

Q Correction in the Spectra of the Iron Group

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A semiempirical correction term, proportional to the "seniority operator" Q , is introduced into the Slater formulas for the configurations $3d^n4s^k$ of the second spectra of V, Cr, and Fe. The agreement with the experimental data, obtained by least squares, is improved by about 20%. The physical meaning of this correction is discussed.

IT was pointed out by Trees¹ that the agreement between the theoretical formulas of the Slater approximation and the experimental data in the d^5s configurations of Mn II and Fe III is greatly improved by the addition of a correction term of the form $\alpha L(L+1)$, and it was later verified that this correction is also very important in many other spectra of the iron group.

This effect was explained by Racah^{2,3} by the assumption that the deviation from the theoretical formulas in the n -electron configurations are the sum of the deviations of the interaction of each couple from the corresponding formulas. Such an assumption seems strange at first sight, but it was already shown by Bacher and Goudsmit⁴ that additivity is to a good approximation a general property of most configuration interactions.

As the configuration d^2 contains five terms, which are expressed by three Slater parameters, one can introduce two correction terms $\alpha\varphi_1(L)$ and $\beta\varphi_2(L)$, where φ_1 and φ_2 are arbitrary functions of L , in order to represent exactly the terms of d^2 . Without any loss of generality, we may represent the deviations from Slater's formulas in d^2 by

$$\delta W(d^2) = 2\alpha(\mathbf{I}_1 \cdot \mathbf{I}_2) + \beta q_{12},$$

where q_{12} is the "seniority operator" of two particles. The additivity assumption now gives:

$$\delta W(d^n) = \sum_{i < k} [2\alpha(\mathbf{I}_i \cdot \mathbf{I}_k) + \beta q_{ik}] = \alpha[L(L+1) - 6n] + \beta Q,$$

where Q is the total "seniority operator."⁵

The first term on the right side is, apart of an additive constant, the $L(L+1)$ correction of Trees. The second term, βQ (which we call the " Q correction") was generally neglected because Q is considerably different from zero only for the higher terms of every configuration and was expected to vanish or to have very small expectation values for almost all the terms which are experimentally known.

The authors of the present paper have recently completed a systematic treatment of the low even con-

figurations of all the second spectra of the iron group.⁶ In this treatment the interaction between the three neighboring configurations $3d^n$, $3d^{n-1}4s$, $3d^{n-2}4s^2$, the spin-orbit interaction and the $L(L+1)$ correction were taken into account, as well as the possibility of using different interaction parameters for each of the three configurations. In the last stage of this work it was found possible to fit all the interaction parameters into simple interpolation formulas. In this way 650 levels of 11 different spectra (405 of them experimentally known) were calculated with the use of 25 interpolative interaction parameters only. The final mean error was 229 cm^{-1} , while the maximum breadth of the configurations treated exceeds 100 000 cm^{-1} . In this way it was possible to get very reliable answers regarding the importance of the various improvements, and the conclusions are very definite. All the three improvements of the electrostatic approximation are very important in the second spectra of the iron group. Similar treatments of the first and third spectra (which are almost completed by now) lead to similar conclusions.

After finishing this work⁶ it seemed worthwhile, for the sake of completeness, to try also the Q correction. In

TABLE I. Parameters of V II—($3d+4s$)⁴.^{a, b}

	Diag.	L. S. Ia	L. S. IIa
A	13 484	13 511±160	13 583±125
S'	4877	4805±185	4802±146
S''	28 955	28 363±478	28 236±373
B	641	648±6	652±5
B'	746	739±6	751±5
B''	851	830*	850*
C	2154	2152±26	2220±23
C'	2629	2625±31	2696±23
C''	3104	3098*	3172*
G	1616	1600±31	1577±25
H	133	130±7	136±6
α	55	52±3	43±3
β	0	...	-334±53
ζ	123	125±51	118±40
ζ'	159	228±55	206±43
ζ''	195	331*	294*
Δ	...	±240	±186

^a Primes and double primes refer to the configurations $d^{n-1}s$ and $d^{n-2}s^2$ respectively.

^b Parameter values indicated by an asterisk were not free to change arbitrarily in the least-squares calculations but were forced to remain in linear progression with the corresponding ones of the other configurations.

⁶ G. Racah and Y. Shadmi, Bull. Research Council Israel **8F**, 1 (1959).

¹ R. E. Trees, Phys. Rev. **83**, 756 (1951); **84**, 1089 (1951).

² G. Racah, Phys. Rev. **85**, 381 (1952).

³ G. Racah, *Rydberg Centennial Conference* [Lunds Univ. Årsskr. **50**, 31-42 (1955)].

⁴ R. F. Bacher and S. A. Goudsmit, Phys. Rev. **46**, 948 (1934).

⁵ G. Racah, Phys. Rev. **63**, 367 (1943).

fact in the iron group many of the higher levels are also known. Furthermore, an examination of the eigenvectors of the calculated levels showed that even in some of the lower levels the expectation value of Q was not negligible at all, and therefore these levels could also be influenced quite considerably by the Q correction.

In order to be sure of the physical meaning of our results, we tried the Q correction in the spectra of V II, Cr II, and Fe II, which have the greatest number of experimentally known levels. For these spectra we compared least-squares calculations without Q correction ("L. S. I") with least-squares calculations where the new parameter was allowed to change freely ("L. S. II"). The least-squares calculation referred as "L. S. Ia" is identical with the final least-squares calculation of the previous paper.⁶ All the least-squares calculations are

TABLE II. Terms of V II considerably changed by the Q correction.

Conf.	Term	J	L. S. Ia	L. S. IIa
d^4	1S	0	61 432	60 468
d^2s^2	1S	0	76 415	75 435

TABLE III. Parameters of Cr II— $(3d+4s)^6$.^a

Diag.	L. S. Ia	L. S. Ib	L. S. IIa	L. S. IIb
A	24 479	24 450±266	24 470±281	24 201±241
S'	11 009	10 612±316	10 486±331	10 816±282
S''	41 510	41 823±413	41 581±429	42 171±372
B	700	701±6	701±7	698±6
B'	805	805±6	798±6	803±5
B''	910	909*	895*	908*
C	2514	2490±26	2490±27	2571±28
C'	2932	2968±22	2970±23	3017±22
C''	3350	3446*	3450*	3463*
G	1605	1588±26	1593±28	1576±24
H	111	113±8	111±8	112±7
α	59	58±3	58±3	50±3
β	0	-267±56
ξ	184	212±80	214±85	188±71
ξ'	227	212±42	212±42	195±37
ξ''	270	212*	210*	202*
Δ	...	±260	±277	±231

^a See footnotes to Table I.

based on the linear equations obtained by the "general diagonalization" of the previous work.⁶

V II— $(3d+4s)^4$

The predicted terms of these configurations are 37. They split into 81 levels. In the compilation by Moore,⁷ 30 terms, which split into 70 levels, are reported. In the previous paper some changes in assignment were performed. All these changes are adopted in the present work.

In L. S. I we got a mean error of 240 cm⁻¹. In L. S. II, the insertion of the Q correction reduced the mean error to 186 cm⁻¹.

The values of the parameters in the various steps of the calculation are given in Table I. Those energy levels

⁷ *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1; *ibid*, 1952, Vol. 2.

TABLE IV. Terms of Cr II considerably changed by the Q correction.

Conf.	Term	J	L. S. Ib	L. S. IIb
d^4s	$(^3F)^2F$	7/2	59 819	59 390
		5/2	59 847	59 419
d^5	2D	3/2	67 828	67 275
		5/2	67 833	67 271
d^4s	$(^1S)^2S$	1/2	96 082	95 027
d^3s^2	2D	5/2	103 474	102 985
		3/2	103 603	103 126

which their calculated values changed because of the Q correction by more than 400 cm⁻¹ are given in Table II.

The symbols for the parameters are the usual ones; primes and double primes refer to the configurations $d^{n-1}s$ and $d^{n-2}s$, respectively. Parameter values indicated by an asterisk were not free to change arbitrarily in the least-squares calculations but were forced to remain in linear progression with the corresponding ones of the other configurations. For detailed definitions, see the previous work.⁶

Cr II— $(3d+4s)^5$

In these configurations 48 terms are predicted, splitting into 119 levels. 91 levels belonging to 36 terms are reported in reference 7. The terms c^4P and b^2P are not complete.

In the previous work some configuration assignments were changed. The terms e^2G and e^2D differed by more than 13 000 cm⁻¹ from their predicted positions, and

TABLE V. Calculated values of $d^4s\ ^4F$ in Cr II.

J	Observed ("e ² G")	L. S. Ia	L. S. Ib	L. S. IIa	L. S. IIb
3/2		55 242	55 081	54 811	54 713
5/2		55 250	55 090	54 819	54 721
7/2	54 444.19	55 250	55 091	54 821	54 724
9/2	54 678.95	55 235	55 078	54 812	54 716

TABLE VI. Parameters of Fe II— $(3d+4s)^7$.^a

Diag.	L. S. Ia	L. S. Ib	L. S. IIa	L. S. IIb
A	13 741	13 756±143	13 761±130	13 785±128
S'	12 082	11 920±197	12 069±178	12 049±179
S''	45 669	45 558±587	46 021±538	45 762±519
B	818	810±9	811±8	815±9
B'	923	918±5	925±5	926±5
B''	1028	1026*	1039*	1037*
C	3234	3244±43	3231±41	3326±40
C'	3539	3525±23	3490±23	3569±23
C''	3844	3806*	3749*	3812*
G	1585	1577±26	1580±24	1578±23
H	67	43±34	61±31	53±30
α	68	74±4	78±4	68±4
β	0	-268±57
ξ	357	368±75	370±68	378±66
ξ'	412	418±55	415±49	434±48
ξ''	467	468*	460*	490*
Δ	...	±302	±271	±266

^a See footnotes to Table I.

TABLE VII. Terms of Fe II considerably changed by the Q correction.

Conf.	Term	J	L. S. Ib	L. S. IIb
d^5s^2	4P	5/2	57 032	56 451
		3/2	57 106	56 521
		1/2	57 185	56 588
d^5s^2	2D	5/2	70 509	70 005
		3/2	71 040	70 618
d^5s^2	2F $^2F+^4F$	7/2	72 402	71 780
		5/2	73 144	72 607
d^5s^2	4F	9/2	73 451	72 947
		7/2	73 501	72 996
	$^4F+^2F$	5/2	73 540	73 061
		3/2	73 657	73 173
d^5s^2	2H	9/2	76 613	76 005
		11/2	76 956	76 235
d^6s	$(^1S)^2S$	1/2	97 808	97 076
d^5s^2	2D	5/2	125 911	125 068
		3/2	125 951	125 116

were not included in calculation. All these changes were adopted as a starting point of the present work.

In L. S. Ia the mean error was 260 cm^{-1} . The introduction of βQ in L. S. IIa reduced the mean error to 231 cm^{-1} . In a detailed examination of the result of L. S. IIa it was found that the calculated values of d^4s^4F (the experimental values of which are not reported in reference 7) changed very considerably, so that we could fit to it the 2 discarded levels of the so called e^2G . The least-squares calculation was therefore repeated with the addition of these two levels. In L. S. Ib (without βQ) the mean error increased to 277 cm^{-1} . While in L. S. IIb (including the Q correction) the mean error remained 231 cm^{-1} . So, the re-inclusion of the two discarded levels was justified. Thus L. S. Ib and IIb must be considered the final; and the Q correction reduced the mean error by 46 cm^{-1} .

The values of the parameters in the various stages of the calculation are given in Table III. Those energy levels which their calculated levels changed because of the Q correction by more than 400 cm^{-1} are given in Table IV. The values of the above-mentioned d^4s^4F in all the stages are given in Table V.

Fe II— $(3d+4s)^7$

In these configurations 48 terms are predicted, splitting into 119 levels. 84 levels belonging to 32 terms are reported in reference 7.

In L. S. Ia we got a mean error of 302 cm^{-1} . In L. S. IIa the mean error was 266 cm^{-1} .

The term d^6s^2S differed by more than 1000 cm^{-1} from its calculated value. In L. S. IIa the difference even increased. We repeated the calculations without this level. L. S. Ib gave a mean error of 271 cm^{-1} while in L. S. IIb the mean error was 222 cm^{-1} .

The values of the parameters in the various stages of the calculation are given in Table VI. Those energy levels which their calculated values changed by the influence of the Q correction by more than 400 cm^{-1} are given in Table VII.

CONCLUSION

The Q correction reduces the mean error by about 20%. This is not a change of the order of magnitude, but nevertheless not a negligible one, if we consider that we are dealing with spectra with a very large number of experimentally known levels.

The meaningfulness of this correction is also confirmed by the consistency of the results in the three different spectra. Not only the values of β are practically equal in the three spectra, but also the effect of the correction on the other parameters is the same: the C 's increase, α decreases, and the other parameters do not change.