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Interpretation of Higher Order Magnetic effects in the Spectra of Transition Metal Ions in Terms of SO(5) and Sp(10)

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Small discrepancies in the fitted energy levels of the configurations $3d^N$ of transition metal ions are ascribed to effective three-electron magnetic operators y_i . Surprisingly it has been found that, of the 16 possible operators with ranks 1 in both spin and orbital spaces, four operators labeled by the irreducible representation (irrep) (11) of SO(5) are sufficient to obtain results which appear to be limited by the errors in the experimental energy levels. An interpretation is given involving products of operators labeled by the irreps of SO(5) and the symplectic group Sp(10). [S0031-9007(97)03013-5]

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The use of group theory for the understanding of physical phenomena has a long and distinguished tradition in quantum mechanics [1]. Group theory has repeatedly been used to elucidate patterns in experimental observations in all areas of modern physics. In particular, atomic spectra have from the beginning been a fertile hunting ground for the effects of symmetry. As simple a configuration as d^3 requires the introduction of a new quantum number, seniority, to distinguish the two 2D terms. However, in contrast to the lowest symmetries represented by the S and L quantum numbers, the higher symmetries are not expected to be connected with constants of the motion and are not represented by “good” quantum numbers. Nevertheless, the advantages of using group theory for understanding the structures of the configurations d^N and f^N are substantial, and the simplifications afforded by the use of the Wigner-Eckart theorem, when applied to the higher groups, are extremely large. Even so, it is clear that it would be very interesting if group theory exposed not only the beauty of the underlying structure, but also the relative importance of the various interactions between the electrons. A demonstration of the connection between these two aspects of atomic physics forms the subject of the present Letter.

The power of group theory is particularly striking when the accuracy of the observations cannot be matched by the available *ab initio* theories. In this respect the unrivaled accuracy of spectroscopic observations, which is far beyond what can be reached in *ab initio* calculations for atoms with more than two electrons, is important. To take advantage of this precision we have recently introduced the “orthogonal operator” method [2–5] for the description of complex configurations. In this method, which is based on parametric fitting to the observed energy level structure, the physical interactions are augmented with “effective interactions” which represent the effects of configuration interaction (CI). In the case of the d shell, all operators are classified with respect to SO(5) and Sp(10). This choice has the advantage that the operators in general

are automatically orthogonal to each other in the sense of the theory; i.e., the matrix elements corresponding to different operators are represented by orthogonal matrices. A practical advantage of orthogonality is that bringing new operators into play entails minimal adjustments to the values of the parameters associated with the operators already in use. More importantly in the present context, the addition of effective operators makes it possible to obtain a much more accurate description of the data and thereby, as we will show, allow the “observation” of very small relativistic and correlation effects that normally would disappear in the “noise” caused by the inability of more conventional methods to take into account even large higher order effects. While any extension of the conventional parameter sets can be expected to lead to a decrease in the remaining discrepancies in the fit, the use of group theory to classify the operators makes it easy to ensure that the additional operators show a minimal correlation to, i.e., are orthogonal to, the old ones; but, as we will show, it also allows us to ascribe physical significance to the remaining discrepancies in the fit. Thus the orthogonal operator technique is crucial for making possible the observations reported here. Although of less significance in the present context it should be mentioned also that the wave functions obtained in fits including the new operators have been shown to be superior to the old ones if used to predict properties such as decay rates [6].

A fruitful area for the use of the orthogonal operator technique has turned out to be the transition metal atoms and ions with an open $3d$ shell, for which complete sets of energy levels are known in many cases. For example, the $3d^N$ configurations have been studied for several degrees of ionization using a complete set of 21 electrostatic operators [7]. “Complete” means, in this context, that CI effects can be included to all orders, if due to the Coulomb interaction. To include magnetic effects to second order, it is necessary to add a set of nine operators [4]. In the transition metals this is sufficient to obtain fits with deviations between observed and calculated energies,

δE , of the order of a few cm^{-1} [7], an improvement with factors between 20 and 80 compared to previous parametric fittings and fairly close to the uncertainties in the experimental energies.

However, the discrepancies between theory and experiment, though small, have been found to display patterns that suggest that further analysis might be useful. For example, the δE 's for the individual J levels of similar terms belonging to mutually conjugate configurations (lying on either side of the half-filled shell) exhibit sign reversals for the spectra that have been studied [7]. In addition, there is an obvious pattern in the δE values within each multiplet with the δE 's decreasing in a regular manner from positive to negative values. Two examples are given in Table I (the columns labeled "no three-body") concerning the 4F term in $3d^3$ (Cr IV [8]) compared to the conjugate term in $3d^7$ (Ni IV [9]) and the 5D terms in $3d^4$ (Fe V [10]) and $3d^6$ (Ni V [11]). We repeat that without a (nearly) complete set of orthogonal operators it would not be possible to expose such minute physical effects from the configuration energies which in Cr IV, for example, cover an energy range of more than $53\,000\text{ cm}^{-1}$ and in Ni V probably more than $130\,000\text{ cm}^{-1}$ (the latter is an estimate since the highest level, 1S_0 , is unknown). The J dependence evident in Table I points to the importance of spin-orbit effects; yet the fitting already includes the normal single-electron spin-orbit interaction as well as the two-electron terms of the spin-other-orbit and electrostatically correlated spin-orbit types. However, operators representing three-electron magnetic effects of the spin-orbit type have been neglected so far. Such operators would be expected to come from a variety of interactions between d^N and excited configurations, and their diagonal matrix elements

would possess the property of reversing signs when going from d^N to the conjugate configuration d^{10-N} . Using group theory to construct operators labeled by irreducible representations (irreps) of $SO(5)$, the matrix elements of a complete set of 16 orthogonal three-electron magnetic operators y_i with rank 1 in both spin and orbital spaces have been calculated for d^3 by Leavitt [12]. We will call the associated parameter values for the normalized operators $p(y_i)$. With this set of operators, where the magnetic ones now are complete to third order, new fits have been made for the $3d^N$ configurations and we report here a remarkable simplification which allows us to obtain fits with deviations which are very close to the experimental energy uncertainties using only four of the 16 operators. This simplification is unexpected since all 16 operators appear in the same order of perturbation theory for a given selection of the perturbing operators [12]. Given the many operators available it is possible to obtain fits with δE essentially zero for each level. However, in this case the experimental errors in the energy level values will influence the parameter values. It is therefore important to use other criteria to determine the most appropriate fit. We use mainly the isoionic and isoelectronic trends in the parameter values and we do not allow all parameters to vary freely but the $y(11)$ set is basically determined after the appropriate values of the larger parameters have been obtained.

Table I shows also the results of adding subsets of the three-body operators to the fitting for the four ions, as well as the residue Δ that gives an indication of the remaining errors in the fit. Δ is defined as $\sum \delta E^2$ where the sum is over all levels of the particular configuration. The 16 operators have, as mentioned, been classified according to the irreps W of $SO(5)$. There are four operators

TABLE I. Differences between experimental and calculated energy level values, δE (in cm^{-1}), for the 4F terms belonging to the $3d^3$ and $3d^7$ configurations in Cr IV and Ni IV as well as for the 5D terms belonging to the $3d^4$ and $3d^6$ configurations in Fe V and Ni V. The observed energy levels are taken from [8] (Cr IV), [9] (Ni IV), [10] (Fe V), and [11] (Ni V). Results are shown obtained without the use of three-body magnetic operators (column labeled "no three-body") and introducing batches of three-body operators characterized by the $SO(5)$ labels (11), (21), and (31) + (32). The residue Δ is calculated by summing δE^2 over all levels belonging to the configuration. For further explanation, see text.

	Cr IV ($3d^3$)				Ni IV ($3d^7$)			
	(11)	(21)	(31) + (32)	No three-body	(11)	(21)	(31) + (32)	No three-body
${}^4F_{9/2}$	-0.23	-0.75	-0.81	-1.24	-0.37	1.51	1.73	1.95
${}^4F_{7/2}$	0.03	0.26	0.19	0.22	0.52	0.89	1.03	0.58
${}^4F_{5/2}$	-0.10	0.59	0.53	0.83	-0.26	-1.78	-1.98	-2.04
${}^4F_{3/2}$	0.10	1.02	0.98	1.42	0.12	-2.98	-3.52	-2.97
Δ	3.9	9.4	10.0	16.8	5.4	41.6	51.5	52.7
	Fe V ($3d^4$)				Ni V ($3d^6$)			
	(11)	(21)	(31) + (32)	No three-body	(11)	(21)	(31) + (32)	No three-body
5D_4	0.11	-1.56	-1.38	-1.92	-0.01	2.74	1.64	4.17
5D_3	-0.46	-0.54	-0.63	-0.63	-0.15	-0.16	-0.25	0.14
5D_2	0.38	1.60	1.48	1.79	0.08	-1.96	-1.15	-2.27
5D_1	-0.28	1.88	1.78	2.29	0.10	-3.20	-1.64	-3.81
5D_0	1.29	3.95	3.86	4.48	0.27	-3.66	-1.64	-4.37
Δ	11.0	33.7	32.8	53.0	14.5	62.2	56.2	97.5

with the label $W = (11)$, which we label $y(11)$, five with (21), three with (31), two with (32), and one of each with the labels (33) and (41). These labels are assumed to have primarily mathematical significance but Table I shows that the effect of introducing the $y(11)$ set is to reduce the residue Δ with factors varying between 4 and 10. In contrast, introducing instead the five (21) operators or the five operators with either (31) or (32) symmetry gives at best an improvement by a factor of 1.8. The most spectacular result is obtained for the $3d^7$ configuration in Ni IV where the $y(11)$ set reduces Δ from 52.7 to 5.4 cm^{-1} while the other sets do not lead to a reduction below 41 cm^{-1} . The larger errors for the $3d^6$ and $3d^7$ configurations compared to the situation for the conjugate configurations, $3d^4$ and $3d^3$, can be expected because the lowest order electrostatic and magnetic interactions are larger thus pointing to larger higher order effects. In Cr IV, Ni IV, and Ni V, the δE 's in the fit including the $y(11)$ set are smaller than the estimated errors in the experimental energies (roughly 0.4 cm^{-1}) signifying that the residues in these cases might be determined by the experimental errors and not by neglected physical effects. However, a closer look at the regularities in the δE 's indicates that the energy level values perhaps are more accurate than the authors' conservative estimates would suggest.

Given that there are 1820 possible combinations of four operators out of the 16 possible, it is clear that it is very difficult to pick the most suitable set of operators by trial and error. Even trying to determine whether it would be useful to add a few of the remaining operators to the $y(11)$ set would be a tedious task. However, the results obtained with the $y(11)$ set indicate that it is unlikely that such an extension would be useful. Table II shows complete results for the $3d^3$ configuration in Cr IV and its conjugate configuration $3d^7$ in Ni IV. Table II shows the δE 's with and without inclusion of the $y(11)$ set. The results obtained *without* the $y(11)$ set show, particularly for the high J values, clearly the sign reversal between $3d^3$ and $3d^7$ which led to the present investigation in the first place. However, when we consider the residuals obtained *with* $y(11)$ included it can be seen that, although most δE 's are smaller than the expected experimental accuracy, there is a remarkable similarity between the two columns *but* this time the deviations fairly consistently have the same sign, allowing us to conclude that the remaining deviations in so far as they are real probably have a different origin.

As mentioned, the finding that a small subset of the y_i operators is sufficient to include the higher order magnetic effects comes as a surprise and it clearly would be interesting to understand why this is so. It is highly suggestive that the irrep (11) of SO(5) is exactly the same as that labeling the ordinary single-electron spin-orbit interaction ζ_d in d^N . Thus a perturbation in which ζ_d is combined with SO(5) scalars would preserve the label (11), since $(00)^n \otimes (11) = (11)$. The Coulomb interaction plays the main role in mixing configurations,

TABLE II. δE values (in cm^{-1}) for the $3d^3$ and $3d^7$ configurations of triply ionized iron group elements, with and without a three-particle magnetic contribution from the $y(11)$ set. The seniorities of the two 2D terms are given as a subscripted prefix to the L value. In the least squares fitting, the levels are weighted with their degeneracy $2J + 1$.

		Cr IV ($3d^3$)		Ni IV ($3d^7$)	
		Without	With	With	Without
$J = 1/2$	2P	1.51	1.08	1.27	2.47
	4P	-0.32	-0.83	-1.53	-2.77
$J = 3/2$	2D	-0.23	0.00	0.06	0.49
	1_2D	1.38	0.16	-0.12	1.21
	2P	-1.76	-0.66	-0.67	-1.67
	4P	-0.02	-0.05	0.12	-0.26
$J = 5/2$	4F	1.42	0.10	0.12	-2.97
	2D	0.16	0.16	-0.01	-0.34
	2F	-0.68	-0.61	0.25	1.13
	3D	-0.21	-0.53	-0.03	-0.73
	4P	0.14	0.69	0.54	1.07
$J = 7/2$	4F	0.83	-0.11	-0.26	-2.04
	2F	0.51	0.20	-0.24	-0.85
	2G	-1.31	0.15	-0.04	1.82
$J = 9/2$	4F	0.22	0.03	0.52	0.58
	2H	-0.92	0.13	-0.08	2.23
	2G	1.06	0.50	0.19	-1.55
$J = 11/2$	4F	-1.24	-0.23	-0.37	1.95
	2H	0.72	-0.27	0.02	-1.66

but, although scalar with respect to S and L , it is not a pure SO(5) scalar. Within d^N , there is a component belonging to the irrep (22) in addition to (00). When configuration interaction is considered, the situation is more complex. The mixing of $d^{N-1}s$ into d^N calls for products of creation and annihilation operators of the types $d^\dagger d^\dagger ds$ and $s^\dagger d^\dagger dd$, and the SO(5) label is the part of $(10)^3(00)$ that contains spin and orbital ranks of zero, namely, the irrep (30). A third-order mechanism involving $d^{N-1}s$ in which two Coulomb operators and ζ_d appear would be expected to lead to contributions to all the y_i , since $(30)^2(11)$ contains all the irreps in the list of operator labels [12].

Another type of single-electron excitation that preserves parity is the mixing of $d^{N-1}d'$ into d^N . It is here that a new feature appears. The group SO(5) can be enlarged to include the d' electron by adding a second set of group generators to those referring to the d electron. The condition that the Coulomb interaction be an SO(5) scalar can now be stated in the form of conditions on the Slater integrals: namely, $X(2) = (5/9)X(4)$, where $X(k) = F^k(d, d), F^k(d, d'), G^k(d, d'),$ or $R^k(dd, dd')$. As is well known, the condition on $F^k(d, d)$ is equivalent to a delta-function interaction [13]. However, this short range interaction may be closer to the Coulomb force than appears at first sight because of screening effects. In fact, the Coulomb energies of the terms of d^2 can be represented by an operator whose largest component o_2 belongs to (00) [14,15]. The dominance of effective

operators belonging to (00) is apparent as we proceed along the d shell: for example, of the effective four-electron operators f_i , the largest in the fits are f_1 , f_3 , and f_8 , all belonging to (00) [7].

If, then, we make the decision to restrict our attention to just those parts of the Coulomb interaction belonging to (00) of SO(5), i.e., restricting the contributions to just the $y(11)$ set, we can calculate the ratios of the parameters $p(y_i)$ that measure the strengths of the normalized operators y_i under various assumptions. A few results are compared to experiment in Table III. Since y_6 is the most reliably determined experimentally, we arbitrarily set $p(y_6) = 1$. Case A is a third-order calculation in which only ζ_d is included (and not $\zeta_{d'}$ or the cross term $\zeta_{dd'}$). However, the null rank of $G^0(d, d')$ leads to large matrix elements when products of the type $R^k(dd, dd')G^0(d, d')\zeta_{dd'}$ are considered, and this gives the ratios of case B. In both cases the absolute signs of $p(y_6)$ agree with experiment, as do the signs of all four $p(y_i)$ for case B. It should be mentioned that such third-order contributions are distinct from second-order effects that come from $d \rightarrow d'$ excitations but have already been included by means of two-electron magnetic operators [4].

Included in Table III is also the result of a more general type of calculation (case C). This involves the symplectic group Sp(10). Within d^N , both o_2 and the delta-function interaction are (different) mixtures of 2 two-electron operators, e_1 and e_2 , whose respective symplectic labels are $\langle 00000 \rangle$ and $\langle 22000 \rangle$ [5]. If we attempt to represent the effects of third-order perturbation theory by effective operators acting solely within d^N , we are led to study products of the types $e_1 \otimes e_1 \otimes \zeta_d$ and $e_2 \otimes e_2 \otimes \zeta_d$. It turns out that the first contributes only to $p(y_1)$. The second, however, contributes to all members of the $y(11)$ set. The results for the symmetrized form, $e_2^2 \zeta_d + \zeta_d e_2^2$, are listed as case C in Table III. The correspondence to the experimental ratios is remarkably good. We should also note that the similarity of several ratios for cases A, B, and C is a direct consequence of the association of each y_i with a given irrep of Sp(10). In particular, the stability of $p(y_6)/p(y_7)$ (which corresponds quite well to the rather uncertain experimental values) is due

TABLE III. Theoretical and experimental ratios $p(y_i)/p(y_6)$ between the $y(11)$ parameters. The three theoretical cases A, B, and C are described in the text; the number of decimals in the experimental ratios reflects the accuracy of the fitted values.

	$p(y_1)$	$p(y_3)$	$p(y_6)$	$p(y_7)$
A	-1.50	2.75	1	-0.54
B	1.20	0.55	1	-0.54
C	0.59	0.55	1	-0.54
Cr IV	0.2	0.5	1	-0.46
Ni IV	0.2	0.2	1	-1.0
Fe V	0.4	0.5	1	-0.1
Ni V	0.1	0.4	1	-0.45

to the shared label $\langle 22110 \rangle$ for y_6 and y_7 , and the fact that $\langle 22110 \rangle$ is formed from symplectic components of similar types for the three cases.

Until a complete third-order calculation is carried out, we cannot properly assess the general applicability of the model based on the irreps (00) of SO(5) and $\langle 22000 \rangle$ of Sp(10). Nevertheless, the evidence clearly points to the excitations of the type $d \rightarrow d'$ as making the most significant contributions to the parameters $p(y_i)$. The extraction of physical information from detailed fits of theory to experiment is a prime justification for the fitting procedure. In fact, it could be argued that any discrepancies that remain in a fit indicate that the experimental information is not being put to full use. The magnitudes of the parameters constitute a separate issue, one that has to be faced with the help of *ab initio* methods. However, at present such methods cannot meet the level of precision demanded by the parametric approach. The two methods are complementary, not competitive.

Our success in reproducing the general trends of the four parameters of Table III provides a rationale for extending the use of effective operators with group labels elsewhere. One rather obvious extension is to the f shell, where group-theoretical methods are well established.

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