

Parameters α and β in the Spectra of the Iron Group

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The parameters α and β in the low even configurations of iron-group spectra are qualitatively explained as effects of the interaction with configurations having two $3p$ electrons excited from the argon-type core to $3d$ states. Quantitatively, the parameters are too large by a factor of two when the interaction integrals are taken equal to the exchange integrals of Watson's self-consistent field calculations. The parameters are too small when the exchange integrals are evaluated from observed data in the $3p^63d$ configuration of Ca III.

IT was shown by Bacher and Goudsmit¹ that a large part of the second-order effect of electrostatic interaction in an n electron atomic system could be evaluated indirectly from the experimental data in appropriate two electron atomic systems.² This was the effect produced by interactions with other configurations having two electrons excited from the configuration under consideration.³ They verified their theory by use of the experimental data for the simple spectra of elements in the first row of the periodic table. The method of applying their procedure was cumbersome, however, and was not applicable if configuration interaction became too strong (i.e., second-order perturbation theory would not apply), or if there were a breakdown of LS coupling sufficient to obscure the term structure of the levels. For these and other reasons, it was impractical to verify the original theory with any precision in more complicated spectra, and so Slater's theory⁴ continued to be the one mainly used; to the extent that it was practical, configuration and spin-orbit interactions were also included, as suggested by Condon.⁵

In recent years a further extension of Slater's theory has been used and briefly described as the "linear theory." It originated in the observation of Trees⁶ and Layzer⁷ that adding a correction proportional to $L(L+1)$ to Slater's formulas greatly improved the accuracy of the theory in even configurations of first long period spectra. Racah recognized that the correction implied a linear behavior of second-order effects of the electrostatic interaction, along with the existence of an additional correction; he introduced the latter as a term proportional to eigenvalues of his operator Q .⁸

¹ R. F. Bacher and S. Goudsmit, *Phys. Rev.* **46**, 948 (1934).

² It is considered that the closed shells forming the appropriate inert-gas type of core are also present.

³ They also showed that second-order effects arising from interactions with configurations having only one electron excited could be evaluated by considering data in appropriate three-electron spectra as well. Since these excitations are not included in the "linear theory," the latter is not expected to apply, except fortuitously, in the spectra where they are important.

⁴ J. C. Slater, *Phys. Rev.* **34**, 1293 (1929).

⁵ E. U. Condon, *Phys. Rev.* **36**, 1121 (1930).

⁶ R. E. Trees, *Phys. Rev.* **83**, 756 (1951); **84**, 1089 (1951).

⁷ D. R. Layzer, dissertation, Harvard University, Cambridge, Mass., May 1, 1950 (unpublished).

⁸ G. Racah, *Phys. Rev.* **85**, 381 (1952).

Later it was recognized that the linear property of second-order perturbations had been demonstrated earlier by Bacher and Goudsmit.^{1,9}

The linear theory augments the usual Hamiltonian of the n electron system with additional two-body scalar interaction terms. Each interaction is multiplied by an adjustable constant that is determined by comparison with the experimental results. It is essential at this point to regard Slater's F and G integrals as adjustable parameters also. The number of additional interactions is the minimum consistent with the requirement that the total number of adjustable parameters be the same, loosely speaking, as the number of allowed terms in all distinct two electron configurations that can be derived by deleting $(n-2)$ of the electrons from the n electron configuration under consideration.⁸ Many sets of additional interactions would satisfy this minimum requirement, but it is natural to choose interactions that have easily evaluated matrix elements. For the even configurations of the first long period, two interactions are introduced corresponding to the two corrections already described. The parameter α multiplies the $L(L+1)$ correction, and the parameter β is associated with the Q correction. Including the three Slater integrals as parameters (i.e., F_0 , F_2 , and F_4), this yields a total of five adjustable parameters corresponding to the five allowed terms in the d^2 configuration.

In the present paper it is shown that the observed values of α and β can be semiquantitatively explained by consideration of the interaction with a configuration having two $3p$ electrons excited from the argon-type core to $3d$ states; i.e., the values of α and β in $3s^23p^63d^n$ originate in the interaction with $3s^23p^43d^{n+2}$. This has been pointed out by Jørgensen, who has discussed these and other configuration interactions in first long period spectra from a more qualitative viewpoint.¹⁰ Excitations of either one or two of the $3s$ electrons to $3d$ states are omitted for simplicity.¹¹ This is the natural generaliza-

⁹ G. Racah, *Lunds Univ. Arsskr.* **50:21**, 31 (1954).

¹⁰ C. K. Jørgensen, *Solid State Physics* (to be published).

¹¹ Interaction with $3p^63d^{n+2}$ would increase β by about 30%, but have no effect on other parameters (excluding F_0). Interactions with $3s3p^63d^{n+1}$ are the nonlinear type referred to in reference 3. The relative contributions to different terms can be easily calcu-

tion to the first long period of the well-known interactions between $2s^2 2p^n$ and $2p^{n+2}$ in the first short period.¹² The interactions in the first short period recently have been investigated in considerable detail by the use of new theoretical techniques.¹³

Regarding $p^6 d^{10}$ as a full shell (and ignoring phase conventions), it follows from first principles that

$$(p^n d^m | G | p^{n-2} d^{m+2}) = (p^{6-n} d^{10-m} | G | p^{8-n} d^{8-m}).$$

Specializing to the case where $n=6$ and $m=8$, we obtain

$$(p^6 d^8 | G | p^4 d^{10}) = (d^2 | G | p^2).$$

The matrix element on the left is the one needed to evaluate the interaction with the configuration having two core electrons excited, the property of linearity making it immaterial which particular $p^6 d^n$ configuration is considered. The equation shows that this element is equal to the easily evaluated¹⁴ element between the d^2 and p^2 configurations. The effects of the interaction, as given by second-order perturbation theory, are then equated to the formulas of the linear theory for the d^8 configuration. By solving this simple set of five simultaneous equations, the following contributions are obtained to the parameters of the linear theory (the contribution to F_0 is omitted, as being irrelevant to the present work). The results apply, of course, to $3d^n$ configurations generally.

$$\alpha = (W^2 + V^2)/40U,$$

$$\beta = -(11W - 3V)(W - V)/20U,$$

$$F_2 = -(W^2 + 1.8V^2)/84U,$$

$$F_4 = -(W^2 - V^2)/175U,$$

where U is the positive number specifying the separation of the configurations,

$$U = E(3p^4 3d^{n+2}) - E(3p^6 3d^n),$$

and V and W are linear combinations of the radial integrals $R^1(3d3d, 3p3p)$ and $R^3(3d3d, 3p3p)$ as follows:

$$V = (5)^{-\frac{1}{2}}(R^1 - 3/7R^3),$$

$$W = (5)^{-\frac{1}{2}}(R^1 + 9/49R^3).$$

The integrals R^k are formally equal to the exchange integrals G^k , and it follows that V and W are positive numbers.¹⁴ The G^k are in turn equal to $D_k G_k$, where the D_k are numerical factors that simplify the form of Slater's formulas. In the notation of *Theory of Atomic Spectra*¹⁵ (TAS), $D_1=15$ and $D_3=245$ while Racah¹⁴ uses $D_1=15$ and $D_3=245/3$.

lated for each value of n by use of matrix elements published by Racah. However, the appropriate radial integrals required to evaluate the absolute effects have not been evaluated with self-consistent field functions.

¹² D. R. Hartree, W. Hartree, and B. Swirles, *Phil. Trans. Roy. Soc. (London)* **A238**, 229 (1939).

¹³ D. R. Layzer, *Ann. Phys. (N. Y.)* **8**, 271 (1959). (See also reference 21).

¹⁴ G. Racah, *Phys. Rev.* **62**, 438 (1942).

¹⁵ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1951).

Utilizing Roothaan's procedure, Watson has carried out many Hartree-Fock calculations for the $3d^n$ configurations of iron group spectra.¹⁶ He has published the values of the F and G integrals obtained from the calculation for the $3d^5$ 6S ground term of Mn III. Using these results, we obtain 39 000 and 58 000 cm^{-1} as the values of V and W respectively. By taking twice the difference of the one electron energies $H(3p)$ and $H(3d)$, U is estimated as 810 000 cm^{-1} . The corresponding values of α , β , F_2 , and F_4 are 150, -630, -90, and -13 cm^{-1} , respectively. Shadmi has evaluated the parameter α in Mn III from a least-squares adjustment to fit all the available observed data for third spectra of the iron group, and finds it has the value 76 ± 2 cm^{-1} , or only half the value just estimated from Watson's calculation.^{17,18} The most reliable estimates of β have been obtained from experimental data in the spectra of V II, Cr II, and Fe II where the values are within the limits -290 ± 50 cm^{-1} .¹⁹ These values are consistent with the value -250 ± 130 obtained by least-squares from the observed data for the $3d^6$ configuration of Fe III.²⁰ It follows that the value of β estimated from the self-consistent field calculations is also twice as large as observed, and contributions from other configurations would make it still larger.¹¹

Watson's calculations indicate that $F_2=1741$ and $F_4=120$. These values would appear reduced in the observed data by 90 and 13 cm^{-1} , respectively, if the corrections evaluated above applied (i.e., $F_2=1651$ and $F_4=107$). The corrected values are still considerably larger than the observed values $F_2=1378 \pm 6$ and $F_4=93 \pm 1$.¹⁸ The corrections are too small by a factor of 2 to 4 to explain these differences, and modifications (i.e., increase of U) leading to better values of α and β tend to make the situation worse for F_2 and F_4 .

The variation of the corrections with atomic number and degree of ionization has been estimated by use of some of Watson's data for $3d^3$ and $3d^5$ isoelectronic sequences reproduced in Tables 3 and 4 of reference 10. The ratio of $(G_1)^2$ to $H(3p) - H(3d)$ indicates that the parameters should decrease by about 15% in going from Mn III to the isoelectronic spectrum of Cr II. In the latter spectrum $\alpha=60$,¹⁷ so an approximately correct percentage variation is obtained. But the self-consistent field calculations yield $F_2=1400$ and $F_4=100$, while the observed values¹⁷ are $F_2=1061$ and $F_4=72$; the differences between corresponding observed and calculated parameters are closely alike in Mn III and Cr II, and the effect of change in degree of ionization is much less

¹⁶ R. E. Watson, *Phys. Rev.* **118**, 1036 (1960).

¹⁷ G. Racah and Y. Shadmi, *Bull. Research Council Israel* **8F**, 15 (1959).

¹⁸ Y. Shadmi, dissertation, The Hebrew University of Jerusalem (unpublished).

¹⁹ G. Racah and Y. Shadmi, *Phys. Rev.* **119**, 156 (1960).

²⁰ In the $3d^8 4s$ configuration of Fe III, it is found that $\beta = -77 \pm 27$. The apparent inconsistency in the two values of β seems to arise from the fact that the standard deviations obtained from statistics are unrealistic. [R. E. Trees (unpublished calculations)].

TABLE I. Calculated and observed energy levels (in cm^{-1}) in the $3p^33d$ configuration of Ca III.

J value	Obs	Calc	Calc-Obs
0		203 230	
1	203 845	203 998	153
4		211 055	
3	213 378	212 428	-950
2	204 835	205 604	769
1	224 552	225 841	1289
2	214 332	213 822	-510
3		224 893	
2	225 823	225 286	-537
3	228 412	228 487	75
2	227 388	226 799	-589
1	232 831	233 188	357

Parameters
 $F_0=215\ 328$; $F_2=1479$; $G_1=1387$
 $G_3=170$; $\zeta_p=2975$; $\zeta_d=172$

than for α . According to the self-consistent field calculations, the parameters should be about 5% smaller in V III than in Mn III, and $F_2=1480$ while $F_4=102$. The observed values¹⁸ are $\alpha=68$, $F_2=1178$, and $F_4=77$. Here the difference of observed and calculated F_2 values shows a larger percentage variation than the α value. This may indicate a dependence on the particular configuration (i.e., $3d^3$ in V III as compared to $3d^5$ in Mn III), but it is also possible that Watson's F_k values are not sufficiently close to exact self-consistent field results to justify our comparison of second-differences.

The variation of α and β is associated with the "near orbital degeneracy" of the interacting configurations $3p^63d^n$ and $3p^43d^{n+2}$. This effect is already well known in simpler spectra,¹³ and has been particularly studied in the $1s^22s^2$ and $1s^22p^2$ configurations of Be I.²¹ In contrast, the "constancy" of differences in the F_k values is expected for interactions with configurations in which the principal quantum numbers of some orbitals differ from the corresponding numbers in the configuration under consideration. In these interactions, the energy denominators increase roughly with the square of the ionization in a way similar to the Rydberg series formulas. More specifically, the excited configuration $3d^{n-2}(\infty d)^2$ has been identified as one of those responsible for the differences in the F_k values.¹⁰ Here the notation " ∞d " refers to a "virtual" d orbital of the type used in simpler configurations.²¹ Because of the presence of a node near the maximum of the $3d$ orbital, this virtual orbital would satisfy the requirements of orthogonality while still yielding large interaction integrals, and hence strong perturbations. These virtual orbitals are obtained from straightforward variation calculations,²¹ or by solving the Fock self-consistent field equations in

the multi-configuration approximation.²² The magnitudes of the effects have not been estimated. However, simple considerations indicate that the major effect will be a reduction in the F_k . It seems that even if this reduction can be made large enough to explain the difference between observed and calculated values of the F_k , the contributions to α and β will be too small to compensate the excess in the values calculated from the $3p^43d^{n+2}$ interaction.

Instead of introducing interactions with configurations other than $3p^43d^{n+2}$, the Hartree-Fock equations might be modified to yield $3d$ orbitals that are slightly expanded. By decreasing both the F_k and the G_k , this should lead to better quantitative agreement. It is known that the $3d$ orbitals are particularly sensitive to small changes in the equations,²³ and core polarization potentials might produce the desired result. The simplest viewpoint indicates that such corrections would contract the $3d$ orbitals still more and make the situation worse. But the form of such a polarization potential is not known in the region of the maximum of the $3d$ orbitals,²³ and the effect in this region may well be repulsive. Whatever the merits of such an approach, it would still be desirable to evaluate the G^k from the experimental data, and see if these parameters are also smaller than those obtained from the self-consistent field calculations.²⁴

The integrals G^k have been determined from the observed data for the $3p^53d$ configuration of Ca III.²⁵ The radial integrals in the matrices of TAS¹⁵ were determined to yield the best fit to the observed data (approximately), as judged by the least-squares criterion. The results are given in Table I. This calculation yields the values $V=1470$ and $W=14\ 190$. We estimate $U=450\ 000\ \text{cm}^{-1}$, and obtain $\alpha=11$, $\beta=-214$, $F_2=-5$, and $F_4=-3$. An extrapolation of Shadmi's results¹⁸ indicates that $\alpha=56$ in Ca III, so that the use of the observed data to estimate this parameter leads to a value that is too small by a factor of 5. However, the assignments of the observed levels are "doubtful"²⁵; even if they are correct, the effects of configuration interaction may be important, so that the results obtained from this calculation are somewhat inconclusive.

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²² A. P. Jucys, Zhur. Eksp. i Teoret. Fiz. **23**, 129 (1952); Trudy Akad. Nauk Litovsko S.S.R. Ser. B, **2**, 3 (1958) (translated by American Meteorological Society).

²³ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), pp. 87, 162.

²⁴ We are indebted to Professor Racah for suggesting this, and for pointing out the possibility of using the observed data in Ca III.

²⁵ *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. I.

²¹ S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950); V. V. Kibartas, V. I. Kavetskis, and A. P. Yutsis, Zhur. Eksp. i Teoret. Fiz. **29**, 623 (1955); R. E. Watson, Phys. Rev. **119**, 170 (1960); A. W. Weiss, Phys. Rev. **122**, 1826 (1961).