

and we obtain  $\Omega = -0.18(6)$  nm b. The value  $T/F_{3/2} = 0.77$  has been obtained from Schwartz.<sup>21</sup>  $c_{3/2} = C' = -0.79(28)$  kc/sec.<sup>14</sup> If we reject the data for the first run for  $f(5/2 \leftrightarrow 7/2)$ , then  $C' = -0.68(20)$  kc/sec and  $\Omega = -0.15(4)$  nm b. The principal source of error in  $\Omega$  is the error in  $c_{3/2}$ . In this value of  $c_{3/2}$  there has been made no correction for configuration mixing of the  $|^3P_2\rangle$  state. The measured  $\Omega$  lies between the Schmidt limits, and it has the sign anticipated; but it is smaller than expected for  $g_s = -3.83$  (see Fig. 3).<sup>21a</sup> Williams<sup>22</sup> has recently given a discussion of the octupole moments of a number of nuclei and of the  $g$  factors.

We calculate the nuclear quadrupole moment from the relation<sup>23</sup>  $Q = -(8/3)(b_{3/2}/a_{3/2})(F_{3/2}/R)(g_{rm}/M_p)(\mu_0^2/e^2) \times 10^{24}$  b, and we obtain  $Q = +0.270(13)$  b. The value  $R/F_{3/2} = 1.028$  has been taken from Schwartz.<sup>21</sup>  $b_{3/2} = B' = -452$  Mc/sec. The source of error in  $Q$  is the error in  $a_{3/2}$ <sup>14</sup> (see footnote i of Table I). We have included no correction for the effect of polarization of the electron core, as discussed by Sternheimer.<sup>24</sup>

### E. $g_J$ Factor for the Krypton Metastable $^3P_2$ State

The ratio  $g_J(^3P_2 \text{ krypton})/g_J(^3P_2 \text{ argon})$  was measured by observations of the  $\Delta M_J = \pm 1$ ,  $\Delta J = 0$  transi-

<sup>21</sup> C. Schwartz, Phys. Rev. **105**, 173 (1957).

<sup>21a</sup> Note added in proof. See final paragraph of Introduction.

<sup>22</sup> S. A. Williams, Phys. Rev. **125**, 340 (1962).

<sup>23</sup> A similar expression was given in reference 2 and again in reference 6 (see errata, Sec. VI of the present paper). The expression applies for  $l \geq 1$ , with a plus sign for a  $p_{3/2}$  electron and with a minus sign for a  $p_{3/2}$  hole.

<sup>24</sup> R. M. Sternheimer, Phys. Rev. **95**, 736 (1954); **105**, 158 (1957).

tions (frequency  $g_J \mu_0 H$ ) for the even isotopes of each gas in the same magnetic field. The result of two measurements is  $g_J(^3P_2 \text{ krypton})/g_J(^3P_2 \text{ argon}) = 1.00007(10)$ . If the known value  $g_J(^3P_2 \text{ argon}) = 1.500964(8)$  is used,<sup>25</sup> there follows  $g_J(^3P_2 \text{ krypton}) = 1.5011(2)$ ; this result is considered to confirm that of Friedburg and Kuiper (see footnote h, Table I),  $g_J(^3P_2 \text{ krypton}) = 1.5009(1)$ .

### VI. ERRATA ON PREVIOUS PAPERS

The expression for  $W_F^2$  in reference 2 should be multiplied by the factor 1/16. The expression relating  $Q$  and  $b_{3/2}$  in reference 6 should be multiplied by the factor  $(-1)$ . (See footnote 23 of the present paper.)

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<sup>25</sup> A. Lurio, G. Weinreich, C. Drake, V. W. Hughes, and J. A. White, Phys. Rev. **120**, 153 (1960).

## Nonlinear Effects in Spectra of the Iron Group

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As known for the last ten years, calculations made with the linear theory agree poorly with the experimental results for the  $3d^6$  configuration of Fe III, compared with the agreement obtained for the  $3d^4s$  configuration of that spectrum. It is shown that effects of  $3s3d^64s$  on  $3s^23d^64s$  satisfy the necessary conditions for linear behavior, consistent with the close agreement obtained in the latter configuration of Fe III. Corresponding effects of  $3s3d^7$  on  $3s^23d^6$  are not linear. When they are included in the calculation, close agreement is obtained in the  $3d^6$  configuration as well; the mean error is reduced from  $\pm 364$  cm<sup>-1</sup> to  $\pm 66$  cm<sup>-1</sup>. An additional parameter,  $\gamma$ , is introduced to define this nonlinear effect. The value of  $\gamma$  obtained from the experimental data by use of least squares is confirmed reasonably well by the value calculated from Watson's self-consistent field results. The parameters of the linear theory are changed considerably when this nonlinear effect is accounted for.

THE present work continues calculations initiated in a recent paper.<sup>1</sup> Introductory material, and most of the references essential to the present work, are

contained in A. Excepting the work in A, since the introduction of the linear theory ten years ago,<sup>2-4</sup> the parameters of the theory have been studied purely in

\* Deceased.

<sup>1</sup> R. E. Trees and C. K. Jørgensen, Phys. Rev. **123**, 1278 (1961). We shall refer to this paper as A.

<sup>2</sup> R. E. Trees, Phys. Rev. **83**, 756 (1951); **84**, 1089 (1951).

<sup>3</sup> D. R. Layzer, dissertation, Harvard University, Cambridge, Massachusetts, 1 May 1950 (unpublished).

<sup>4</sup> G. Racah, Phys. Rev. **85**, 381 (1952).

contexts where they are empirically defined by comparison with the experimental data.<sup>2,3,5-7</sup> In A, an attempt was initiated to calculate the parameters *ab initio*, by simple application of second-order perturbation theory. Such a calculation became a reasonable possibility only recently, largely as a result of the application of digital computers in making Hartree-Fock calculations for complex spectra of the iron group.<sup>8,9</sup> But a calculation of parameters in close quantitative agreement with those obtained from the experimental data was not obtained (in all instances, as in A, we refer to the parameters in the  $3s^23p^63d^n$  configuration). The results were encouraging, but two of the four parameters (i.e.,  $\alpha$  and  $\beta$ ) were calculated twice as large as observed, and the two others (i.e.,  $F_2$  and  $F_4$ , respectively) were a quarter and a half as large as expected. To obtain better quantitative agreement, it is clear that additional interactions must be considered, and some of these have already been suggested.<sup>10,11</sup> In the present work, we consider the *nonlinear* interaction with<sup>11</sup>  $3s3p^63d^{n+1}$ .

This nonlinear interaction explains the objection raised<sup>12</sup> when the  $L(L+1)$  correction was first generalized by interpreting it as a linear effect.<sup>4</sup> In the  $3d^54s$  configuration of Fe III, the mean deviation between calculated and observed term values is  $852\text{ cm}^{-1}$  when Slater's theory is applied<sup>2</sup> and a comparable mean deviation of  $876\text{ cm}^{-1}$  is obtained with this theory in the  $3d^6$  configuration of the same spectrum.<sup>13</sup> When the  $L(L+1)$  correction is included, the mean deviation in  $3d^54s$  is reduced to  $105\text{ cm}^{-1}$ ,<sup>2</sup> but it is reduced to only  $439\text{ cm}^{-1}$  in the  $3d^6$  configuration<sup>12</sup>; i.e., there is a marked systematic dependence of the mean deviation on the configuration when a linear theory is assumed. It was concluded that, in general, the linear theory was only "approximately" correct, but that it was "quantitatively justifiable" for the  $3d^54s$  (and  $3d^6$ ) configurations. The additional discussion,<sup>12</sup> intended to make this somewhat unexpected conclusion theoretically plausible, was pure conjecture, which is not, incidentally, confirmed by the results in the present work; this accounts in part for the fact that the conclusion has been ignored. But once the relationship of the linear theory to the earlier theory of Bacher and Goudsmit was understood,<sup>14,15</sup> the possibility that nonlinear effects might be important was implicitly recognized.<sup>16</sup> The preceding discussion illustrates this importance explicitly, but the main purpose is to point out the essential difference in the behavior of nonlinear effects in the two configurations.

The matrix elements of the interaction between  $3s3d^{n+1}$  and  $3s^23d^n$  have been evaluated as multiples of an interaction integral  $H_2(3s,3d)$  (5). Since the configurations are widely separated, the interaction can be evaluated accurately with second-order perturbation theory. In this way, it is easy to verify that in  $3s^23d^5$  (this result applies also for  $3s^23d^54s$ ) the parameters of the linear theory can fully absorb the effects of this interaction, and that it makes the following contributions to these parameters.

$$\begin{aligned} A &= 0, \\ B &\equiv F_2 - 5F_4 = 0, \\ C &\equiv 35F_4 = -40\gamma, \\ \alpha &= 7.5\gamma, \\ \beta &= 80\gamma, \end{aligned}$$

$$[F_2 = -(40/7)\gamma \text{ and } F_4 = -(8/7)\gamma],$$

where the (positive) parameter  $\gamma$  is equal to the square of  $H_2(3s,3d)$  divided by the separation of the centers of gravity of the configurations  $3s^23d^n$  (here we have  $n=5$ ) and  $3s3d^{n+1}$ . It will be shown below that  $\gamma$  has a value of the order of 5 to  $8\text{ cm}^{-1}$ , so these contributions are by no means negligible. The major point is that, insofar as this interaction is considered, a linear treatment is valid. This is consistent with the close agreement obtained in the  $3d^54s$  configuration of Fe III, described above. These contributions are referred to as being "quasi-linear," since it is simple to show that the parameters in  $3s^23d^6$  cannot absorb the corresponding effects of the configuration interaction with  $3s3d^7$ . By considering the separation of the  $^3D$  and  $^3H$  (in  $3s^23d^6$ ) one obtains as a condition for the linear treatment to apply

$$B - 2\alpha = -5\gamma;$$

but the separation of the  $^1F$  and  $^1I$  leads to the inconsistent condition,

$$B - 2\alpha = -15\gamma.$$

However, it is simple to make a straightforward calculation with the matrices of the complete interaction, and show that this nonlinearity accounts for the poor agreement obtained in the  $3d^6$  configuration of Fe III, described above. This calculation is presented below, the parameter  $\gamma$  is determined from the experimental data by use of least squares, and a reasonably good confirmation is obtained by comparison with the value calculated from Watson's Hartree-Fock self-consistent field (s.c.f.) results.<sup>9</sup>

The numerical values quoted so far have been based on calculations of term positions (i.e., second-order effects of the spin-orbit interaction were ignored) and the  $\beta Q$  correction<sup>4</sup> was omitted. Shadmi has included the effects of spin-orbit interaction in his calculations,<sup>6,17</sup> but he has likewise omitted the  $\beta Q$  correction. In the

<sup>5</sup> G. Racah and Y. Shadmi, Bull. Res. Council Israel **8F**, 15 (1959).

<sup>6</sup> Y. Shadmi, Bull. Res. Council Israel **10F**, 109 (1962).

<sup>7</sup> G. Racah and Y. Shadmi, Phys. Rev. **119**, 156 (1960).

<sup>8</sup> R. E. Watson, Phys. Rev. **118**, 1036 (1960).

<sup>9</sup> R. E. Watson, M. I. T. Technical Report No. 12, 1959 (unpublished).

<sup>10</sup> C. K. Jørgensen, "Solid State Physics" (to be published).

<sup>11</sup> See footnote 11 of reference 1 for discussion.

<sup>12</sup> R. E. Trees, Phys. Rev. **85**, 382 (1952).

<sup>13</sup> R. E. Trees, Phys. Rev. **82**, 683 (1951).

<sup>14</sup> R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

<sup>15</sup> G. Racah, Lunds Univ. Arsskr. **50**: 21, 31 (1954).

<sup>16</sup> See footnote 3 of reference 1.

<sup>17</sup> I am indebted to Y. Shadmi for a discussion of Edlén's arguments in respect to the reality of the  $a^1S$  level, and for bringing the Cr II calculation to my attention.

TABLE I. Calculated and observed energy levels (in  $\text{cm}^{-1}$ ) in the  $3d^6$  configuration of Fe III.  $E_0$ =observed energy;  $E_L$ =energy calculated with linear theory;  $E_{NL}$  and  $E_{NL}'$ =energy calculated with linear theory and nonlinear configuration interaction.

Term	$J$	$E_0$	$E_L$	$E_L - E_0$	$E_{NL}$	$E_{NL} - E_0$	$E_{NL}'$	$E_{NL}' - E_0$
$a^5D$	4	0	-61	-61	-25	-25	-37	-37
	3	436	386	-50	428	-8	416	-20
	2	739	699	-40	744	5	732	-7
	1	932	900	-32	948	16	936	4
	0	1027	999	-28	1048	21	1035	8
$a^3P$	2	19 405	19 767	362	19 366	-39	19 365	-40
	1	20 688	21 088	400	20 699	11	20 698	10
	0	21 208	21 626	418	21 254	46	21 254	46
$a^3H$	6	20 051	20 184	133	20 114	63	20 099	48
	5	20 301	20 402	101	20 337	36	20 323	22
	4	20 482	20 558	76	20 497	15	20 482	0
$a^3F$	4	21 462	21 564	102	21 473	11	21 471	9
	3	21 700	21 806	106	21 714	14	21 712	12
	2	21 857	21 981	124	21 886	29	21 883	26
$a^3G$	5	24 559	24 427	-132	24 519	-40	24 514	-45
	4	24 941	24 825	-116	24 917	-24	24 913	-28
	3	25 142	25 006	-136	25 103	-39	25 098	-44
$a^1I$	6	30 356	30 466	110	30 498	142	30 474	118
$a^3D$	1	30 726	30 390	-336	30 720	-6	30 721	-5
	2	30 716	30 410	-306	30 726	10	30 727	11
	3	30 858	30 541	-317	30 872	14	30 873	15
$a^1G$	4	30 886	30 364	-522	30 892	6	30 873	-13
$a^1S$	0	34 812	33 691	-1121	34 829	17	34 810	-2
$a^1D$	2	35 804	36 734	930	35 797	-7	35 775	-29
$a^1F$	3	42 897	42 979	82	42 792	-105	42 776	-121
$b^3P$	0	49 148	49 325	177	49 250	102	49 253	105
	1	49 577	49 750	173	49 674	97	49 676	99
	2	50 412	50 617	205	50 546	134	50 549	137
$b^3F$	2	50 185	50 072	-113	50 142	-43	50 133	-52
	3	50 295	50 163	-132	50 234	-61	50 225	-70
	4	50 276	50 123	-153	50 193	-83	50 184	-92
$b^1G$	4	57 222	57 316	94	57 125	-97	57 133	-89
$^1D$	2		76 218		76 382		76 381	
$^1S$	0		97 367		97 644		97 639	

$3d^54s$  configuration of Fe III, he obtains excellent agreement, so that his calculations are a more rigorous basis for establishing the statements made above. The better agreement that inclusion of the  $\beta Q$  correction would necessarily yield is not likely to be significant, considering the close agreement that he has already obtained. To clarify this theoretically, we point out two reasons why the  $\beta Q$  correction is not needed in  $3d^54s$ ; (a) as based on calculations of term positions, the parameter  $\beta$  ( $= -77 \text{ cm}^{-1}$  with a standard deviation of  $\pm 27 \text{ cm}^{-1}$ ) has a small value, and (b) the significant difference  $Q(5,3) - Q(5,5) = 2$  (see Racah<sup>18</sup>) is also small. One may also refer to Shadmi's calculations for more rigorous confirmation of the statement that the agreement obtained with the linear theory is relatively poor in the  $3d^6$  configuration of Fe III. However, a

<sup>18</sup> G. Racah, Phys. Rev. **63**, 367 (1943).

rigorous confirmation requires a demonstration that the agreement remains poor when the  $\beta Q$  correction is included. Unpublished data were referred to in A which indicated that in the  $3d^6$  configuration, the parameter  $\beta$  ( $= -250 \text{ cm}^{-1}$  with a standard deviation of  $\pm 130 \text{ cm}^{-1}$ ) is larger. (These data are now given in Table I, as described in the next paragraph.) The significant difference  $Q(6,2) - Q(6,4) = 3$  is also larger in this configuration.

The energy levels calculated with the linear theory are given in the column headed " $E_L$ " in Table I, and the corresponding parameters are in Table II. The mean error is  $\pm 364 \text{ cm}^{-1}$ , which shows that the agreement is still relatively poor when spin-orbit interaction is included rigorously along with the  $\beta Q$  correction. The error of  $-1121$  in the calculated position of the  $a^1S$  is particularly large, being more than three times the mean

error. In general, we do not expect the largest individual errors to be much larger than twice the mean error, so that this statistical consideration would dictate the omission of this level in the calculation by least squares. (Shadmi has omitted this level because the error exceeds five times the mean error for the sequence<sup>17</sup>.) However, Edlén considers the level is real, and he has pointed out the same sort of error in calculations<sup>5</sup> for the  $a^2S$  of Fe II, which has the  $a^1S$  as parent.<sup>17</sup> The observed position of the  $a^1S$  agrees well with calculations based on Slater's theory.<sup>13</sup> This disagreement for the  $a^1S$  is a striking example of the strange behavior of nonlinear effects on terms of the same configuration. Jørgensen's conjecture, that the linear theory requires additional corrections (10), is directed at this kind of behavior.

Effects of the interaction with  $3s3d^7$  are included in the two calculations under the columns headed  $E_{NL}$  and  $E_{NL}'$  in Table I. In making these calculations, the parameters of the linear theory and the additional interaction parameter  $H_2(3s,3d)$  were determined by least squares. The parameters in  $3s3d^7$  were assigned fixed values, as given in Table II and discussed more fully later. The essential equivalence of the two calculations simply demonstrates that the results do not depend on assumptions about the location of levels in the  $3s3d^7$  configuration (which is, of course, experimentally unknown), and that second-order perturbation theory is applicable. The mean errors are  $\pm 65$  and  $\pm 66$   $\text{cm}^{-1}$ , and the largest error for an individual level is  $142$   $\text{cm}^{-1}$  (about twice the mean error). Along with the confirmation obtained from s.c.f. calculations, also discussed below, the calculations establish the fact that this nonlinear effect is responsible for the poor agreement that is obtained with the linear theory in the  $3d^6$  configuration of Fe III. Since the required matrix elements are available,<sup>18</sup> this nonlinear effect can be included explicitly in calculations for  $3d^a4s^b$  configurations generally, and other important interactions can be included in the linear theory. As already noted,<sup>12</sup> we then expect that the largest errors will not exceed  $200$   $\text{cm}^{-1}$ .

Before discussing the results in more detail, a few technical points will be presented. The calculations are similar to ones carried out for the  $(4d+5s)^8$  configurations in Ru I.<sup>19</sup> The principal quantum numbers are irrelevant, and the coefficient matrices described in reference 19 were applied in the present work to the  $(3d+3s)^8$  configurations of Fe III. For simplicity, the linear effects of  $3d^8$  were ignored by setting the appropriate configuration interactions equal to zero, this being slightly simpler than (and exactly equivalent to) removing the unnecessary cards from the coefficient matrices. Two calculations were made to test the possibility that the spread in energy of the two remaining configurations could have an observable influence on the calculations for the levels of the  $3s^23d^6$  configuration. The calculation described as " $E_{NL}$ " is expected to show

TABLE II. Parameters and mean errors for the  $3d^6$  configuration of Fe III. The parameters correspond to the three calculations in Table I as indicated. Parameters enclosed in parentheses were fixed in the calculation by least squares. Units are  $\text{cm}^{-1}$ .

Parameter	$E_L$	Calculation $E_{NL}$	$E_{NL}'$
$3s^23d^6$			
A	20 414±234	20 507±41	20 495±41
B	972± 9	965± 1	965± 1
C	3633± 44	3835±10	3833±10
$\zeta$	432± 76	437±14	437±14
$\alpha$	67± 7	34± 2	34± 2
$\beta$	-249±129	-581±26	-576±27
$H_2(3s,3d)$		2000±38	3892±72
$3s3d^7$			
A		(836 680)	(3 164 300)
B		(1190)	(0)
C		(4400)	(0)
$\zeta$		(430)	(0)
$G_2$		(18 616)	(0)
Mean error	±364	±65	±66

the maximum effect that this energy spread could produce. In this case, the centers of gravity of the  $3s3d^7$  and  $3s^23d^6$  configurations<sup>20</sup> are separated by  $783\,900$   $\text{cm}^{-1}$ , in close agreement with the value of  $H(3d)-H(3s) = 783\,600$   $\text{cm}^{-1}$  obtained in Watson's s.c.f. calculation for the  $3d^6$  configuration of Fe III (p. 185 of reference 9). The values of B, C, and  $G_2$  were obtained from the same source.<sup>9</sup> The spin-orbit parameter,  $\zeta$ , was assigned the value obtained in the calculation " $E_L$ ." The s.c.f. calculations overestimate this parameter, as shown for instance in calculations carried out for the  $3s^23d^5$  configuration of Mn III.<sup>21</sup> At least a part of this inaccuracy is a result of inadequacy in the basic theory which can be remedied by more careful consideration of the effects of mutual magnetic interactions.<sup>22</sup> An attempt was made to evaluate certain parts of the latter interactions by comparison with the experimental data in the  $3d^6$  configuration of Fe III (4). Since results of s.c.f. calculations have become available, a more thorough consideration of effects of these interactions has been initiated.<sup>22</sup> From the viewpoint of this paper, the calculation " $E_{NL}$ " leads to results that are essentially the same as the calculation " $E_{NL}'$ ," about to be described. The two calculations are presented to demonstrate also the less obvious fact that this equivalence applies if term intervals are compared, thus making it plausible that the fine structure can be studied independently of detailed considerations of polarization energy, as already attempted.<sup>13</sup> The calculation presented as " $E_{NL}'$ " in Table I is expected to show negligible effects arising from spread in the energy of the configurations. In this

<sup>20</sup> Formulas relating the center of gravity of the configuration to the parameters in Table II are given, for example, in (5). In  $3s^23d^6$ , two-thirds of  $\beta$  must be added to the formula.

<sup>21</sup> J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, Proc. Roy. Soc. (London) A264, 503 (1961).

<sup>22</sup> M. Blume and R. E. Watson (unpublished). I am indebted to the authors for a preprint of this work, and to Dr. Blume for a communication discussing the work which is still in progress.

<sup>19</sup> R. E. Trees, J. Opt. Soc. Am. 49, 838 (1959).

case, the separation of the centers of gravity of the configurations ( $= 3\ 134\ 750\ \text{cm}^{-1}$ ) is four times as large as expected from the s.c.f. calculations, and the levels in  $3s3d^7$  coincide, since all parameters, excepting  $A$ , have been set equal to zero. As expected when second-order perturbation theory is applicable, and the spread of configurations is unimportant, the interaction parameter  $H_2$  is doubled, but the parameters in  $3s^23d^6$  remain the same (all within the standard deviations of these parameters), and the calculated levels are the same (well within the limits of the mean error). As already indicated, term intervals are also the same (within  $2\ \text{cm}^{-1}$  in the worst case).

Both calculations yield the value 5.0 for the parameter  $\gamma$ , with a standard deviation of  $\pm 0.3\ \text{cm}^{-1}$ . By making use of the s.c.f. orbitals (2), and another code which was written for the 7090, we calculate  $R^2(3d3d,3d3s) = 0.80838\ \text{Ry}$ , corresponding to the value  $H_2(3d,3s) = 2535\ \text{cm}^{-1}$ . This is 25% greater than the value  $H_2 = 2000\ \text{cm}^{-1}$  obtained in the calculation " $E_{NL}$ ," and the value of  $\gamma$  calculated from the s.c.f. orbitals is 8.2, about 50% greater than the value obtained from the observed data. Hartree-Fock orbitals are probably not accurate enough to lead to closer agreement than this, so the result confirms the calculation in Table I as well as expected.<sup>23</sup> However, other explanations of the discrepancy can be readily conceived which would not imply inherent inaccuracy in the Hartree-Fock orbitals. Values of  $\gamma$  seem to be defined rather uniquely in terms of this single configuration interaction, so they should provide a simple and straightforward test of one-electron orbitals. This is in contrast to the linear parameters, which originate in a cumulative effect of several configuration interactions, as is implicit in the disagreement between calculated and observed linear parameters which is discussed in the next paragraph. Somewhat more important than the linear effects considered in reference 1 are the compensating *linear* effects produced by interaction with  $3s^23p^33d^n$  ( $\infty f$ ); a manuscript is now being prepared in which this effect is described.

The parameters, obtained in the calculation " $E_{NL}$ ," differ considerably from the parameters obtained in the calculation " $E_L$ ." Since  $\alpha$  is halved, this parameter is now about a quarter the value of 150 calculated in A. On the other hand,  $\beta$  is more than doubled, and, partly by coincidence, happens to agree well with the value of  $-630$  obtained in A (there is negligible discrepancy when the calculations for Mn III, described in A, are compared directly with the present results in Fe III). From parameters  $B$  and  $C$ , one finds that  $F_2$  and  $F_4$  are increased by about 30 and 6  $\text{cm}^{-1}$ , respectively, explaining part of the disagreement not explained in<sup>1</sup> (the improvement is rather negligible with respect to  $F_2$ ).

Despite the considerable changes in values of the parameters, no significant error seems to be present in assuming a smooth *variation* of parameters in related

configurations, as done in the work of Shadmi.<sup>6,8</sup> If  $\gamma$  is assumed to have the same value in  $3d^54s$  as it was found to have in  $3d^6$ , then the quasi-linear effects in the former configuration are about the same as the changes of parameters that are present in  $3d^6$  when one compares the calculations " $E_L$ " and " $E_{NL}$ ." For instance, the parameter  $B$  is left unaltered, the quasi-linear effect in  $C$  is  $40\ \gamma = 200\ \text{cm}^{-1}$ , and the effect in  $\alpha$  is equal to  $7.5\gamma = 38\ \text{cm}^{-1}$ ; these effects agree in magnitude (within limits set by the standard deviations) with the changes calculable from the parameters in Table II. Shadmi's calculations for third spectra of the iron group<sup>17</sup> place all the even configurations on an equal basis; i.e., in his terminology a general least-squares (G.L.S.) calculation was carried out. Because of this restraint on the parameters, it might be expected that a redistribution of errors (from  $3d^64s$  of Co III,  $3d^44s$  of Mn III, etc.) would be present, and that full significant agreement would not be obtained for levels in  $3d^54s$  of Fe III. However, it appears that full significant agreement has been obtained for the reason just noted. On the other hand, in second spectra the interaction between  $3d^n$  and  $3d^{n-1}4s$  must be considered, and the possibility of a redistribution of errors is increased. In calculations for Cr II,<sup>5</sup> the redistribution of nonlinear effects in  $3d^44s$  may explain several large errors present in terms of the  $3d^5$  configuration; otherwise, this calculation would contradict our conclusions by indicating that nonlinear effects have about equal importance in  $3d^5$  and  $3d^44s$ .<sup>17</sup>

On a finer scale, nonlinear effects do seem to produce departures from a smooth variation of parameters that are significant, since they are outside the limits specified by the standard deviations.<sup>24</sup> For example, in the  $3d^64s + 3d^5$  configurations of Fe III, Shadmi finds that  $\alpha = 81\ \text{cm}^{-1}$ , with a "statistical error" of  $\pm 2\ \text{cm}^{-1}$ .<sup>2</sup> This agrees exactly with a value published for the  $3d^54s$  configuration alone.<sup>2</sup> However, it disagrees with the value of  $\alpha$  given in Table II for the  $3d^6$  configuration (according to reference 12, the same disagreement is present when the  $\beta Q$  correction is omitted). A more striking example of disagreement is shown in the values of  $\beta$  for these two configurations, noted earlier in this paper. (This disagreement is inconsistent with the smooth variation of  $\beta$  obtained by use of other procedures.<sup>7</sup>) These departures from smooth variation would be more apparent than real if the standard deviations were misleadingly small. In isolated examples that have been published elsewhere, we have not found this to be the case. However, there is a reasonable basis for considering that the standard deviations are underestimated,<sup>5</sup> and this accounts for the fact that we did not consider the difference in values of  $\beta$  significant before.<sup>25</sup>

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<sup>23</sup> I am indebted to A. W. Weiss for suggesting this viewpoint of the discrepancy.

<sup>24</sup> The standard deviations are calculated as outlined in footnote 11 of reference 19.

<sup>25</sup> See discussion in footnote 20 of reference 1.