

³⁰J. E. Turner, V. E. Anderson, and K. Fox, Oak Ridge National Laboratory Report No. ORNL-4297 (unpublished).

³¹The angular momentum of the electron about the z axis being zero in the ground state, we have omitted this operator from Eq. (5).

³²In plotting $\log z$ along the abscissa, the values $z = \pm 0.01$ were given the same position. The values of ψ^2 at these two points were very nearly equal.

³³H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Atoms (Academic Press Inc., New York, 1957), p. 17.

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Magnetic Parameters for the Configuration f^3 [†]

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The energy-level schemes of several atomic configurations f^3 are analyzed in terms of effective operators. These include all possible Hermitian two-electron scalar operators and six three-body spin-independent scalar operators. This collection of operators allows for spin-spin and spin-other-orbit interactions as well as for the most important effects of configuration interaction. Several alterations and extensions are suggested for the terms of Pr III $4f^3$. The positions of the free-ion levels of Nd IV $4f^3$ and Er IV $4f^{11}$ are inferred from the crystal spectra of Nd³⁺ in LaCl₃, and analyses with restricted sets of operators are carried out.

I. INTRODUCTION

It is often useful to introduce effective operators in the analysis of the energy-level systems of electronic configurations for free atoms and ions. This method avoids the construction of accurate eigenfunctions. Instead, the eigenfunctions of a particular configuration under study are assumed pure, and the responsibility for getting a good fit with experiment rests with the choice of an effective Hamiltonian. It is convenient to express this as a sum of coupled tensors, for then a wide variety of effects can be taken into account by comparatively few operators. The coefficients of these operators can be treated as parameters, through which the experimental data can be represented in a more concise and significant form. This approach works best for configurations that are comparatively isolated from their neighbors.

Considerable work has been carried out by Shadmī¹ on the configurations $(d+s)^N$. Our own interest in the spectra of the doubly and triply ionized rare earths has led us to investigate the configurations f^N . These are more appealing from a theoretical standpoint, because there are many more levels to be fitted. The only difficulty is in finding experimental data that have been analyzed extensively enough. Preliminary analyses for several configurations of the type f^N have been reported recently.² Although only partial-term schemes are known in some cases, it was found to be highly desirable to introduce an operator that would represent magnetic interactions between the f electrons. The success of this approach has encouraged us to attempt an analysis of several $4f^3$ species in which the number of experimentally determined levels makes it feasible to go beyond the conventional analysis and include operators

that represent not only the direct magnetic interactions but also certain kinds of configuration interaction. We shall pay particular attention to the Pr III free-ion levels of Sugar.³

II. EFFECTIVE OPERATORS

A straightforward first-order analysis of the levels of a configuration f^N involves the Slater parameters F^k (where $k=0, 2, 4$, and 6) and the spin-orbit coupling constant ζ . To allow for two-electron excitations (as well as certain electrostatic shielding effects and the magnetic orbit-orbit interaction), the three parameters α , β , and γ are required. Rajnak and Wybourne^{4,5} introduced certain scalar three-electron operators to take into account single-electron excitations; it was shown later⁶ that a complete parametrization is possible with just six parameters T^k . The inclusion of magnetic spin-spin and spin-other-orbit interactions introduces three parameters M^k (where $k=0, 2$, and 4). Rather than treat these interactions as they stand, it is highly advantageous to decompose them into parts that have irreducible representations of certain continuous Lie groups as their labels. Four operators z_i ($1 \leq i \leq 4$) are required for the spin-spin interaction,⁷ and ten ($5 \leq i \leq 14$) for the spin-other-orbit interaction.² Of the latter, z_{13} has matrix elements proportional to the ordinary spin-orbit interaction, and a linear relationship exists that allows us to replace z_{12} and z_{14} by a combined operator z_c , where, for the states of f^2 , the equivalence

$$z_c \equiv (13/3)z_{12} - 40z_{13} + (4/3)z_{14}$$

is valid. In addition to satisfying many selection rules, the operators z_i are effective operators

for many types of configuration interaction in which the spin-orbit coupling, as well as the Coulomb interaction, plays a role. In fact, if a further operator z_0 is included, all possible Hermitian one-electron and two-electron scalar operators are represented. The reduced matrix elements of z_0 (which possesses spin and orbital ranks both equal to 2) are given in Table I. The total number of parameters a_i associated with z_i are $4 + 8 + 1$, that is, 13; with ζ , α , β , γ , and the four F^i , a total of 21 is obtained. This is precisely the number of cells in the energy matrices for f^2 , if each off-diagonal cell is counted just once. The six three-electron operators T^k raise the number of parameters to 27.

In order to analyze the empirical data, the matrix elements of the z_i for f^3 are required. They can be calculated from the results for f^2 by standard techniques [e.g., by the use of Eq. (4) of Ref. 2]. The results are set out in Table II for the operators z_i for which $0 \leq i \leq 4$. These operators possess spin and orbital ranks of 2. The matrix elements for z_i ($5 \leq i \leq 11$) and z_c are given in Table III; the spin and orbital ranks are both 1. Reduced matrix elements that reverse their sign when Ψ and Ψ' are interchanged are indicated by an asterisk. Duplicated terms are distinguished by a suffix (either 1 or 2); the notation is identical to that of Rajnak,⁵ who gives the correspondence with the group-theoretical description. With two exceptions, namely $({}^2F \parallel z_{10} \parallel (20) {}^2G)$ and $({}^2G \parallel z_{10} \parallel (21) {}^2G)$, the vanishing matrix elements can be given simple explanations in terms of group theory. Whether the exceptions are merely accidentally zero or whether a new selection rule remains to be discovered is not known.

Each operator z_i is associated with a parameter a_i so that its contribution to the effective Hamiltonian is a $a_i z_i$. The parameter a_c is used for z_c .

III. COMPARISON WITH EXPERIMENT

The only f^3 free-ion configuration on which any extensive analysis is available is that of Pr III, for which Sugar³ has reported 38 of the 41 levels that are theoretically possible. The parameter analysis was given by Trees⁸ in terms of the Racah E^k 's and ζ , plus the electrostatic two-body parameters α and β (our β , equivalent to twelve times his γ). In this work we use the convention in which β is the parameter which multiplies the matrix elements of the Casimir operator $G(G_2)$. The third two-body parameter γ [associated with $G(R_7)$] directly affects only the high (100) (10) 2F states, which Sugar did not find. One of Sugar's levels,

the nominal (210) (21) ${}^2F_{5/2}$ (2F2 in the Tables) at $34\,193.20 \text{ cm}^{-1}$ contains a small admixture of the higher ${}^2F_{5/2}$ and thus could be used for a rough determination of γ , but it was found only after Tree's analysis was complete. He therefore made no attempt to evaluate γ .

In a subsequent study, Rajnak⁵ introduced several three-body operators representing the effects of certain kinds of configuration interaction, and she also included the $34\,193 \text{ cm}^{-1}$ level. Reasonable results were obtained with five three-body operators, but the calculations showed a serious discrepancy for the level at $27\,597.13 \text{ cm}^{-1}$, nominally (210)(21) ${}^2D_{5/2}$ (2D_2). Since this level appears to be very well defined experimentally and the level at $34\,193$ does not, and since Rajnak's analysis leads to a negative value of γ which is in conflict with determinations for other rare-earth spectra, we have examined the alternative approach of keeping the ${}^2D_{5/2}$ level and suppressing the ${}^2F_{5/2}$ level. A preliminary diagonalization shows, in fact, that ${}^2D_{5/2}$ also contains a moderate admixture (8%) of the higher ${}^2F_{5/2}$ level, and requires a positive γ of about 2200 cm^{-1} . This same calculation places the high 2F levels about 4000 cm^{-1} lower than Tree's prediction and more than 9000 cm^{-1} lower than that of Rajnak. Using lines from Sugar's data which were not otherwise classified, we have made a search in this neighborhood and have uncovered levels at $53\,092.80 \text{ cm}^{-1}$ for ${}^2F_{7/2}$ and $54\,184.37 \text{ cm}^{-1}$ for ${}^2F_{5/2}$; the lower ${}^2F_{7/2}$ level was also located at $31\,787.93 \text{ cm}^{-1}$. The two ${}^2F_{7/2}$ levels appear to be well established and the ${}^2F_{5/2}$ a little less so. No satisfactory replacement for the rejected $34\,193 \text{ cm}^{-1}$ level could be found. In the course of the parameter analysis, we also found that Sugar's $26\,979.66 \text{ cm}^{-1}$ level, nominally (210) (11) ${}^2H_{9/2}$ (2H1), also could not be fitted satisfactorily into the parameter analysis; a search for a substitute revealed another level at $27\,178.80 \text{ cm}^{-1}$ which appears to be as good experimentally as Sugar's original one. We have used these 40 levels, one short of the complete set, in this parametrization. The results are set out in Table IV: column 2 for a 14-parameter fit with ζ as the only magnetic variable; column 3 for the full 27-parameter fit; and column 4 for a 25-parameter fit with the insignificant operators z_0 and z_3 deleted. The mean error is defined as $\sigma = [\sum_i \Delta_i^2 / (n-k)]^{1/2}$, where Δ_i is the difference between observed and calculated energies, n is the number of levels, and k the number of variable parameters. The parameters generally have the same sign and the same order of magnitude which they would have if the interactions were entirely attributable to spin-other-orbit and spin-spin effects (see Ref. 2 for the relationship of the a_i to Marvin's M^k integrals), but an analysis in just these terms, although suggestive, was not very satisfactory.

The physical significance of this type of parametrization has been confirmed by a similar treatment of levels derived from Nd^{3+} and Er^{3+} in LaCl_3 crystals. These ions are situated in crystal sites of high symmetry (hexagonal), and because for the rare earths the crystal-field effects can be treated as a static Stark-effect perturbation on the

TABLE I. Reduced matrix elements of z_0 for f^2 .

Φ	Φ'	$(\Phi \parallel z_0 \parallel \Phi')$
3P	3P	9
3P	3F	$3(3)^{1/2}$
3F	3F	$-2(14)^{1/2}$
3F	3H	$(22)^{1/2}$
3H	3H	$-(143)^{1/2}$

TABLE II. Reduced matrix elements $(\psi||z_i||\psi')$ for f^3 ($0 \leq i \leq 4$).

ψ	ψ'	F^2	(z_0)	(z_1)	(z_2)	(z_3)	(z_4)
4S	4D	6	-1	-4	-112	0	0
	$^2D1^*$	42	1	1	-32	0	0
	$^2D2^*$	154	0	0	0	1/22	0
4D	4D	14	11/7	34/7	47/7	2/21	1/7
	$^4F^*$	3	0	8	-96	1/2	0
	4G	231	-4/7	8/7	44/7	-13/1386	-4/77
	2P	2	0	3/2	72	1/2	0
	$^2D1^*$	2	31/7	67/14	-167/7	5/42	-1/7
	$^2D2^*$	66	-6/7	3/7	-51/7	-19/462	1/77
	2F1	3	6	0	0	0	0
	2F2	66	0	1	3	1/132	-1/11
	$^2G1^*$	33	4/7	-2/7	244/7	47/693	4/77
	$^2G2^*$	130	6/7	-3/7	51/7	-1/84	9/91
	4F	4F	21	-2	-2	-56	0
$^4G^*$		11	0	6	-72	-2/11	0
$^2P^*$		6	-3	-3	96	1/12	0
2D1		21	-6/7	8/7	384/7	-1/28	0
2D2		77	9/14	9/14	117/14	5/154	-1/22
$^2F1^*$		21	3/2	0	0	0	0
$^2F2^*$		462	-1/4	-1/4	-13/4	-1/33	-1/44
2G1		77	9/14	-6/7	-288/7	-1/77	0
2G2		2730	3/140	3/140	39/140	-1/105	3/260
$^2H1^*$		11	-2	-2	64	-3/44	0
$^2H2^*$		5005	1/10	1/10	13/10	-1/110	-3/1430
4G	4G	77	-18/77	-6/77	72/77	-68/847	80/847
	4I	858	-2/11	-8/11	-14/11	7/2178	-14/1573
	$^2D1^*$	33	4/7	-2/7	244/7	-23/252	4/77
	$^2D2^*$	1	39/14	-93/14	111/14	-73/462	123/154
	2F1	11	-9/2	0	0	0	0
	2F2	2	21/4	9/4	237/4	8/33	3/4
	2G1	11	-27/154	-30/77	720/77	-85/847	-80/847
	$^2G2^*$	390	-39/140	93/140	-111/140	2/385	-367/20020
	2H1	3	0	-4	-192	-29/132	0
	2H2	1365	3/10	-1/10	27/10	-1/110	-21/1430
	$^2I^*$	6006	-1/11	-1/11	2/11	-47/4356	2/1573
4I	4I	2002	-5/11	2/11	31/11	2/363	31/1573
	$^2G1^*$	6006	-1/11	-1/11	2/11	13/1089	2/1573
	$^2G2^*$	35	6/5	6/5	78/5	29/330	-18/715
	2H1	182	0	1/2	24	-1/22	0
	2H2	10	18/5	-17/5	129/5	-1/110	159/715
	$^2I^*$	286	-1/11	-13/22	233/11	5/726	-31/1573
	2K	1	-9	15	-45	-3/11	9/13
$^2L^*$	51	1	1	13	-1/11	-3/143	

free-ion levels, to first order the effect is merely to split a free-ion level (in this case) into $J + \frac{1}{2}$ components, each of them doubly degenerate. In higher order, the crystal field will also induce mixing between different free-ion levels, with resultant shifts in their mean position. This can be calculated if the details of the crystal-field parameters are sufficiently well known. Eisenstein⁹ has made this calculation for these cases, using the experimental data of Dieke and his students.¹⁰ His interest was principally in the crystal-field effects themselves, but Rajnak¹¹ was able to infer from his results the unperturbed free-ion positions and to extend the earlier analyses to include her three-body operators, in a similar manner to her

treatment of Pr III. We have applied the magnetic corrections also to her adjusted sets of crystal levels, with the results given in the last two columns of Table IV. Since the z_i with $0 \leq i \leq 11$ possess even quasispin ranks (see Ref. 2), their matrix elements for $4f^{11}$ have the same sign as the corresponding matrix elements for $4f^3$. We may imagine that the same is true of z_C , since the part that possesses an odd quasispin rank has the same matrix elements (apart from a constant factor) as the ordinary spin-orbit interaction. This interaction, and also the three-body interactions, possess matrix elements that reverse signs in going from f^3 to f^{11} .

IV. CONCLUSION

The introduction of the parameters a_i has led to a better understanding of several configurations f^3 . Although the range of parametrization is considerably widened, most of the new parameters are quite well determined. Three instances (a_0 , a_3 , and a_c) where this is not so can be readily understood. The parameter a_0 is not required to represent the spin-spin interaction; a_3 involves only off-diagonal matrix elements of the spin-spin interaction in f^2 ; and the coefficients of a_c differ from those of ζ only through matrix elements involving the high levels with seniority 1.

For other f^N configurations for which Russell-Saunders coupling is a good approximation, the most important contribution to the terms of max-

imum multiplicity will be from a_5 and a_6 . For these terms, the diagonal elements of a_7 and a_8 are identical to those of a_5 and a_6 , respectively, and hence will give an equivalent result in this limit; a_9 and a_c have diagonal elements which are equivalent to those of ζ ; and a_{10} and a_{11} have only zero diagonal elements. The diagonal matrix elements for terms of maximum multiplicity can be calculated from the symmetry properties of quarter-filled¹² and half-filled shells. A systematic chain calculation such as that described here for f^3 will be required for more detailed results. Such calculations for f^4 are now under way.

We wish to thank Dr. E. Reilly for sending us tables of her matrix elements of the spin-spin interaction for f^3 prior to publication.¹³

TABLE III. Reduced matrix elements ($\psi || z_i || \psi'$) for f^3 ($i \geq 5$).

ψ	ψ'	F^2	(z_5)	(z_6)	(z_7)	(z_8)	(z_9)	(z_{10})	(z_{11})	(z_c)
4S	2P	2	4	0	-8	0	-4/3	0	0	4
4D	4D	2	5/9	-7/9	5/9	-7/9	10/3	0	0	10/3
	$^4F^*$	6	50/9	2/9	50/9	2/9	0	0	0	0
	2P	30	-29/9	-1/45	11/18	1/90	-2/9	1/15	-2/45	2/3
	$^2D1^*$	70	-1/63	1/45	-4/9	1/45	2/63	2/15	4/105	-2/21
	$^2D2^*$	2310	2/63	2/495	1/18	7/990	-4/63	-1/165	-26/3465	4/21
	2F1	30	2/3	-2/15	0	0	0	0	0	32/3
4F	2F2	165	0	8/165	0	8/165	0	-8/165	16/495	0
	4F	35	-2	0	-2	0	4/3	0	0	4/3
	$^4G^*$	165	10/9	-4/99	10/9	-4/99	0	0	0	0
	2D1	210	-2/9	-2/63	-32/63	8/315	-4/21	0	0	4/7
	2D2	770	-1/3	17/1155	11/84	17/4620	2/63	17/330	1/165	-2/21
	$^2F1^*$	7	-6	0	0	0	0	0	0	32/3
	$^2F2^*$	154	-7/6	1/66	11/24	1/264	1/9	7/132	-1/66	-1/3
4G	2G1	231	2/9	-20/693	32/63	16/693	4/21	0	0	-4/7
	2G2	910	1/2	1/70	-11/56	1/280	-1/21	1/20	-1/390	1/7
	4G	3	10/9	56/99	10/9	56/99	20/3	0	0	20/3
	2F1	33	-2/3	-4/33	0	0	0	0	0	-32/3
	2F2	6	7/18	-1/198	49/72	227/792	-7/9	-25/132	-1/66	7/3
	$^2G1^*$	105	-2/63	-8/495	-8/9	-8/495	4/63	-16/165	32/1155	-4/21
4I	$^2G2^*$	2002	1/42	-1/66	1/24	-17/1320	-1/21	3/220	139/30030	1/7
	2H1	10	58/9	-62/495	-11/9	31/495	4/9	62/165	-4/165	-4/3
	2H2	182	-1/9	-5/99	-7/36	59/1980	2/9	-1/330	67/2145	-2/3
	4I	910	1/9	-1/99	1/9	-1/99	2/3	0	0	2/3
	2H1	26	-29/9	-7/99	11/18	7/198	-2/9	7/33	14/429	2/3
	2H2	70	-2/9	82/495	7/18	-73/990	4/9	-1/165	-14/715	-4/3
2P	$^2I^*$	26	-1/9	1/99	-28/9	1/99	2/9	2/33	-20/429	-2/3
	2K	15	4/9	148/495	7/9	-83/495	-8/9	2/165	668/6435	8/3
	2P	1	-10/3	2/3	-4/3	-1/3	8/9	4/3	0	0
	$^2D1^*$	105	-1/9	1/315	19/18	-1/630	2/9	-1/105	2/315	-2/3
	$^2D2^*$	385	0	-12/385	0	6/385	0	-6/385	4/385	0
	2D1	2D1	5	-88/63	-4/9	-88/63	7/45	52/63	-8/15	8/105
2D2		165	-34/63	2/495	8/63	-2/99	8/63	2/165	4/3465	-8/21
$^2F1^*$		105	32/21	4/105	0	0	0	0	0	32/21
$^2F2^*$		2310	0	4/1155	0	-2/165	0	2/1155	-4/3465	0
2D2	2D2	5	-22/21	2/165	41/21	-43/165	2/7	-2/11	-76/385	38/21
	$^2F1^*$	385	-1/7	17/385	0	0	0	0	0	32/21
	$^2F2^*$	70	1	-39/385	-3/4	-13/220	2/9	13/462	5/231	-2/3

TABLE III (continued)

ψ	ψ'	F^2	$(\ z_5\)$	$(\ z_6\)$	$(\ z_7\)$	$(\ z_8\)$	$(\ z_9\)$	$(\ z_{10}\)$	$(\ z_{11}\)$	$(\ z_c\)$
2F_1	2F_1	14	0	0	0	0	0	0	0	40/3
	2F_2	77	1/2	-1/22	0	0	0	0	0	-16/3
	${}^2G_1^*$	462	16/21	-4/231	0	0	0	0	0	16/21
	${}^2G_2^*$	455	-3/14	-3/70	0	0	0	0	0	16/7
2F_2	2F_2	14	8/3	-2/33	-5/6	4/33	10/9	4/33	4/33	-2/3
	${}^2G_1^*$	21	17/18	1/1386	-2/9	8/99	-2/9	-32/231	-16/231	2/3
	${}^2G_2^*$	10010	0	2/385	0	1/110	0	1/385	2/15015	0
2G_1	2G_1	30	-88/63	16/99	-88/63	-28/495	52/63	32/165	32/1155	4/21
	2G_2	143	-17/42	-1/66	2/21	8/165	2/21	0	272/15015	-2/7
	${}^2H_1^*$	35	-2/9	-62/3465	19/9	31/3465	4/9	62/1155	-4/1155	-4/3
	${}^2H_2^*$	13	17/9	-5/99	-4/9	8/495	-4/9	8/33	112/2145	4/3
2G_2	2G_2	30	184/105	14/75	-31/210	11/75	286/315	-2/75	-24/2275	-2/35
	${}^2H_1^*$	6006	0	4/1155	0	-2/1155	0	2/1155	172/45045	0
	${}^2H_2^*$	330	3/5	23/825	-9/20	-37/3300	2/15	-43/1650	49/2925	-2/5
2H_1	2H_1	55	-10/3	-2/165	-4/3	1/165	8/9	-4/165	0	0
	2H_2	1001	0	4/165	0	-2/165	0	2/165	4/2145	0
	${}^2I^*$	91	-1/9	1/99	19/18	-1/198	2/9	-1/33	-2/429	-2/3
2H_2	2H_2	55	-2/15	-18/275	19/15	3/275	22/45	14/275	196/10725	6/5
	${}^2I^*$	5	-34/9	-82/495	8/9	10/99	8/9	118/165	-12/143	-8/3
2I	2I	91	-88/63	-20/693	-88/63	1/99	52/63	-8/231	-40/3003	4/21
	${}^2K^*$	210	-34/63	74/3465	8/63	-4/495	8/63	-116/1155	136/45045	-8/21
2K	2K	35	59/42	43/462	215/168	-109/1320	85/63	-541/4620	157/10010	9/7
	${}^2L^*$	85	3/2	-1/110	-9/8	1/88	1/3	3/220	-73/1430	-1
2L	2L	51	11/6	-5/66	23/24	1/264	13/9	7/132	-7/286	1

TABLE IV. Parameters for $4f^3$ and $4f^{11}$ configurations. (Values in square brackets are fixed estimates.)

	Pr III	Pr III	Pr III	Nd ³⁺ in LaCl ₃	Er ³⁺ in LaCl ₃
E_{av}	8520 ± 42	8535 ± 17	8534 ± 16	12835. ± 17	20479 ± 26
E^1	3811 ± 6	3810 ± 3	3812 ± 2	5024 ± 132	6683 ± 12
E^2	20.22 ± 0.07	20.17 ± 0.04	20.16 ± 0.03	23.9 ± 0.5	31.8 ± 0.2
E^3	408.5 ± 0.5	408.8 ± 0.2	408.8 ± 0.2	497 ± 9	661 ± 3
ζ	662 ± 3	661 ± 2	661 ± 2	884 ± 2	2367 ± 4
α	30.6 ± 0.4	31.1 ± 0.2	31.1 ± 0.2	25 ± 14	19.7 ± 0.8
β	-810 ± 27	-820 ± 12	-821 ± 11	-735 ± 336	-427 ± 52
γ	2219 ± 33	2206 ± 12	2207 ± 12	[750]	[750]
T^2	449 ± 16	444 ± 6	443 ± 6	[0]	[0]
T^3	33 ± 8	39 ± 3	39 ± 3	44 ± 3	[0]
T^4	92 ± 12	81 ± 6	80 ± 5	43 ± 8	455 ± 77
T^6	-217 ± 19	-209 ± 8	-210 ± 7	-189 ± 28	-256 ± 46
T^7	312 ± 29	314 ± 12	311 ± 11	168 ± 30	168 ± 92
T^8	254 ± 33	282 ± 15	286 ± 13	[0]	[0]
a_0		0.04 ± 4	[0]	[0]	[0]
a_1		8.8 ± 4.5	9.3 ± 3.9	[0]	15 ± 5
a_2		-0.21 ± 0.20	-0.22 ± 0.19	[0]	[0]
a_3		70.5 ± 87.3	[0]	[0]	[0]
a_4		-93 ± 90	-87 ± 69	[0]	[0]
a_5		16 ± 2	17 ± 2	14 ± 3	13 ± 7
a_6		-176 ± 29	-173 ± 27	-127 ± 50	-180 ± 71
a_7		-5.3 ± 2.6	-5.3 ± 2.5	-5.0 ± 2.1	[0]
a_8		-113 ± 33	-116 ± 31	-137 ± 48	[0]
a_9		-3.2 ± 3.5	-3.7 ± 3.2	-20 ± 3	-27 ± 6
a_{10}		67 ± 23	67 ± 22	[0]	[0]

TABLE IV (continued)

	Pr III	Pr III	Pr III	Nd ³⁺ in LaCl ₃	Er ³⁺ in LaCl ₃
a_{11}		317 ± 105	340 ± 95	355 ± 240	[0]
a_c		-1.0 ± 0.7	-1.1 ± 0.7	[0]	[0]
σ	31 cm ⁻¹	11 cm ⁻¹	11 cm ⁻¹	7 cm ⁻¹	18 cm ⁻¹
No. of levels	40	40	40	22	20
No. of parameters	14	27	25	17	14
Largest deviation	74 cm ⁻¹	17 cm ⁻¹	18 cm ⁻¹	9 cm ⁻¹	23 cm ⁻¹

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Accurate Atomic and Molecular Wave Functions Without Exchange

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A perturbation-theoretic procedure is developed for obtaining the spatial function Φ_0 for the many-electron problem, from which the total wave function can be projected by the relation $\Psi = \sum_i \mathcal{D}_{i0}(r) D_{i0}(\sigma) \Phi_0(r) \chi_0(\sigma)$. This function is expanded in a perturbation series in which the Φ_0^0 contains a sufficient set of pair symmetries of Φ_0 itself, such as in the Hartree nonantisymmetrized wave function for closed-shell atoms. When the expansion converges, the remaining symmetries are introduced exactly. The energy eigenvalue does not contain the usual "exchange" terms, since the zeroth-order Hamiltonian, unlike the Hartree-Fock H_0 , has no degeneracies. Applications to interaction energies in molecular crystals and asymmetric wave functions are discussed briefly.

I. INTRODUCTION

The exact wave function for a many-electron system can be written as the sum of products of spatial functions with spin functions.¹ In this paper a perturbation expansion for a single one of these spatial functions is derived. The remaining spatial functions and hence the exact wave function

can be obtained directly from this single function by utilizing the symmetry properties of these functions under the operations of the permutation group for the N electrons.^{1,2} The spatial function solved for here possesses complicated symmetry properties except with respect to a small number of permutations under which, for closed-shell sys-