PHYSICAL REVIEW A VOLUME 4, NUMBER 2 AUGUST 1971

Effective Electrostatic Operators for Two Inequivalent Electrons*

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(Received 17 March 1971)

Parameter analyses of f^nd configurations of rare-earth ions generally result in mean errors in excess of 200 cm^{-1} when conventional Slater operators only are used. We introduce tensor operators whose mathematical structure is similar to those of the Slater angular functions f_k and g_k, except that intermediate values of k are allowed. We may therefore assume that, for the fd and $f^{13}d$ configurations, if we parametrize four new operators f_1, f_3, g_2, and g_4, we will get a complete description of the ten LS terms. The orthogonality properties of the 6-j symbols insure that the new operators are independent of the previous ones. We find a reduction of the mean error to less than 10 cm^{-1} for Pr IV and Ce III, and to about 30–60 cm^{-1} for La II, Yb III, and Th III. The effects of spin-spin and spin–other-orbit interactions are negligible.

When rare-earth configurations of the type $4f^N5d$ are treated by parametrization of the conventional Slater integrals, it is usual to have residual errors in excess of 200 cm^{-1}. A similar problem with equivalent-electron configurations has been solved in the last decade by application of the theory of effective operators[1] in which interaction effects between configurations are replaced by operators acting within the nominal configuration under study. A transformation to a new set of basis functions is implied. These will have S and L still as good quantum numbers, but with the sum over the principal quantum number n taken in an unspecified way, in general differently for the various SL states. Rajnak and Wybourne have discussed the f^N case in some detail,[2] and the new operators are now part of the accepted convention. Wybourne also discussed the $nl\,n'l'$ case,[3] but recommended against its use for two-electron problems, on the ground that the number of parameters equals the number of electrostatic terms. Our view is that in fact this full description of the electrostatic energy can lead to a much sharper interpretation of the fine-structure interactions, such as spin-orbit, spin–other-orbit, spin-spin, and electrostatically correlated spin-orbit effective operators induced by configuration mixing.[4]

For inequivalent electrons having orbital angular momentum quantum numbers l_1 and l_2, the two-electron configuration l_1l_2 contains (with l_2 the smaller of the two values) $2l_2+1$ singlet and $2l_2+1$ triplet SL terms, with the total angular momentum taking on the $2l_2+1$ values from l_1-l_2 to l_1+l_2 inclusive. A complete description of the electrostatic energy can be given by the introduction into the Hamiltonian of $2(2l_2+1)$ independent effective operators defined through their matrix elements by the expressions

$$f_k(L)=(-1)^{L+l_1+l_2}\begin{Bmatrix} l_1 & l_1 & k \\ l_2 & l_2 & L \end{Bmatrix}, \quad 0\le k\le 2l_2 \qquad \text{(1a)}$$

$$g_k(S,L)=(-1)^{S+l_1+l_2}\begin{Bmatrix} l_1 & l_2 & k \\ l_1 & l_2 & L \end{Bmatrix}, \quad l_1-l_2\le k\le l_1+l_2\,. \qquad \text{(1b)}$$

The independence of these operators follows from the orthogonality properties of the 6-j symbols (see, for instance, Edmonds[5]) which for these cases may be expressed as

$$(2k+1)\sum_L (2L+1)\,f_k(L)f_{k'}(L)=\delta(k,k')$$

and

$$(2k+1)\sum_L (2L+1)g_k(S,L)g_{k'}(S,L)=\delta(k,k')$$

for either value of S.

In addition we have

$$\sum_{S,L} f_k(L)\,g_{k'}(S,L)=0$$

for all k and k' because of the phase dependence of $g_{k'}$ on S.

For f_k with k even and g_k with $k+l_1+l_2$ even, these operators have a one-to-one correspondence with the conventional Slater operators. If the usual fitting procedures are used, the Slater integrals are treated as freely varying parameters, and the corresponding configuration-mixing operators will be automatically absorbed. We are then left with the $2l_2$ additional operators to accommodate the residual effects.

These additional "illegal" operators are proportional to those for the orbit-orbit interaction discussed by Feneuille and Pelletier-Allard,[6] but the experimental structures are too large to be attributed to purely relativistic effects and we have therefore suppressed the associated scaling factors. This situation is analogous to that for equivalent-electron configurations.[2]

The operator f_1 can be expressed in the closed form[5]

TABLE I. Illegal operators for $l_1 l_2$ configurations.

	dp			*fp*	
	f_1	g_2		f_1	g_2
^1P	−6	3	^1D	−8	−4
^1D	−2	−5	^1F	−2	11
^1F	4	−2	^1G	6	3
Denom	$12\sqrt{5}$	30	Denom	$12\sqrt{14}$	84

	fd			
	f_1	f_3	g_2	g_4
^1P	−16	−6	2	120
^1D	−12	3	−5	−90
^1F	−6	4	7	−105
^1G	2	−4	−5	−41
^1H	12	1	−5	−6
Denom	$12\sqrt{70}$	$14\sqrt{15}$	70	1260

	ff′					
	f_1	f_3	f_5	g_1	g_3	g_5
^1S	−24	−6	−132	−24	−6	−132
^1P	−22	−3	33	22	3	−33
^1D	−18	1	55	−18	1	55
^1F	−12	3	−66	12	−3	66
^1G	−4	1	34	−4	1	34
^1H	6	−3	−9	−6	3	9
^1I	18	1	1	18	1	1
Denom	168	42	924	168	42	924

	fg					
	f_1	f_3	f_5	g_2	g_4	g_6
^1P	−15	−55	−143	−15	−275	−3003
^1D	−13	−11	143	41	495	1001
^1F	−10	25	26	−70	−315	2366
^1G	−6	31	−130	90	−191	1638
^1H	−1	1	95	−85	369	623
^1I	5	−35	−31	35	315	131
^1K	12	14	4	84	70	12
Denom	$12\sqrt{105}$	$42\sqrt{165}$	$132\sqrt{273}$	1260	6930	36036

$$\frac{L(L+1)-l_1(l_1+1)-l_2(l_2+1)}{[l_1(2l_1+1)(2l_1+2)l_2(2l_2+1)(2l_2+2)]^{1/2}}$$

and is proportional to one of the operators discussed by Sack[7] in connection with $d^n p$ configurations. It is often seen in the contracted form $\alpha L(L+1)$ in analogy to Trees's correction operator for d^n configurations,[8] but we prefer to keep the full form in our calculations for more convenient comparison of magnitudes with the conventional operators.

Matrix elements for these illegal operators are given in Table I for the commonly occurring cases. Values for the conventional operators can be found in standard works such as Condon and Shortley[9] and (for *fg*) Shortley and Fried.[10] All entries for the exchange operators g_k are for singlet terms, as noted. The corresponding triplet values are of opposite signature, according to Eq. (1b). The f_k operators representing the direct interactions of course do not have a spin dependence [see Eq. (1a)]. Note that for the conventional f_k (k even) an additional multiplicative factor

$$(-1)^{l_1+l_2}(2l_1+1)(2l_2+1)\begin{pmatrix} l_1 & l_1 & k \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_2 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix} \quad (k \text{ even})$$

has been used; and for the g_k, the factor

$$(-1)^{l_1+l_2}(2l_1+1)(2l_2+1)\begin{pmatrix} l_1 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (k+l_1+l_2 \text{ even}),$$

to bring them into agreement with the conventional definitions (see, for instance, Wybourne[11] or Judd[12]).

The coefficient matrices of the direct integrals F^k for the $f^{13}d$ configuration are related to those for *fd* by the relation

$$(f^{13}d, SL\,|\,f_k\,|\,f^{13}d, SL) = (-1)^{k+1}(fd, SL\,|\,f_k\,|\,fd, SL),$$

derived from Racah.[13] The new operators are therefore identical to those of the conjugate configuration *fd*, since for these we take k odd.

The matrices for the g_k of $f^{13}d$ are not so simply related to those of *fd*, but for this special case the calculation is also given by Racah.[13] These are given in Table II. Note that this treatment is slightly different than that given by Condon and Shortley and Shortley and Fried, in that in their case a constant has been added to all elements of a given g_k such that the only nonzero element is that for the ^1L term with $L = k$.

Table III shows the comparison of these calculations with experimental energy levels for La II,[14] Ce III,[15] Pr IV,[16] Yb III,[17] and Th III.[18] The associated parameters are given in Table IV. The values are all in cm^{-1}, the parenthetical numbers being the estimated errors. The quantities σ and σ_S represent the mean errors as determined with and without inclusion of the illegal operators, respectively. In the case of Th III it was necessary to include the $5f6d$-$5f7s$ configuration interaction explicitly, but for the others the residual errors are not great

TABLE II. Exchange matrix elements for the $f^{13}d$ configuration.

k	$g_k(^1L)$ ($L = k$)	$g_{k'}$ (all other terms)
1	$\frac{7}{5}$	$-\frac{3}{5}$
2	$-\frac{1}{5}$	$\frac{1}{5}$
3	$\frac{12}{105}$	$-\frac{4}{15}$
4	$-\frac{1}{45}$	$\frac{1}{5}$
5	$-\frac{10}{363}$	$-\frac{10}{33}$

TABLE III. Residual errors in $f(d+s)$ configurations.

			$4f(5d+6s)$				$4f^{13}(5d+6s)$		$5f(6d+7s)$	
Desig	La II		Ce III		Pr IV		Yb III		Th III	
$4f5d$	En	O-C	En	O-C	En	O-C	En	O-C	En	O-C
$^3P_0$	22 684	36	11 577	−4	70 843	−8	45 277	37	12 043	1
$^3P_1$	22 705	10	11 613	2	70 756	2	39 721	78	11 933	−1
$^3P_2$	23 247	−38	12 642	2	72 185	6	33 386	−114	14 018	0
$^1P_1$	27 424	−5	18 433	0	78 776	0	53 365	−8	21 035	−1
$^1D_2$	18 895	11	6 571	3	65 322	6	40 288	2	7 098	−17
$^3D_1$	21 442	−97	8 922	7	66 968	9	50 029	22	8 731	9
$^3D_2$	22 106	−9	9 900	−10	68 412	−15	48 415	−1	10 991	−6
$^3D_3$	22 537	104	10 127	5	68 496	9	39 141	6	11 551	−4
$^3F_2$	17 212	5	3 822	−7	61 457	−11	51 463	−17	1 321	40
$^3F_3$	18 216	−17	5 502	0	63 356	7	43 019	−24	5 637	−38
$^3F_4$	19 215	−6	7 150	4	66 518	4	42 425	23	8 952	13
$^1F_3$	24 523	5	12 501	−2	71 725	−5	53 123	−72	16 263	−4
$^1G_4$	16 599	4	3 277	−2	61 171	−3	40 160	65	810	5
$^3G_3$	20 403	−3	6 265	4	64 124	3	51 582	57	5 871	−53
$^3G_4$	21 332	−4	7 837	−2	65 640	−5	53 736	−38	9 790	36
$^3G_5$	22 283	−2	9 326	−3	67 899	−3	43 623	−8	12 087	19
$^3H_4$	17 826	28	5 127	7	63 581	5	47 057	−23	3 990	−3
$^3H_5$	18 580	4	6 361	−7	65 239	−4	37 020	−15	5 299	17
$^3H_6$	19 750	−28	8 350	2	68 078	1	43 623	−8	9 247	−18
$^1H_5$	28 526	1	16 152	0	75 266	0	50 357	18	18 820	−1
$4f6s$										
$^3F_2$	14 148	−66	19 236	−5	100 258	−1	44 854	−25	3 991	0
$^3F_3$	14 375	67	19 464	5	100 544	1	45 207	25	3 337	15
$^3F_4$	15 699	36	21 476	2	103 271	1	34 656	22	7 121	−25
$^1F_3$	15 774	−36	21 849	−2	103 754	−1	34 991	−22	8 310	21

enough to warrant this procedure (although further reduction of the mean error can in fact be found). Note the striking correlation of the residuals given in Table III for Ce III and Pr IV. Since for Pr IV the $4f5d$ and $4f6s$ are well separated from other configurations (and from each other), there appears to be

TABLE IV. Parameters for $f(d+s)$ configurations.

		$4f(5d+6s)$		$4f^{13}(5d+6s)$	$5f(6d+7s)$	$4f6d$
Par	La II	Ce III	Pr IV	Yb III	Th III	Ce III
$4f5d\zeta_f$	389(16)	637(2)	858(3)	2 923(9)	1 171(8)	641(4)
ζ_d	415(30)	687(4)	1 067(4)	1 151(15)	1 552(18)	203(8)
F^2	13 886(159)	19 435(21)	22 428(28)	20 117(219)	20 578(118)	3479(66)
F^4	12 028(258)	15 702(37)	18 046(54)	12 325(490)	18 175(291)	2937(139)
G^1	11 037(67)	10 620(9)	10 520(11)	6 965(45)	15 271(46)	1501(36)
G^3	9 205(234)	10 963(31)	11 936(42)	7 272(460)	14 072(189)	1827(135)
G^5	4 577(168)	6 876(26)	7 947(36)	4 765(600)	7 504(162)	944(112)
F^1	4 252(173)	1 027(22)	1 064(29)	739(256)	2 445(122)	1 563(82)
F^3	2 373(292)	396(40)	158(56)	437(452)	2 026(285)	0
G^2	2 379(265)	3 008(36)	2 671(50)	2 213(337)	3 038(243)	0
G^4	0	1 947(48)	2 328(67)	3 075(913)	1 546(379)	0
$4f6s\zeta_f$	414(18)	638(3)	860(3)	2 927(19)	1 178(17)	•••
G^3	842(406)	2 085(54)	2 683(63)	2 385(466)	3 448(610)	•••
C.I. R^2	0	0	0	0	1 792(429)	•••
R^3	0	0	0	0	9 777(544)	•••
σ	61	8	10	67	33	27
σ_s	511	226	211	179	310	139

TABLE V. Parameters of higher configurations of Ce III.

	$4f5g$		$4f5f$	$4f6f$
ζ_f	643.32(0.05)	ζ_f	634(2)	638(0.5)
ζ_g	0.11(0.05)	$\zeta_{f'}$	25(2)	17(0.6)
F^2	424 (1)	F^2	3110(23)	1640(16)
F^4	45 (3)	F^4	1384(62)	940(30)
F^6	14 (4)	F^6	960(80)	232(73)
G^1	16 (1)	G^0	1174(3)	642(2)
G^3	9 (3)	G^2	1544(25)	850(17)
G^5	0	G^4	1034(67)	706(39)
G^7	0	G^6	832(62)	340(68)
F^1	151 (2)	F^1	154(31)	68(26)
F^3	29 (3)	F^3	0	0
F^5	9 (4)	F^5	0	0
G^2	9 (4)	G^1	−112(38)	33(24)
G^4	0	G^3	0	0
G^6	0	G^5	0	0
σ	0.5		9	3
σ_s	10		39	13

no need to introduce specific interactions directly. The remaining effects, therefore, appear to be magnetic (or pseudomagnetic) in origin. However, attempts to include a spin–other-orbit interaction between the $4f$ and $5d$ electrons[19] have given negative results. Configuration-mixing effects are too complicated for a general parametrization to be attempted, but there is an indication in the Yb III case that the leading terms are significantly present (see below).

Extending this analysis to more complex configurations, for $4f^2(5d+6s)$ of Pr III we get $F^1=1000$ (100), $F^3=459$ (210), $G^2=2456$ (192), and $G^4=1671$ (258), similar to the results of Feneuille and Pelletier-Allard[6]; for the $4f^{12}(5d+6s)$ levels of Tm III reported by Sugar[20] we get in a similar way $F^1=733$ (120), $F^3=0$, $G^2=2236$ (268), and $G^4=2141$ (429). The fact that the new operators appear to be fairly constant across the periodic series suggests that, as a first approximation in dealing with the more complex cases in between, one may make a fixed correction by assuming a mean of the values of the extremes. Similar values would appear to be appropriate for the fourth spectra. The La II results are probably disturbed by the overlapping $5d6p$ configuration, and these results should be extended to other cases with caution.

Results for some of the higher configurations of Ce III are given in Table V. Note that for $4f5g$ some of the new operators (especially F^1 and F^3) are more significant than the conventional ones of high rank.

The Yb III $4f^{13}5d$ case requires special consideration, since the interactions with the only known close configuration ($4f^{13}6s$) are not sufficient to absorb the effects. Electrostatically correlated spin-orbit operators analogous to those investigated[21] for $4f^2$ may be generated and tested for efficacy. After some experimentation we arrive at the conclusion that only the leading terms of the type $F^2(fd,fd')\cdot\zeta(d,d')$ and $G^1(fd,d'f)\cdot\zeta(d,d')$ are of significance; but both take precedence over the conventional configuration interactions $R^2(fd,fs)$ and $R^3(fd,sf)$. If these four variables are added to the previous set, and the $4f^{12}6s$ levels are also included, a mean error of some 15 cm^{-1} is obtained.

If these two-body magnetic operators scale approximately as ζ_d times F^2, they will be of vanishing significance for left-hand-side ions. Further study of the right-hand-side cases is needed before these results can be taken as definitive.

We wish to thank B. R. Judd for several helpful discussions.

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*Work supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, U.S. Air Force, under AFOSR Contract No. F44620-29-C-0027, and by the U. S. Atomic Energy Commission.

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PHYSICAL REVIEW A VOLUME 4, NUMBER 2 AUGUST 1971

Variational-Bound Methods for Auto-Ionization States. II. Three-Electron Atoms*

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(Received 18 January 1971)

Singly auto-ionizing (SAI) states of three-electron atoms below the first core excitation threshold are defined as eigenfunctions of an operator QHQ. It is shown that a particular type of multiconfiguration calculation provides upper-energy-bound estimates of such states, subject to a certain definition of Q (and the assumption that a certain set of equations has a solution). For SAI states with $L \neq 0$, Q is the proper Feshbach operator which projects out all wave-function components which overlap the exact ground state of the two-electron core. For SAI states with $L=0$, the bound is only established by adopting a modified, approximate Q which projects out only those wave-function components which overlap the angle-independent part of the core ground state. It is proposed that doubly auto-ionizing (DAI) states be defined as eigenfunctions of $Q'HQ'$, where Q' is the projection operator which eliminates all wave-function components which overlap the known 1s hydrogenic ground state of the one-electron system. The explicit form of P' and Q' is given, and a brief summary is given of various upper-energy-bound computational methods for DAI states; these closely parallel methods discussed previously for SAI states of two-electron atoms.

I. INTRODUCTION AND DISCUSSION

There are two general types of auto-ionization states, which may be readily distinguished.[1,2] Within the nonrelativistic approximation, which is adopted throughout this paper, these may be classified as stationary and quasistationary states, respectively. The former present no special theoretical or computational difficulty; they can be calculated with ordinary variational methods such as used for stationary states lying below the ionization threshold.[1,3] In treating quasistationary states, which are of primary interest herein, one must first adopt a mathematical definition and then attempt to develop suitable computational methods. In a previous paper[4] (hereinafter referred to as I) there was given a discussion of this problem for two-electron atoms; the present paper describes attempts to extend the same general approach to three-electron atoms. It happens that the QHQ definition which we adopt also encompasses nonrelativistically stationary states which are subject to auto-ionization through spin-dependent forces. This generality is of no practial usefulness, but should be borne in mind in connection with stages of energy-bound proofs in which the auto-ionization states are enumerated in order of increasing energy without regard to symmetry type. In actual calculations, the trial function will usually be restricted to a selected symmetry type, and the conclusions to be reached herein are primarily of interest with respect to those symmetry types corresponding to quasistationary states. Similar remarks are also applicable to the two-electron auto-ionization-state problem, though they were not given in I.

We will separately consider singly auto-ionizing (SAI) states and doubly auto-ionizing (DAI) states of three-electron atomic systems. Although there presumably exist SAI states lying between various discrete levels of the two-electron core,[5] attention is herein limited to states below the first core excitation threshold. Of particular experimental and historical interest is the SAI state of He$^-$ lying some 19.3 eV above the core ground state. This state was first observed by Schulz,[6] is thought to be of ^2S symmetry, and can be roughly classified as arising from a 1s(2s)^2 configuration.[7] There is also some experimental evidence for a P state at slightly higher energy,[8] and for a number of other states of undetermined symmetry.[9,10]

The DAI states lie within the continuum of the two-electron core, i.e., above the ground state of the associated one-electron system; for simplicity we limit attention to DAI states lying below the first excitation level of the one-electron system. Resonances associated with DAI states in He$^-$ have been observed by Kuyatt *et al.*[9] and by Simpson *et al.*[11] Fano and Cooper[12] have argued that these states are of $^2P^\circ$ and ^2D symmetry, roughly classifiable as arising from (2s)^{2}2p and 2s(2p)^2 configurations,