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Spin-Dependent Interactions in the $3d^N$ Configurations of the Third Spectra of the Iron Group*

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A systematic investigation was conducted on the effects of spin-dependent interactions on the energy-level schemes of the $3d^N$ configurations ($N=2, 3, \ldots, 8$) in the third spectra of the iron group. The spin-dependent interactions considered were the spin—other-orbit, the spin-spin, and the effective electrostatic-spin-orbit interactions. The appropriate radial integrals M^k ($k=0, 2$) and Q^k ($k=2, 4$) were considered as adjustable parameters and evaluated by means of diagonalization-least-squares procedures. The introduction of the spin-dependent interactions greatly improved the fit between calculated and observed multiplet splittings in all investigated configurations. Reliable and consistent values of the appropriate parameters were obtained, which agree with available theoretical predictions. In particular, the M^k values are in excellent agreement with corresponding values obtained by the Hartree-Fock method. The variation of the various parameters with k and their dependence on the effective nuclear charge were determined.

I. INTRODUCTION

Energy-level calculations of heavy atoms are usually based on a Hamiltonian comprising only the Coulomb interaction between the electrons and their individual spin-orbit interactions. These interactions are, respectively, represented by the Slater parameters F^k and G^k, or, equivalently, by their linear combinations A, B, C introduced by Racah[1] for d^N configurations, and by the spin-orbit constants ζ_{nl}. Such calculations generally result in a rather poor agreement between calculated and observed energy levels, even when the parameters are considered as freely adjustable. Recently, substantially better fits for l^N configurations were obtained by the inclusion in their energy matrices of two- and three-electron effective electrostatic interactions, which represent, to second-order perturbation theory, electrostatic interactions with distant configurations.[2-6] These interactions are represented by "effective electrostatic parameters," e.g., α, β (two-electron effective parameters), T and Tx (three-electron effective parameters) for d^N configurations.[6] The mean error was thereby decreased to several tens of cm^{-1}. The remaining deviations often were of a pronounced magnetic character, thus suggesting the need for inclusion in the Hamiltonian of the still missing mutual magnetic interactions. These interactions are provided by the Breit equation,[7] which, in the nonrelativistic limit, breaks up into terms which can be given a simple physical interpretation.[7,8] All of these terms that are spin independent (such as the orbit-orbit interaction, the retardation of the Coulomb interaction, and the relativistic correction due to the mass variation with velocity) are absorbed by the electrostatic parameters (real and effective, including the additive constant) already included in the calculations. Into this category also falls the spin-spin contact term, which is diagonal with respect to the total spin angular momentum of the electrons. The terms which are not absorbed are the spin-dependent spin-spin and spin—other-orbit interactions, which, respectively, represent the mutual interaction between the magnetic dipole moments of the electrons and between the dipole moment of one electron and the orbital motion of another.

In view of the importance of the effective electrostatic interaction as compared to the real one, it was considered worthwhile to include in the theoretical calculations a spin-dependent effective interaction along with the above mentioned real spin-dependent interactions. This interaction originates by considering the two dominant terms of the Hamiltonian for heavy atoms, which are the electrostatic interaction G and the spin-orbit interaction F. The effective Hamiltonian is therefore given, to second order of perturbation theory, by the following equation:

$$H_{\text{eff}} = -(G+F)(G+F)/\Delta E , \tag{1}$$

ΔE being the (positive) energy separation between the perturbing and the perturbed configurations. This Hamiltonian decomposes into three parts:

$$\begin{aligned} H_A &= -GG/\Delta E , \\ H_B &= -(GF+FG)/\Delta E , \\ H_C &= -FF/\Delta E . \end{aligned} \tag{2}$$

H_A represents the effective electrostatic interaction already included in the calculations. H_C turns out to have the same angular dependence as the usual spin-orbit interaction.[9,10] H_B is an independent effective interaction which has the property of being spin dependent, and has been called "effective electrostatic-spin-orbit interaction" (effective EL-SO) in previous papers.[11,12] There are, therefore, three types of spin-dependent interactions to be considered: the mutual magnetic spin-spin, and spin–other-orbit interactions, and the effective EL-SO interaction.

Investigations of the effects of the mutual magnetic interactions on the energy-level structures of atomic spectra date from the work of Breit on the He I $1snp\,^3P$ terms.[13] Marvin[14] computed the matrix elements of these interactions for two-electron configurations comprising s, p, or d electrons. Horie[15] derived formulas in which the matrix elements of the spin-spin and spin–other-orbit interactions for l^N configurations were expressed in terms of the unit tensor operators defined by Racah.[1] Jucys and his collaborators[16] investigated from a theoretical standpoint the properties of these interactions in various complex configurations, thereby extending and correcting earlier results. Trees[17] computed the matrix elements of the spin-spin interaction for d^N configurations and applied them to his analysis of Fe III $3d^6$. Blume and Watson[18] obtained Hartree-Fock values for the radial integrals representing the mutual magnetic interactions for various d^N and f^N configurations in transition-element and rare-earth ions, respectively. These values can be used for estimating the strengths of these interactions.[19]

In a more recent work, Jucys and his collaborators[20–23] calculated the energy levels of some $3d^N$ and $3d^Nnl$ configurations of the spectra of ions belonging to the iron group (ranging from the first to the twelfth spectra). They have first[20–22] calculated the radial integrals by the Hartree-Fock method. No configuration interactions were included in the energy-level calculations. Later[23] the radial integrals were determined by a least-squares calculation, and the two-body effective electrostatic interaction represented by the $\alpha L(L+1)$ correction was included. In all their calculations the only spin-dependent interactions which were taken into account were the spin-orbit interaction and that part of the spin–other-orbit interaction which has the same angular dependence as the spin-orbit interaction. The remaining parts of the spin–other-orbit interaction and the spin-spin interaction were considered, but were found too small to be included in such rough approximation.

Lately, in the light of the good agreement obtained between theory and experiment due to the inclusion in the calculations of effective electrostatic interactions, new interest has been aroused in the investigation of the magnetic interactions. Goldschmidt included the mutual magnetic interactions in the energy-level calculations of Pr IV $4f^4$ and Pr III $4f^3$.[24,25] His analysis of these configurations was later extended by the present authors by including also the effective EL-SO interaction.[11,26] Recently, Judd, Crosswhite, and Crosswhite[27,28] investigated the spin-dependent interactions in various $4f^N$ configurations. They also extended the list of parameters representing these interactions to a complete set of parameters associated with all two-electron scalar operators possessing spin and orbital ranks of 1 (like the spin–other-orbit interaction) and 2 (like the spin-spin interaction) and carried out a group-theoretical analysis of these operators. A summary of the studies in the field of the spin-dependent interactions in heavy atoms up to the beginning of 1970 was published by Judd.[29]

The present paper presents the results of a systematic investigation of the effects of the spin-dependent interactions on isolated configurations belonging to a whole group of neighboring spectra. The configurations chosen for this purpose were the $3d^N$ configurations of the third spectra of the iron group listed below: Ti III $3d^2$, V III $3d^3$, Cr III $3d^4$, Mn III $3d^5$, Fe III $3d^6$, Co III $3d^7$, and Ni III $3d^8$.

The inclusion of the spin-dependent interactions in the energy-level calculation of these configurations greatly improved the fit between calculated and observed multiplet splittings. Reliable and consistent values of the appropriate parameters were determined, which agree remarkably well with available theoretical predictions.

II. OPERATORS AND MATRIX ELEMENTS

A. Mutual Magnetic Interactions

The operators representing the spin-spin (ss) and the spin-other-orbit (soo) interactions for l^N configurations can be described in tensor form by the following formulas:

$$H_{\mathrm{ss}} = -\beta^2 (5)^{-1/2} \sum_k (-1)^k \left(\frac{(2k+5)!}{(2k)!} \right)^{1/2} \times \sum_{i \neq j} \left(\frac{r_j^{\,k}}{r_i^{\,k+3}} \left([\underline{C}_i^{(k+2)} \times \underline{C}_j^{(k)}]^{(2)} \cdot [\underline{s}_i \times \underline{s}_j]^{(2)} \right) + \frac{r_i^k}{r_j^{k+3}} \left([\underline{C}_i^{(k)} \times \underline{C}_j^{(k+2)}]^{(2)} \cdot [\underline{s}_i \times \underline{s}_j]^{(2)} \right) \right), \quad (3)$$

with

$$\beta = e\hbar/2mc \,,$$

$$H_{\mathrm{soo}} = \beta^2 2(3)^{-1/2} \sum_k (-1)^k \sum_{i\neq j} \left(\frac{r_i^{k-2}}{r_j^{k+1}} (2k+1)(2k-1)^{1/2} [\underline{C}_j^{(k)} \times [\underline{C}^{(k)} \times \underline{1}]^{(k-1)}]^{(1)} - \frac{r_j^k}{r_i^{k+3}} (2k+1)(2k+3)^{1/2} [\underline{C}_j^{(k)} \times [\underline{C}^{(k)} \times \underline{1}]_i^{(k+1)}]^{(1)} \right) \cdot (\underline{s}_i + 2\underline{s}_j) . \qquad (4)$$

The appropriate radial integrals are those defined by Marvin,[14]

$$M^k = \frac{\beta^2}{2} \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+3}} R_{nl}^2(r_1) R_{nl}^2(r_2)\, dr_1\, dr_2 ,$$

where $r_< = \min(r_1, r_2)$ and $r_> = \max(r_1, r_2)$. For d^N configurations k may take the values 0 and 2.

It is both analytically and computationally convenient to express the operator representing the spin–other-orbit interaction in terms of the unit tensor operators $\underline{u}_i^{(k)}$ defined by Racah[1]:

$$H'_{\mathrm{soo}} = 2 \sum_{k,K} M^k (l \| \underline{C}^{(K)} \| l)(l \| \underline{U}^{(K;k+1)} \| l) \times \left[(-1)^K \left(\frac{3}{2K+1} \right)^{1/2} (\underline{U}^{(K)} \cdot \underline{T}^{(1\,k+1)K}) + 2(-1)^{k+1} \left(\frac{3}{2k+3} \right)^{1/2} (\underline{U}^{(k+1)} \cdot \underline{T}^{(1K)\,(k+1)}) \right] , \qquad (5)$$

where

$$K = k,\ k+2,$$

$$\underline{U}^{(k)} = \textstyle\sum_i \underline{u}_i^{(k)} ,$$

with

$$(nl \| \underline{u}_i^{(k)} \| nl) = 1 ,$$

$$\underline{T}^{(1t)k} = \textstyle\sum_i \underline{t}_i^{(1t)k} = \sum_i [\underline{s}_i \times \underline{u}_i^{(t)}]^{(k)} ,$$

and

$$\underline{U}^{(k;k+1)} = 3^{-1/2}(2k+1)(2k+3)^{1/2}[\underline{C}^{(k)} \times \underline{1}]^{(k+1)} ,$$

$$\underline{U}^{(k+2;k+1)} = -3^{-1/2}(2k+5)(2k+3)^{1/2}[\underline{C}^{(k+2)} \times \underline{1}]^{(k+1)} .$$

The prime over the H_{soo} in the left-hand side of Eq. (5) indicates that a term proportional to the spin-orbit interaction has been omitted from the expression given in Eq. (4). The remaining expression in Eq. (5) has the property that it remains invariant under the conjugation process $l^N \to l^{4l+2-N}$.

The formulas for the matrix elements of the ss and soo-interactions for l^N configurations derived by Horie[15] are cited below:

$$(l^N \alpha SLJM | H_{\mathrm{ss}} | l^N \alpha' S' L' JM) = (-1)^{S'+L+J} \begin{Bmatrix} S & S' & 2 \\ L' & L & J \end{Bmatrix} (l^N \alpha SL \| H_{\mathrm{ss}} \| l^N \alpha' S' L') , \qquad (6)$$

where

$$(l^N \alpha SL \| H_{\mathrm{ss}} \| l^N \alpha' S' L') = (-1)^{S+S'+L+L'+1} \sum_k 2 \left(5 \frac{(2k+5)!}{(2k)!} \right)^{1/2} (l \| \underline{C}^{(k)} \| l)(l \| \underline{C}^{(k+2)} \| l) M^k \times \sum_{\alpha'' S'' L''} (l^N \alpha SL \| \underline{V}^{(1k)} \| l^N \alpha'' S'' L'')(l^N \alpha'' S'' L'' \| \underline{V}^{(1k+2)} \| l^N \alpha' S' L') \begin{Bmatrix} S & S' & 2 \\ 1 & 1 & S'' \end{Bmatrix} \begin{Bmatrix} L & L' & 2 \\ k+2 & k & L'' \end{Bmatrix} , \qquad (7)$$

and $V^{(1k)}$ is the double tensor defined by Racah,[1]

$$\underline{V}^{(1k)} = \textstyle\sum_i \underline{s}_i \underline{u}_i^{(k)} .$$

For the soo interaction it is shown that

$$(l^N \alpha SLJM | H'_{\mathrm{soo}} | l^N \alpha' S' L' JM) = (-1)^{S'+L+J} \begin{Bmatrix} S & S' & 1 \\ L' & L & J \end{Bmatrix} (l^N \alpha SL \| H'_{\mathrm{soo}} \| l^N \alpha' S' L') , \qquad (8)$$

where

$$(l^N \alpha SL \| H'_{\mathrm{soo}} \| l^N \alpha' S' L') = 2(3)^{1/2} (-1)^{L+L'} \sum_{k,K} M^k (l \| \underline{U}^{(K;k+1)} \| l)(l \| \underline{C}^{(K)} \| l) \times \left[\sum_{\alpha'' L''} (l^N \alpha SL \| \underline{U}^{(K)} \| l^N \alpha'' SL'')(l^N \alpha'' SL'' \| \underline{V}^{(1k+1)} \| l^N \alpha' S' L') \begin{Bmatrix} L & K & L'' \\ k+1 & L' & 1 \end{Bmatrix} + 2 \sum_{\alpha'' L''} (l^N \alpha SL \| \underline{U}^{(k+1)} \| l^N \alpha'' SL'')(l^N \alpha'' SL'' \| \underline{V}^{(1K)} \| l^N \alpha' S' L') \begin{Bmatrix} L & k+1 & L'' \\ K & L' & 1 \end{Bmatrix} \right] . \qquad (9)$$

The first sum in the square brackets of (9) yields, for $k=0$, matrix elements which are proportional to those of the spin-orbit interaction, and is therefore omitted.

B. Effective EL-SO Interaction

Since the spin-orbit operator is a sum of one-electron operators each of which is diagonal in the orbital quantum number l, the perturbing configurations can differ from the perturbed configuration $(nl)^N$ by the principal quantum number n of one-electron state only. Three kinds of perturbing configurations can thus occur: (i) $(nl)^{N-1}n'l$, (ii) $(n'l)^{4l+1}(nl)^{N+1}$, and (iii) $(n'l')^{4l'+1}(nl)^N n''l'$.

The contributions to the effective EL-SO operator due to these kinds of perturbing configurations have been obtained. It has been shown that, after omitting terms proportional to the spin-orbit interaction, the contributions of the configurations $(nl)^{N-1}n'l$ and $(n'l)^{4l+1}(nl)^{N+1}$ have the same angular dependence, whereas that of $(n'l')^{4l+1}(nl)^N n''l'$ vanishes.

The expression for the effective EL-SO operator is

$$H_{\text{EL-SO}} = -2 \sum_{k\ \text{even}} Q^k [l(l+1)(2l+1)]^{1/2} (2k+1)^{-1/2} \times \sum_{t\ \text{odd}} (2t+1) \begin{Bmatrix} 1 & k & t \\ l & l & l \end{Bmatrix} (\underline{\mathrm{U}}^{(k)} \cdot \underline{\mathrm{T}}^{(1t)k}) , \quad (10)$$

where the parameters Q^k are defined as follows:

$$Q^k = (l \| \underline{\mathrm{C}}^{(k)} \| l)^2 \sum_{n'} \frac{R^k(nlnl, nln'l)\zeta_l(nn')}{\Delta E_{nn'}} , \quad (11)$$

with $R^k(nlnl, nln'l)$ and $\zeta_l(nn')$, respectively, a Slater and a spin-orbit parameter. The first kind of perturbing configuration has also been studied by Stein.[10] Equation (10) agrees with formula (E23) of Stein, except for his double tensor $\underline{\mathrm{V}}^{(t,1)}$, which should be replaced by the "coupled" tensor $\underline{\mathrm{T}}^{(1t)k}$

The matrix elements of the effective EL-SO interaction are given by

$$(l^N \alpha SLJM | H_{\text{EL-SO}} | l^N \alpha' S' L' JM) = (-1)^{S'+L+J} \begin{Bmatrix} S & S' & 1 \\ L' & L & J \end{Bmatrix} (l^N \alpha SL \| H_{\text{EL-SO}} \| l^N \alpha' S' L'), \quad (12)$$

where

$$(l^N \alpha SL \| H_{\text{EL-SO}} \| l^N \alpha' S' L') = -2 \sum_{\substack{k\ \text{even} \\ t\ \text{odd}}} Q^k [l(l+1)(2l+1)]^{1/2} (2t+1) \begin{Bmatrix} 1 & k & t \\ l & l & l \end{Bmatrix}$$

$$\times \sum_{\alpha'' L''} (-1)^{L+L'} \begin{Bmatrix} L & L' & 1 \\ t & k & L'' \end{Bmatrix} (l^N \alpha SL \| \underline{\mathrm{U}}^{(k)} \| l^N \alpha'' SL'') (l^N \alpha'' SL'' \| \underline{\mathrm{V}}^{(1t)} \| l^N \alpha' S' L') . \quad (13)$$

Detailed derivation of the effective EL-SO operator and its matrix elements will be given elsewhere.[30]

The algebraic matrices of the spin-dependent interactions were computed for all d^N configurations and added to the already existing energy matrices. They are available in the magnetic-tape library of the department of theoretical physics in the Hebrew University of Jerusalem.

III. CALCULATION OF THE ENERGY LEVELS

The energy levels of the $3d^N$ configurations belonging to the third spectra of the iron group were calculated by using diagonalization-least-squares procedures. The calculations were conducted in two stages. In the first stage each spectrum was treated separately. Such calculations will from now on be referred to as LS calculations. In these calculations it was found that the parameters representing the various interactions vary regularly from one spectrum to another along the row. Thus, it was possible in the next stage to perform a general least-squares (GLS) calculation, treating all the $3d^N$ configurations as a single problem,[3] the radial parameters being restricted to change from one spectrum to another according to a simple interpolation formula. For any interaction parameter P, the interpolation formula was of the form $P = P_0 + P_1 x + P_2 y$, in which $x = N - 5$ and $y = x^2 - 4$. The coefficients of the interpolation formulas took the role of the free parameters. In most cases a linear change was sufficient ($P_2 = 0$).

The investigated $3d^N$ configurations were recently treated by Shadmi, Caspi, and Oreg.[6] These authors calculated the energy levels of these configurations by including the effective electrostatic interactions in addition to the traditional interactions, but neglecting the additional spin-dependent interactions. However, the interaction-parameter values obtained by them could not be used straightaway as a starting point for the present work, since they treated the configurations $3d^N$ and $3d^{N-1}4s$ simultaneously—some parameter values of $3d^N$ being held equal to the corresponding ones of $3d^{N-1}4s$. A preliminary calculation of the energy levels, which did not include the additional spin-dependent interactions, was therefore carried out.

The observed energy levels are those considered by Shadmi, Caspi, and Oreg, except for the following changes: The two levels 29 207.6 and 32 384.0 cm^{-1} of Mn III $3d^5$ have been added[31]; the ground level $^6S_{5/2}$ of Mn III $3d^5$ has been omitted, because of the large deviation between its calculated and observed values (this deviation, of about 200 cm^{-1}, contributed about one-third of the total sum of the squares of the deviations of all the spectra).

In some of the separate LS calculations, the values

TABLE I. Interaction-parameter values, in cm^{-1} (GLS 1 and GLS 2).

Parameter	GLS 1	GLS 2
A_2	5 808 ± 25	5 809 ± 23
A_3	11 998 ± 24	11 999 ± 22
A_4	18 185 ± 18	18 184 ± 17
A_5	31 666 ± 12	31 659 ± 11
A_6	20 453 ± 20	20 446 ± 19
A_7	15 549 ± 11	15 546 ± 10
A_8	9 045 ± 20	9 039 ± 18
B_0	919.6 ± 0.5	919.5 ± 0.4
B_1	54.3 ± 0.3	54.3 ± 0.3
C_0	3457.9 ± 4.1	3458.6 ± 3.8
C_1	304.9 ± 1.3	305.4 ± 1.2
α_0	32.17 ± 0.55	32.14 ± 0.50
α_1	3.76 ± 0.21	3.78 ± 0.19
β_0	−421.6 ± 9.7	−421.2 ± 8.9
β_1	[0][a]	[0][a]
T_0	−4.60 ± 0.06	−4.60 ± 0.05
T_1	[0][a]	[0][a]
Tx_0	−1.82 ± 0.11	−1.80 ± 0.10
Tx_1	−0.43 ± 0.05	−0.41 ± 0.04
ζ_0	353.2 ± 2.9	348.3 ± 5.5
ζ_1	91.5 ± 1.5	85.8 ± 2.1
ζ_2	9.0 ± 1.0	7.7 ± 1.3
$M^0_{\mathrm{ss}_0}=M^0_{\mathrm{soo}_0}$	[0][a]	1.452 ± 0.379
$M^0_{\mathrm{ss}_1}=M^0_{\mathrm{soo}_1}$	[0][a]	0.318 ± 0.302
$M^2_{\mathrm{ss}_0}=M^2_{\mathrm{soo}_0}$	[0][a]	0.808 ± 0.333
$M^2_{\mathrm{ss}_1}=M^2_{\mathrm{soo}_1}$	[0][a]	0.193 ± 0.186
$Q^2_0=Q^4_0$	[0][a]	40.5 ± 13.0
$Q^2_1=Q^4_1$	[0][a]	13.9 ± 10.3
Δ	26	24

[a] Fixed value.

of several parameters had to be fixed, so that the number of free electrostatic parameters would not exceed the number of observed terms. The values of the following parameters were fixed on values interpolated from neighboring spectra: β, T, and Tx for Ti III $3d^2$, Mn III $3d^5$, and Ni III $3d^8$ and β for Co III $3d^7$. The value of β was fixed because of the lack of experimental levels having low-seniority quantum numbers. The values of T and Tx were fixed because in two-electron configurations and, to a good approximation, also in half-filled-shell configurations these parameters are linear combinations of other electrostatic parameters.

The preliminary separate LS calculations are denoted by LS 1 and the preliminary simultaneous calculation of all the spectra is denoted by GLS 1.

The results obtained for the parameters in GLS 1 served as initial values for a second diagonalization-least-squares iteration. In this iteration, initial values of zero were used for the parameters representing the additional spin-dependent interactions, their final values being determined by the least-squares calculations. The separate LS calculations are denoted by LS 2 and the simultaneous calculation of all the spectra is denoted by GLS 2. In GLS 2 all the parameters except ζ_{3d} were constrained to change linearly with N; for ζ_{3d} a quadratic correction term was also included. The linearity of the M^k's and the Q^k's was deduced from the results of the separate LS calculations. In addition, the following restrictions were imposed upon the spin-dependent interaction parameters: (i) $M^k_{\mathrm{ss}}=M^k_{\mathrm{soo}}$, and (ii) $Q^2=Q^4$. These relations were deduced from the results of a set of calculations in which all spin-dependent parameters were permitted to vary independently, the first one also being suggested by the definition of the M^k's.

The radial parameters obtained in GLS 1 and GLS 2 are given in Table I, together with the appropriate mean errors Δ. It can be seen that the electrostatic and spin-orbit interaction parameters have not changed significantly by the introduction of the additional spin-dependent interactions.

The spin-dependent interaction parameters obtained for each spectrum in LS 2 and GLS 2 are given in Table II. The values of ζ_{3d} and the M^k's obtained by Blume and Watson[18] using the Hartree-Fock method are also given for comparison, with the subscript HF. The ratio M^0/M^2 and the mean error Δ are also given. The mean errors obtained in LS 1 and GLS 1 (without the additional spin-dependent interactions) are given at the bottom of Table II for comparison.

The calculated energy levels of GLS 2 are given in Tables III–IX, together with the observed levels, the deviations of the calculated levels from the observed ones $(o_i - c_i)$, the composition percentages of the eigenstates, and the calculated Landé g factors. In the last column of each table the $o_i - c_i$ values of GLS 1 are given for comparison. Table V presents also the $o_i - c_i$ values for the individual LS 2 of Cr III $3d^4$, which rendered especially good results, and the $o_i - c_i$ values of the corresponding LS 1 for comparison.

IV. RESULTS AND CONCLUSIONS

A. Improvement of the Calculated Multiplet Structures

The coupling in the $3d^N$configurations of the third spectra of the iron group is close to Russell-Saun-

TABLE II. Magnetic and effective EL–SO parameters, in cm^{-1} (LS 2 and GLS 2).

Parameter	Ti III $3d^2$	V III $3d^3$	Cr III $3d^4$	Mn III $3d^5$	Fe III $3d^6$	Co III $3d^7$	Ni III $3d^8$
ζ_{LS}	130 ± 0	179 ± 2	241 ± 1	323 ± 9	414 ± 9	522 ± 9	651 ± 0
ζ_{GLS}	129	177	239	318	411	520	644
ζ_{HF}	126	184	258	333	426	539	672
M^0_{LS}	1.328 ± 0.002	1.059 ± 0.198	1.219 ± 0.078	1.452 ± 0.176	1.699 ± 0.986	1.796 ± 0.971	2.160 ± 0.000
M^0_{GLS}	0.498	0.816	1.134	1.452	1.770	2.088	2.406
M^0_{HF}	0.704	0.915	1.156	1.433	1.704	2.022	2.375
M^2_{LS}	0.197 ± 0.001	0.467 ± 0.147	0.674 ± 0.099	0.820 ± 0.232	1.097 ± 1.091	1.193 ± 0.427	1.283 ± 0.000
M^2_{GLS}	0.229	0.422	0.615	0.808	1.001	1.194	1.387
M^2_{HF}	0.384	0.499	0.631	0.783	0.930	1.103	1.295
$Q^2 = Q^4_{\mathrm{LS}}$	16.3 ± 0.1	23.9 ± 6.0	30.5 ± 2.6	39.3 ± 7.9	51.7 ± 31.1	59.3 ± 41.5	38.0 ± 0.0
$Q^2 = Q^4_{\mathrm{GLS}}$	−1.2	12.7	26.6	40.5	54.4	68.3	82.2
$(M^0/M^2)_{\mathrm{LS}}$	6.741	2.268	1.809	1.771	1.521	1.505	1.684
$(M^0/M^2)_{\mathrm{GLS}}$	2.175	1.934	1.844	1.797	1.768	1.749	1.735
$(M^0/M^2)_{\mathrm{HF}}$				1.832			
Δ_{LS}	0	5	2	4	31	12	0
Δ_{GLS}				24			
$\Delta_{\mathrm{LS}\,1}$	6	11	11	14	32	20	27
$\Delta_{\mathrm{GLS}\,1}$				26			

TABLE III. Observed and calculated energy levels of Ti III $3d^2$, in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS 1
^3F 100%	2	0.0	−34	34	0.667	27
100%	3	183.7	161	23	1.083	21
100%	4	421.9	412	10	1.250	13
^1D 99%	2	8 472.6	8 472	1	1.003	−1
^3P 100%	0	10 536.4	10 554	−18	0.000	−16
100%	1	10 603.5	10 624	−21	1.500	−15
99%	2	10 721.1	10 757	−36	1.496	−35
^1G 100%	4	14 398.5	14 392	7	1.000	7
^1S 100%	0		32 541		0.000	

ders coupling. Therefore, the electrostatic interaction determines the term values, whereas the spin-dependent interactions determine the multiplet splittings. The effect of the introduction of the additional spin-dependent interactions on the calculated energy levels can, therefore, be best studied by considering the multiplet structures.

Indeed, the results which are summed up in Tables III–IX show that the introduction of the additional spin-dependent interactions substantially improved the calculated multiplet splittings in all the investigated configurations. This improvement is reflected by the deviations of all the levels of the same multiplet which became equal. The remaining deviations are therefore of electrostatic character, and are due to the lack of higher-order electrostatic corrections. These deviations prevent the mean error of the GLS calculation from decreasing upon the introduction of the additional spin-dependent interactions (see Tables I and II). Evidently, the mean error is not an adequate criterion for estimating the improvement of the fit between the calculated and observed energy levels due to the introduction of the additional spin-dependent interactions. A new criterion, which measures the fit between the calculated and observed multiplet splittings, has therefore been introduced, and is called "observed minus calculated ($o-c$) spread." This is defined as the absolute value of the difference between the maximum and minimum deviations for levels belonging to the same multiplet.

TABLE IV. Observed and calculated energy levels of V III $3d^3$ in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS 1
^4F 100%	$\frac{3}{2}$	0.0	26	−26	0.400	−22
100%	$\frac{5}{2}$	145.5	172	−27	1.029	−23
100%	$\frac{7}{2}$	341.5	369	−28	1.238	−27
100%	$\frac{9}{2}$	583.8	612	−28	1.333	−35
^4P 100%	$\frac{1}{2}$	11 513.8	11 516	−2	2.661	−13
99%	$\frac{3}{2}$	11 591.8	11 591	1	1.730	−2
100%	$\frac{5}{2}$	11 769.7	11 767	3	1.600	11
^2G 100%	$\frac{7}{2}$	11 966.3	11 964	2	0.889	1
100%	$\frac{9}{2}$	12 187.0	12 182	5	1.110	3
^2P 67% + ^2_3D 25%	$\frac{3}{2}$	15 550.3	15 563	−13	1.164	−16
^2P 100%	$\frac{1}{2}$	15 579.8	15 610	−30	0.672	−33
^2_3D 52% + ^2P 32% + ^2_1D 16%	$\frac{3}{2}$	16 330.5	16 319	12	0.972	20
^2_3D 77% + ^2_1D 22%	$\frac{5}{2}$	16 374.7	16 342	33	1.200	32
^2H 100%	$\frac{9}{2}$	16 810.9	16 800	11	0.910	15
100%	$\frac{11}{2}$	16 977.6	16 962	16	1.091	12
^2F 100%	$\frac{7}{2}$	27 727.8	27 713	15	1.143	4
100%	$\frac{5}{2}$	27 846.8	27 833	14	0.857	30
^2_1D 77% + ^2_3D 22%	$\frac{5}{2}$	42 267.4	42 239	28	1.200	30
^2_1D 77% + ^2_3D 23%	$\frac{3}{2}$	42 371.2	42 357	14	0.800	14

TABLE V. Observed and calculated energy levels of Cr III $3d^4$, in cm^{-1} (GLS 2).

Term composition	*J*	Obs	Calc	*o − c*	*g* Calc	*o − c* GLS 1	*o − c* LS 2	*o − c* LS 1
${}^5D$ 100%	0	0.0	−30	30	0.000	35	4	4
100%	1	59.9	33	27	1.500	33	1	2
100%	2	181.9	155	27	1.500	32	1	3
100%	3	355.8	329	27	1.500	27	−1	0
100%	4	575.0	550	25	1.500	16	−4	−8
${}^3_4P$ 59%+${}^3_2P$ 41%	0	16 770.9	16 785	−14	0.000	−17	−1	−13
${}^3_4P$ 59%+${}^3_2P$ 41%	1	17 167.4	17 179	−12	1.499	−6	−2	4
${}^3_4P$ 59%+${}^3_2P$ 41%	2	17 850.0	17 855	−5	1.499	−9	2	9
${}^3H$ 99%	4	17 272.8	17 285	−12	0.803	4	−1	14
99%	5	17 395.5	17 406	−11	1.034	−10	−1	3
100%	6	17 528.8	17 537	−8	1.166	−29	1	−15
${}^3_4F$ 77%+${}^3_2F$ 23%	2	18 451.0	18 452	−1	0.667	2	0	1
${}^3_4F$ 76%+${}^3_2F$ 22%	3	18 510.0	18 510	0	1.078	2	0	2
${}^3_4F$ 76%+${}^3_2F$ 21%	4	18 581.6	18 580	2	1.245	−5	1	−5
${}^3G$ 98%	3	20 702.0	20 731	−29	0.755	−16	−2	7
98%	4	20 851.3	20 877	−26	1.052	−27	0	−3
99%	5	20 994.6	21 018	−23	1.199	−33	2	−6
${}^1_4G$ 64%+${}^1_2G$ 35%	4		25 062		1.001			
${}^3D$ 100%	3	25 725.8	25 721	5	1.333	0	0	−5
100%	2	25 781.0	25 775	6	1.167	2	1	−3
100%	1	25 848.2	25 842	6	0.501	15	−1	10
${}^1I$ 100%	6		25 943		1.000			
${}^1_4S$ 78% + ${}^1_0S$ 22%	0		27 257		0.000			
${}^1_4D$ 77% + ${}^1_2D$ 22%	2		32 087		1.000			
${}^1F$ 100%	3		36 933		1.000			
${}^3_2F$ 78%+${}^3_4F$ 22%	4	43 286.4	43 287	−1	1.250	12	1	17
${}^3_2F$ 77%+${}^3_4F$ 22%	3	43 321.7	43 326	−4	1.083	−4	1	2
${}^3_2F$ 77% + ${}^3_4F$ 23%	2	43 304.1	43 312	−8	0.671	−24	−1	−19
${}^3_2P$ 59% + ${}^3_4P$ 41%	2		43 347		1.496			
${}^3_2P$ 59% + ${}^3_4P$ 41%	1		43 816		1.500			
${}^3_2P$ 59% + ${}^3_4P$ 41%	0		44 038		0.000			
${}^1_2G$ 65% + ${}^1_4G$ 35%	4		49 588		1.000			
${}^1_2D$ 78% + ${}^1_4D$ 22%	2		65 584		1.000			
${}^1_0S$ 78% + ${}^1_4S$ 22%	0		83 913		0.000			

TABLE VI. Observed and calculated energy levels of Mn III $3d^5$, in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS1
^6S 100%	$\frac{5}{2}$		−229		2.000	
^4G 100%	$\frac{11}{2}$	26 824.5	26 797	28	1.273	3
100%	$\frac{9}{2}$	26 852.4	26 823	29	1.172	25
100%	$\frac{7}{2}$	26 860.3	26 830	30	0.984	43
100%	$\frac{5}{2}$	26 856.9	26 827	30	0.572	57
^4_3P 97%	$\frac{5}{2}$	29 168.9	29 161	8	1.593	10
98%	$\frac{3}{2}$	29 207.6	29 199	9	1.723	10
99%	$\frac{1}{2}$	29 243.0	29 232	11	2.650	5
^4D 100%	$\frac{7}{2}$	32 308.9	32 295	14	1.428	8
97%	$\frac{5}{2}$	32 385.7	32 372	14	1.376	7
98%	$\frac{3}{2}$	32 384.0	32 376	8	1.210	11
99%	$\frac{1}{2}$	(32 368.9)[a]	32 358	(11)	0.016	
^2I 99%	$\frac{11}{2}$		39 121		0.924	
100%	$\frac{13}{2}$		39 125		1.077	
^2_5D 58% + ^2_3F 22% + ^2_1D 22%	$\frac{5}{2}$	(41 238.1)[a]	41 177	(61)	1.124	
^2_5D 73% + ^2_1D 24%	$\frac{3}{2}$	(41 569.8)[a]	41 505	(65)	0.788	
^2_3F 98%	$\frac{7}{2}$	(42 606.5)[a]	42 535	(71)	1.143	
^2_3F 74% + ^2_5D 15%	$\frac{5}{2}$	(43 105.4)[a]	43 040	(65)	0.933	
^4_3F 99%	$\frac{9}{2}$	43 574.2	43 624	−50	1.331	−44
99%	$\frac{7}{2}$	43 604.2	43 652	−48	1.237	−43
93%	$\frac{5}{2}$	43 670.5	43 708	−38	1.029	−38
97%	$\frac{3}{2}$	43 675.6	43 719	−43	0.413	−54
^2_3H 92%	$\frac{9}{2}$	(46 515.9)[a]	46 444	(72)	0.925	
99%	$\frac{11}{2}$	(46 670.7)[a]	46 598	(73)	1.090	
^2_5G 99%	$\frac{7}{2}$	(47 842.0)[a]	47 775	(67)	0.890	
91%	$\frac{9}{2}$	(48 005.2)[a]	47 935	(70)	1.097	
^2_5F 99%	$\frac{5}{2}$	(51 002.7)[a]	50 933	(70)	0.858	
99%	$\frac{7}{2}$	(51 059.7)[a]	50 993	(67)	1.143	
^2S 100%	$\frac{1}{2}$		55 611		2.000	
^2_3D 100%	$\frac{3}{2}$	(61 580.2)[a]	61 474	(106)	0.800	
100%	$\frac{5}{2}$	(61 603.8)[a]	61 491	(113)	1.199	
^2_3G 100%	$\frac{9}{2}$		68 797		1.111	
100%	$\frac{7}{2}$		68 785		0.889	
^2_3P 100%	$\frac{3}{2}$		83 161		1.332	
100%	$\frac{1}{2}$		83 147		0.667	
^2_1D 76% + ^2_5D 24%	$\frac{5}{2}$		89 525		1.200	
^2_1D 75% + ^2_5D 24%	$\frac{3}{2}$		89 514		0.802	

[a] See Ref. 32.

TABLE VII. Observed and calculated energy levels of Fe III $3d^6$, in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS 1
^5D 100%	4	0.0	−20	20	1.500	11
100%	3	436.2	421	15	1.500	15
100%	2	738.9	727	12	1.500	15
100%	1	932.4	922	10	1.500	13
100%	0	1 027.3	1 018	9	0.000	12
${}^3_4P$ 61% + ${}^3_2P$ 38%	2	19 404.8	19 420	−15	1.499	−20
${}^3_4P$ 62% + ${}^3_2P$ 38%	1	20 688.4	20 711	−23	1.499	−11
${}^3_4P$ 62% + ${}^3_2P$ 37%	0	21 208.5	21 232	−24	0.000	−25
^3H 100%	6	20 051.1	20 078	−27	1.166	−49
99%	5	20 300.8	20 323	−22	1.036	−16
97%	4	20 481.9	20 500	−18	0.810	8
${}^3_4F$ 74% + ${}^3_2F$ 21%	4	21 462.2	21 487	−25	1.237	−28
${}^3_4F$ 77% + ${}^3_2F$ 21%	3	21 699.9	21 721	−21	1.077	−17
${}^3_4F$ 79% + ${}^3_2F$ 20%	2	21 857.2	21 876	−19	0.668	−17
^3G 99%	5	24 558.8	24 585	−26	1.198	−40
97%	4	24 940.9	24 967	−26	1.053	−34
98%	3	25 142.4	25 168	−26	0.757	−15
^1I 100%	6	30 356.2	30 340	16	1.000	15
^3D 100%	1	30 725.8	30 742	−16	0.501	−5
99%	2	30 716.2	30 731	−15	1.165	−24
100%	3	30 857.8	30 875	−17	1.333	−20
${}^1_4G$ 65% + ${}^1_2G$ 34%	4	30 886.4	30 864	22	1.001	20
${}^1_4S$ 76% + ${}^1_0S$ 23%	0	34 812.4	34 758	54	0.000	58
${}^1_4D$ 77% + ${}^1_2D$ 22%	2	35 803.7	35 785	19	1.002	20
^1F 99%	3	42 896.9	42 840	57	1.001	55
${}^3_2P$ 62% + ${}^3_4P$ 38%	0	49 148.0	49 153	−5	0.000	−19
${}^3_2P$ 62% + ${}^3_4P$ 38%	1	49 576.9	49 580	−3	1.500	5
${}^3_2P$ 61% + ${}^3_4P$ 39%	2	50 412.3	50 412	0	1.499	5
${}^3_2F$ 80% + ${}^3_4F$ 20%	2	50 184.9	50 173	12	0.667	−26
${}^3_2F$ 78% + ${}^3_4F$ 21%	3	50 295.2	50 291	4	1.083	1
${}^3_2F$ 78% + ${}^3_4F$ 22%	4	50 276.1	50 283	−7	1.249	21
${}^1_2G$ 65% + ${}^1_4G$ 35%	4	57 221.7	57 138	84	1.001	92
${}^1_2D$ 78% + ${}^1_4D$ 22%	2		76 796		1.000	
${}^1_0S$ 77% + ${}^1_4S$ 23%	0		98 293		0.000	

TABLE VIII. Observed and calculated energy levels of Co III $3d^7$, in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS 1
^4F 100%	$\frac{9}{2}$	0.0	−13	13	1.333	4
100%	$\frac{7}{2}$	841.2	833	8	1.238	12
100%	$\frac{5}{2}$	1 451.3	1 446	5	1.029	12
100%	$\frac{3}{2}$	1 866.8	1 863	4	0.401	10
^4P 100%	$\frac{5}{2}$	15 201.9	15 217	−15	1.599	7
^4P 95% + ^2P 5%	$\frac{3}{2}$	15 428.2	15 438	−10	1.715	−14
^4P 98%	$\frac{1}{2}$	15 811.4	15 819	−8	2.632	−43
^2G 98%	$\frac{9}{2}$	16 977.7	16 989	−11	1.108	−3
100%	$\frac{7}{2}$	17 766.2	17 775	−9	0.889	−13
^2P 87% + ^2_3D 6% + ^2P 4%	$\frac{3}{2}$	20 194.9	20 203	−8	1.306	−7
^2P 98%	$\frac{1}{2}$	20 918.5	20 924	−6	0.701	−15
^2H 100%	$\frac{11}{2}$	22 720.3	22 718	2	1.091	3
98%	$\frac{9}{2}$	23 434.3	23 425	9	0.913	7
^2_3D 76% + ^2_1D 23%	$\frac{5}{2}$	23 058.8	23 051	8	1.201	9
^2_3D 72% + ^2_1D 19% + ^2P 8%	$\frac{3}{2}$	24 236.8	24 238	−1	0.844	6
^2F 100%	$\frac{5}{2}$	37 021.0	37 011	10	0.858	41
100%	$\frac{7}{2}$	37 316.5	37 309	8	1.143	−18
^2_1D 79% + ^2_3D 21%	$\frac{3}{2}$		57 138		0.800	
^2_1D 76% + ^2_3D 23%	$\frac{5}{2}$		57 628		1.200	

Table X contains several examples which show the improvement in the calculated multiplet splittings through the introduction of the additional spin-dependent interactions, and its estimation by the $o-c$ spread. The over-all improvement can be demonstrated by comparing the sum of $o-c$ spreads for all the terms of all the investigated configurations in GLS 2, which is 274 cm^{-1}, to the corresponding sum of 786 cm^{-1} obtained in GLS 1. This clearly shows that the introduction of the additional spin-dependent interactions substantially improves the calculated multiplet structures.[32]

TABLE IX. Observed and calculated energy levels of Ni III $3d^8$ in cm^{-1} (GLS 2).

Term composition	J	Obs	Calc	$o-c$	g Calc	$o-c$ GLS 1
^3F 100%	4	0.0	−11	11	1.250	14
100%	3	1 360.7	1 349	12	1.083	10
99%	2	2 269.6	2 255	15	0.669	1
^1D 83% + ^3P 16%	2	14 031.6	14 045	−13	1.078	−19
^3P 84% + ^1D 16%	2	16 661.6	16 672	−10	1.420	−44
^3P 100%	1	16 977.8	16 987	−9	1.500	23
^3P 100%	0	17 230.7	17 238	−7	0.000	16
^1G 100%	4	23 108.7	23 106	3	1.000	−0
^1S 100%	0		52 523		0.000	

TABLE X. $o-c$ spread for some specific multiplets (in cm^{-1}).

Ion and configuration	Level	Obs	GLS 1 $o-c$	GLS 1 $o-c$ spread	GLS 2 $o-c$	GLS 2 $o-c$ spread
V III $3d^3$	$^2F_{7/2}$	27 727.8	4	26	15	1
	$^2F_{5/2}$	27 846.8	30		14	
Cr III $3d^4$	$^3H_4$	17 272.8	4	33	−12	4
	$^3H_5$	17 395.5	−10		−11	
	$^3H_6$	17 528.8	−29		−8	
Mn III $3d^5$	$^4G_{11/2}$	26 824.5	3	54	28	2
	$^4G_{9/2}$	26 852.4	25		29	
	$^4G_{7/2}$	26 860.3	43		30	
	$^4G_{5/2}$	26 856.9	57		30	
Fe III $3d^6$	$^3H_6$	20 051.1	−49	57	−27	9
	$^3H_5$	20 300.8	−16		−22	
	$^3H_4$	20 481.9	8		−18	
Fe III $3d^6$	$^3G_5$	24 558.8	−40	25	−26	0
	$^3G_4$	24 940.9	−34		−26	
	$^3G_3$	25 142.4	−15		−26	
Co III $3d^7$	$^2F_{5/2}$	37 021.0	41	59	10	2
	$^2F_{7/2}$	37 316.5	−18		8	
Ni III $3d^8$	$^3P_2$	16 661.6	−44	67	−10	3
	$^3P_1$	16 977.8	23		−9	
	$^3P_0$	17 230.7	16		−7	

TABLE XI. Separate contributions of the various spin-dependent interactions to the splittings of some specific multiplets (in cm^{-1}).

Ion and configuration	Level	ΔE SS	ΔE SOO	ΔE MMI	ΔE EL–SO	ΔE total	$o-c$ GLS 1	$o-c$ GLS 2
Fe III $3d^6$	$^3H_6$	−1	−47	−48	22	−26	−49	−27
	$^3H_5$	1	9	10	−4	6	−16	−22
	$^3H_4$	−2	56	54	−26	28	8	−18
	$^3H_4-{}^3H_6$	−1	103	102	−48	54	57	9
	$^3H_4-{}^3H_5$	−3	47	44	−22	22	24	4
Fe III $3d^6$	$^3_2F_2$	−3	22	19	−61	−42	−26	12
	$^3_2F_3$	3	4	7	−12	−5	1	4
	$^3_2F_4$	−1	−17	−18	43	25	21	−7
	$^3_2F_4-{}^3_2F_2$	2	−39	−37	104	67	47	−19
	$^3_2F_4-{}^3_2F_3$	−4	−21	−25	55	30	20	−11
Ni III $3d^8$	$^3P_2$	−1	−29	−30	21	−9	−44	−10
	$^3P_1$	10	28	38	12	50	23	−9
	$^3P_0$	−20	57	37	10	47	16	−7
	$^3P_0-{}^3P_1$	−30	29	−1	−2	−3	−7	2
	$^3P_0-{}^3P_2$	−19	86	67	−11	56	60	3

B. Properties of the Spin-Dependent Parameters

The results of the calculations (see Tables I and II) lead to the following conclusions concerning the spin-dependent parameters:

(a) The values of the spin-spin interaction parameters M^k_{ss} turn out to be equal to the values of the corresponding spin–other-orbit interaction parameters M^k_{soo}, as required by their definition.

(b) Both the M^k's and the Q^k's are positive. The M^k values form decreasing functions of k, whereas the Q^k's seem to be approximately independent of k.

(c) Both the M^k's and the Q^k's increase with N (along the row) in a regular way, agreeing with their theoretical dependence on the effective nuclear charge Z_{eff}. On assuming a Coulomb potential and hydrogenic eigenfunctions one obtains that[33] (i) the electrostatic interaction parameters (Slater parameters) R^k are proportional to Z_{eff}, (ii) the spin-orbit parameter ζ_{nl} is proportional to Z^4_{eff}, (iii) the mutual magnetic interaction parameters M^k are proportional to Z^3_{eff}, and (iv) the effective EL-SO interaction parameters Q^k, which comprise sums of products of $\zeta_l(nn')$ and R^k, are proportional to Z^5_{eff}.

A comparison of the values of B, ζ, M^0, and Q^2 $(=Q^4)$ in Co III $3d^7$ and in Cr III $3d^4$ yields the ratios

$$(B)_{\text{Co III}}/(B)_{\text{Cr III}} = 1.19\ ,$$

$$[(\zeta)_{\text{Co III}}/(\zeta)_{\text{Cr III}}]^{1/4} = 1.21\ ,$$

$$[(M^0)_{\text{Co III}}/(M^0)_{\text{Cr III}}]^{1/3} = 1.23\ ,$$

$$[(Q^2)_{\text{Co III}}/(Q^2)_{\text{Cr III}}]^{1/5} = 1.21\ .$$

The equality of these ratios shows the predicted theoretical behavior of the various interaction parameters, and, as a by product, the rate of increase of Z_{eff} along the row can be approximated. Notice that while the relative effect of the M^k's diminishes on raising the effective nuclear charge, the Q^k's gain in importance.

(d) The M^k values are in excellent agreement with the corresponding values obtained by Blume and Watson[18] using the Hartree-Fock method. The ratio M^0/M^2 tends to be constant and very close to the Hartree-Fock ratio. Thus, the results of calculations from first principles are confirmed by semiempirical calculations.

C. Strengths of the Spin-Dependent Interactions

The contribution of each interaction to a certain energy level can be calculated by multiplying the interaction-parameter value by the derivative of this energy level with respect to that parameter. The derivatives are computed in the diagonalization program together with the energy levels. The strengths of the additional spin-dependent interactions, that is, their contributions to the various

TABLE XII. Magnetic parameter values when the effective EL-SO interaction is omitted (in cm^{-1}).

Parameter	Ti III $3d^2$	V III $3d^3$	Cr III $3d^4$	Mn III $3d^5$	Fe III $3d^6$	Co III $3d^7$	Ni III $3d^8$
ζ_{LS}	126 ± 3	175 ± 3	237 ± 2	284 ± 11	423 ± 7	533 ± 5	657 ± 2
ζ_{GLS}	128	174	237	318	418	535	670
ζ_{HF}	126	184	258	333	426	539	672
M^0_{LS}	1.059 ± 0.447	0.468 ± 0.218	0.437 ± 0.138	0.645 ± 0.132	0.222 ± 0.480	0.526 ± 0.418	1.850 ± 0.205
M^0_{GLS}	0.501	0.475	0.449	0.423	0.397	0.371	0.345
M^0_{HF}	0.704	0.915	1.156	1.433	1.704	2.022	2.375
M^2_{LS}	0.380 ± 0.078	0.559 ± 0.237	0.996 ± 0.323	0.158 ± 0.392	1.297 ± 1.127	1.521 ± 0.383	1.233 ± 0.161
M^2_{GLS}	0.140	0.438	0.736	1.034	1.332	1.630	1.928
M^2_{HF}	0.384	0.499	0.631	0.783	0.930	1.103	1.295
$(M^0/M^2)_{LS}$	2.787	0.837	0.439	4.082	0.171	0.346	1.500
$(M^0/M^2)_{GLS}$	3.579	1.084	0.610	0.409	0.298	0.228	0.179
$(M^0/M^2)_{HF}$				1.832			
Δ_{LS}	2	8	8	8	32	12	2
Δ_{GLS}				25			

multiplet splittings, were thus estimated to be spin-spin interaction—several cm^{-1}, spin-other-orbit and effective EL-SO interactions—several tens of cm^{-1}.

The contributions of the additional spin-dependent interactions to several multiplets, as calculated from GLS 2, are given in Table XI. The deviations $o_i - c_i$ before and after the introduction of the additional spin-dependent interactions are also given for comparison, and all the above quantities are also calculated for the splittings of the multiplets. It is clearly seen how the various contributions combine to reduce the $o - c$ spread of the multiplets. Notice that the contribution of the soo interaction to the total splitting of a term can reach 100 cm^{-1} (^3H of Fe III $3d^6$) and the same is true for the effective EL-SO interaction (^3_2F of Fe III $3d^6$).

D. Importance of the Simultaneous Introduction of all the Spin-Dependent Interactions

All the above results crucially depend on the simultaneous introduction of all the three additional spin-dependent interactions. Various calculations in which these interactions were partly omitted have been carried out, and their results proved to be much worse than the above results. For example, the results of a calculation which included the mutual magnetic interactions but not the effective EL-SO interaction are given in Table XII, which contains information similar to that of Table II. It can be seen that the M^k values vary irregularly along the row and do not agree with the Hartree-Fock values, M^0 being too small and M^2 being too large. The ratio M^0/M^2 varies wildly along the row and in most cases is much smaller than the Hartree-Fock ratio. Also, when the constraint $M^k_{ss} = M^k_{soo}$ was removed, this equality was not retained. Another calculation in which only the effective EL-SO interaction was considered yielded completely unreasonable values for the Q^k's.

V. ADDITIONAL INVESTIGATIONS OF THE SPIN-DEPENDENT INTERACTIONS

The spin-dependent interactions have been included in the analysis of the $3d^N$ configurations of the fourth spectra of the iron group.[12,34] The results are consistent with those of the present work. The spin-dependent interactions are now being included by the present authors in the analyses of the $3d^N$ configurations of the isoelectronic sequences Ti III $3d^2$–Fe VII $3d^2$, V III $3d^3$–Ni VIII $3d^3$, and Cr III $3d^4$–Ni VII $3d^4$.

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