, A', and A'' were replaced by the centers of gravity of the configurations M, M', and M''; then the differences $D'=M'-M$, and $D''=M''-M'$ were introduced, and M' and M'' were replaced by $M'=M+D'$ and $M''=M+D'+D''$. Thus, M became the additive parameter for a whole spectrum, while D' and D'' were expressed by interpolation formulas like the interaction parameters.

$G=G_2(3d4s)$ measures the exchange interaction between $3d$ and $4s$ electrons, and is also the parameter of interaction between the configurations $3d^n$ and $3d^{n-2}4s^2$. $H=R^2(3d3d,3d4s)/35$ is the parameter of the interaction of the configuration $3d^{n-1}4s$ with the configurations $3d^n$ and $3d^{n-2}4s^2$. It should be noted that the parameter H defined here and the parameter H' which is defined in Eq. (2) are analogous, but differ in the principal quantum number of the s electron.

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

Δ is the *mean error*. It is defined by

$$\Delta=[(\textstyle\sum_i \delta_i^2)/(n-m)]^{1/2}\,. \tag{9}$$

In Eq. (9), δ_i is a difference between the observed and calculated values of a level; n is the number of observed levels; and m is the number of free parameters.

The mean error is essentially different from the mean

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TABLE I. General parameters in the various stages of calculation.

	L.S. 1	L.S. 2*a*	L.S. 2*b*	L.S. 2*c*	L.S. 2*d*	L.S. 2*e*	L.S. 3*a*
D_0'	8112±58	8105±29	8105±30	8094±33	8112±50	8115±57	8110±29
D_0''	35 972±76	36 035±39	36 033±39	36 002±44	36 001±65	36 961±76	36 035±39
D_1'	3943±18	3944±9	3944±9	3944±10	3943±15	3946±18	3946±9
D_1''	5886±29	5859±15	5867±15	5856±16	5859±25	5889±28	5857±15
D_2'	−114±7	−112±4	−113±4	−112±4	−112±6	−112±7	−111±4
D_2''	−118±10	−115±5	−117±5	−112±6	−113±8	−118±10	−114±5
B_0	763±3	759±2	756±2	759±2	765±3	762±3	759±2
B_0'	862±2	864±1	865±1	863±1	862±2	859±2	864±1
B_1	59±2	56±1	56±1	55±1	60±1	58±2	56±1
B_1'	60±1	52±1	52±1	54±1	60±1	60±1	52±1
C_0	2841±15	3039±22	3069±11	3082±13	2908±14	2854±15	3037±21
C_0'	3226±10	3439±9	3437±8	3427±9	3285±10	3238±11	3442±9
C_1	339±9	347±10	364±5	366±6	343±7	341±9	349±10
C_1'	306±7	344±6	340±4	332±4	310±6	308±7	345±6
G_0	1595±11	1588±5	1589±5	1590±6	1591±9	1596±10	1588±5
G_1	−5±7	1±3	1±4	−0.4±3.9	−3±6	−6±7	2±3
H_0	85±6	100±3	101±3	96±3	87±5	85±6	95±3
H_1	−26±3	−22±2	−22±2	−24±2	−26±3	−26±3	−24±1
α_0	67±2	37±3	31±1	33±2	60±1	64±2	38±3
α_0'		30±2					30±2
α_1	7±1	8±2	5±1	7±1	7±1	7±1	7±2
α_1'		5±2					5±1
β_0	...	−515±40	−557±18	−538±20	−249±22	...	−511±37
β_0'	...	−551±20				...	−556±20
β_1	...	49±23	...	...	...	...	48±23
β_1'	...	−13±14	...	...	...	...	−15±14
T_0	...	−1.9±0.4	−2.4±0.2	−3.5±0.2	...	−0.5±0.2	−1.8±0.3
T_0'	...	−4.4±0.2	−4.3±0.2		...		−4.4±0.2
T_1	...	0.2±0.2	...	...	...	...	0.2±0.2
T_1'	...	−0.1±0.1	...	...	...	...	0.0±0.1
ζ_0	367±33	365±17	365±17	369±19	374±29	365±33	364±17
ζ_0'	402±26	396±13	395±13	393±15	400±22	403±25	393±13
ζ_1	88±12	87±6	86±6	86±7	91±11	87±12	88±6
ζ_1'	95±7	97±4	97±4	97±4	97±6	94±7	97±4
$\zeta_2=\zeta_2'$	8±3	7±2	7±2	7±2	8±3	7±3	7±2
Δ	±229	±115.8	±117.0	±131.6	±196.4	±227.3	±114.6

deviation

$$\bar{\delta}=[(\textstyle\sum_i\delta_i^2)/n]^{1/2}$$

because it takes into account the statistical effect of the number of free parameters. Therefore, an addition of free parameters reduces the mean deviation, but does not reduce the mean error if the parameters are not significant. In the present paper only the mean error is used.

The "general parameters" used in Table I are the coefficients of the interpolation formulas for the parameters defined in the present section. Their exact definition is given by Eqs. (10) and (11) in the following section.

THE TECHNICAL PROCEDURE

The algebraic energy matrices for the configurations $d^{n-k}s^k$ were calculated long ago; in the scheme we use, Q is diagonal and its eigenvalues are given in Ref. 13; the elements t_{ik} were calculated by using formula (7). Having the algebric matrices, it is possible to give reasonable values to the interaction parameters, to calculate the energy matrices numerically and to diagonalize them. Then one can improve the values of the parameters by comparison with the observed levels in a least-squares calculation. Of course, all this is done by an electronic computer. To get best results it is usually necessary to iterate this process.

In our calculations we express each parameter P by an interpolation formula having the form

$$P=P_0+P_1x+P_2y\,, \tag{10}$$

where

$$x=n-6\,;\quad y=x^2-10 \tag{11}$$

and n is the total number of electrons in the states $3d$ and $4s$.

In fact, for the electrostatic parameters linear formulas are good enough. For D', D'', ζ, ζ', ζ'' only, a small quadratic correction is necessary.

We call the coefficients of the interpolation formulas (10) "general parameters." We first choose starting values for these general parameters, and by substituting in (10) calculate the parameters for each spectrum. These interpolated parameters are used in the diagonalization of the energy matrices of each spectrum. In the least-squares calculation, all the spectra of the sequence are treated as one problem and the role of free parameters is given to the general parameters. The improved set of general parameters obtained in the L.S. can be used for a second iteration of the calculation.

The number of known levels in the configuration $3d^{n-2}4s^2$ is so small that in most cases it is impossible to determine the values of its parameters by direct comparison with experiment. Thus, for each parameter P'', we required

$$P''-P'=P'-P \quad \text{(linear progression)}\,. \qquad (12)$$

Only D'', which is the difference between the centers of two configurations, remains a free parameter. The list of the free general parameters in the L.S. is given in the first column of Table I.

In the L.S. we transfer from A, A', and A'' to M, M', and M''. To do that, we have to express each M as a function of the other parameters. The matrix is linear in the parameters, therefore M also is a linear function of them. The coefficients of this function, except $\partial M/\partial\beta$ and $\partial M/\partial T$, were already calculated.[4] In order to calculate $\partial M/\partial\beta$, one should remember that Q is a pure two-body operator. For the configuration d^2 one can see by direct calculation that $\partial M/\partial\beta=\frac{1}{9}$; thus for d^n,

$$\partial M/\partial\beta=\tfrac{1}{2}n(n-1)\tfrac{1}{9}\,; \quad (n\leq 5)\,. \qquad (13\text{a})$$

For $n>5$ one should replace n by $(10-n)$. T represents essentially a three-body interaction; hence, $\partial M/\partial T$ is a polynomial of degree 3 in n. This polynomial vanishes for $n=0$, 9, 10, since, in these cases, there is no interaction of s^2d^n with sd^{n+1}. For $n=1$, the configuration d^n consists of the one term ^2D so that one sees directly that $\partial M/\partial T=70$. Thus, for d^n, we get

$$\partial M/\partial T=(35/36)n(9-n)(10-n)\,. \qquad (13\text{b})$$

THE STAGES OF THE CALCULATION

The final parameters of the previous work on the second spectra of the iron group[4] were used as initial parameters for the present work; they are given in Table I under the column "L.S. 1." In that work β and T were not included and α had the same value for all configurations. In the previous work, 405 observed levels were fitted to the calculated levels with a mean error of ± 229 cm^{-1}.

In the new diagonalization, β and T were given the value zero, but we got the derivatives of the levels with respect to these parameters which could be used in the following least-squares calculation. This calculation included four variations. In L.S. 2*a*, the parameters α, β, and T were allowed to be different for d^n and d^{n-1} and to change linearly with n. The mean error was reduced to 115.8 cm^{-1}; the deviation of the above-mentioned $(^1S)^2S$ of Fe II decreased from 1039 to -59 cm^{-1}; also, it was found possible to include in the L.S., three observed levels belonging to the Cr II spectrum, which were discarded in the previous work.

Owing to the fact that in L.S. 2*a* the difference between β_0 and β_0' and the n dependence of β and T appear to be almost zero within the statistical errors, two variations were performed in order to eliminate unnecessary parameters. In L.S. 2*b*, the n dependence of β and T was neglected, and β was also forced to be equal for all configurations. The mean error was 117.0 cm^{-1}. In L.S. 2*c* the parameter T also was forced to be equal for all configurations. The mean error was 131.6 cm^{-1}.

In order to check the relative importance of the two new parameters and their interconnections, two more variations were performed. In L.S. 2*d*, the parameter T was neglected and the restrictions on β were the same as in L.S. 2*c*. We got a mean error of 196.4 cm^{-1}. In L.S. 2*e*, the parameter β was neglected and the restrictions on T were the same as in L.S. 2*c*. We got a mean error of 227.3 cm^{-1}.

The parameters of the above-mentioned variation are given in Table I.

In order to check the convergence of the calculation, a second iteration was performed. In the new diagonalization the general parameters were given the values achieved in L.S. 2*b*. The derivatives of this diagonalization were used for two L.S. calculations; L.S. 3*a* and L.S. 3*b*. In L.S. 3*a*, the parameters were subjected to the same conditions as in L.S. 2*a*. We got a mean error of 114.6 cm^{-1} which is practically equal to the mean error of L.S. 2*a*. Also, the values of the parameters in L.S. 3*a* and L.S. 2*a* are practically equal. The parameters of L.S. 3*a* are given in Table I.

At this stage a new feature in the behavior of the parameter H was noticed. In the previous work, the value of H tended to zero for the spectra in the right side of the sequence; this fact manifested itself in the interpolation formula (L.S. 1) and in the separate L.S. calculations of Fe II, Co II, and Cu II as well. In the present work, the interpolation formula for H still showed the same tendency; but in the separate L.S. of Fe II we got $\text{H}=95\pm 11$, while the interpolated value is 71. This situation was explained as follows: The inclusion of β and T canceled the tendency of H towards zero in the right side; on the other hand, H is still more important in spectra of the left side; hence, the coefficients of the interpolation formula are mainly determined by the "left" spectra. The above-mentioned assumption was checked in L.S. 3*b*, where a quadratic dependence of H on n was allowed. The assumption was justified; the new interpolation formula gives practically the same values for H on the left side, but H does not tend to zero on the right. In L.S. 3*b*, the mean error is ± 113.8 cm^{-1}. All the parameters assume the same values as in L.S. 3*a*, except H_0, H_1, H_2 which are

$$H_0=125\pm 13\,,\quad H_1=-15\pm 4\,,\quad H_2=3\pm 1\,.$$

The interpolated value for Fe II is $H=83\pm 13$.

DISCUSSION OF THE RESULTS

The mean error of the present work is ± 115 cm^{-1} which is one-half the mean error of the previous work.[4] The range of values of the observed levels in the sequence we treat is from 0 to 95 560 cm^{-1}; hence the mean error is about 0.12% of the experimental range.

Comparing the values of the parameters of L.S. 3*a* or 2*a* (which are practically identical) with the parameters of the previous work, one sees that D', D'', B, B', G, ζ, and ζ' did not change considerably. The parameters C and C' changed; in particular, the linear coefficients of C and C' became equal within their statistical errors. In the previous work only the linear coefficients of B and B' were equal. The different behavior of H has already been mentioned in the previous section.

In the present work, α_0 is one-half α_0 of the previous work. The new linear coefficients of α and α' are not much smaller than the previous ones, so that on the left side of the sequence α is now very small.

Comparing the results of L.S. 2*a* to Ref. 9 and to L.S. 2*d* we see that the introduction of T also doubles the value of β. The parameter β is practically constant for all the spectra and for all configurations.

The parameter T is very different in the configurations $3d^n$ and $3d^{n-1}4s$: $T_0=-1.9\pm0.3$ while $T_0'=-4.4+0.2$; both T and T' can be considered constant for all the spectra of the sequence.

Let us examine L.S. 2*b* more carefully. In this variation of the L.S. calculations, the β and T corrections are introduced simultaneously by the use of only three new parameters which appear to be the only meaningful ones: $\beta_0=\beta_0'$,T_0, and T_0'. The mean error of L.S. 2*b* is ±117.0 cm^{-1}, while in the previous work it was ±229 cm^{-1}. The total number of free parameters is 39 (in the previous work we had 36 parameters) which is rather small comparing with 408 observed data. In L.S. 2*c*, only two new parameters are used and the mean error is ±131.6 cm^{-1}.

Since the definition of the mean error takes into account the number of free parameters, the fact that two parameters are sufficient to reduce the mean error from 229 to 132 is definite proof of the importance of β and T. The fact that the separation of T and T' again reduces the mean error by 16 shows that there is some meaning in assuming that they are different.

The change in the old parameters because of the introduction of the new ones has already been described. In principle this fact could be foreseen since T is not a pure three-body interaction and a part of its effect can be described as a linear combination of the parameters of two-body and one-body interactions. Nevertheless, it is striking to compare L.S. 2*b* with L.S. 2*c* and 2*d*. The parameters β and T together decrease the mean error Δ by about 100 cm^{-1}, while β alone decreases Δ by 33 cm^{-1} only, and T alone practically does not decrease Δ at all. It turns out that in order to get a significant improvement of the approximation both β and T are necessary. In his paper[12] on Fe III, Trees mentioned that the βQ correction alone did not improve the results very much, but he did not realize that T alone would not improve them either.

Having new values for α and β, it is desirable to reexamine whether it is possible to explain them as two-body model interactions which represent the interaction of $3d^n$ (or $3d^n4s$) with configurations having the same set of principal quantum numbers, and differing from $3d^n$ by the states of two electrons. For $3d^n$ these configurations are $3s^23p^43d^{n+2}$ and $3s^03p^63d^{n+2}$; the contribution of the first configuration to α and β was calculated for Ca III by Trees and Jørgensen.[11] They got $\Delta\alpha=11$ cm^{-1}, $\Delta\beta=-200$ cm^{-1}. Considering the results of the present work, it seems that their $\Delta\alpha$ fits with the actual value of α. The interaction with $3s^03p^63d^{n+2}$ contributes only to the value of β; a contribution of about -300 cm^{-1} is necessary in order to fit with the experimental β. Taking for $G_2(3d,3s)$ and for the distance $(3s^03p^63d^{n+2}-3s^33p^63d^n)$ the values calculated by Watson[16] by self-consistent-field methods, one actually gets the correct contribution. It is not very desirable to mix two methods of calculation, but unfortunately we were not able to estimate $G_2(3d,3s)$ from the experimental material.

The results of the present work, as well as some previous papers,[11,12] emphasize the importance of the interaction with configurations in which the electrons have the same set of principal quantum numbers. This fact was first pointed out by Layzer.[17] This feature suggests a hydrogenic spectrum in which states belonging to the same principal quantum number are degenerate. Hence, it is plausible that the above mentioned effects will become more important for higher ionizations, where the central field becomes more "Coulombic." A similar treatment of the third spectra in the iron group is now in progress in order to check this assumption.

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