(Oxford U.P., New York, 1956), pp. 272 and 277.

[8] W. J. Childs, L. S. Goodman, and D. von Ehrenstein, Phys. Rev. 132, 2128 (1963).

[9] W. J. Childs and L. S. Goodman, Phys. Rev. 148, 74 (1966).

[10] L. S. Goodman and F. O. Salter, Rev. Sci. Instr. 37, 769 (1966).

[11] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D. C., 1949), Vol. 3, p. 136.

[12] See *Nuclear Data Tables*, edited by K. Way (Academic, New York, 1969).

[13] J. Stein, J. Opt. Soc. Am. 57, 333 (1967).

[14] The $l^N \alpha SL$ scheme is used throughout this paper, although the conventional phrases "LS limit," "LS basis," etc., are used. The phases of the LS eigenvector components of Ref. 4 were suitably modified before use.

[15] B. R. Judd and I. Lindgren, Phys. Rev. 122, 1802 (1961).

[16] P. G. H. Sandars and J. Beck, Proc. Roy. Soc. (London) A289, 97 (1965).

[17] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).

[18] These factors are conveniently tabulated by H. Kopfermann, *Nuclear Moments*, translated by E. E. Schneider (Academic, New York, 1958), pp. 445–449.

[19] W. J. Childs and L. S. Goodman, Phys. Rev. 170, 50 (1968).

[20] Y. W. Chan, W. J. Childs, and L. S. Goodman, Phys. Rev. 173, 107 (1968).

[21] W. J. Childs, Phys. Rev. 156, 71 (1967).

[22] G. K. Woodgate, Proc. Roy. Soc. (London) A293, 117 (1966).

[23] M. Wilson and M. Fred, J. Opt. Soc. Am. 59, 827 (1969).

[24] An outline of the theory of the calculation is given in, for example, B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York 1965), pp. 130–131.

[25] R. E. Trees, Phys. Rev. 92, 308 (1953).

[26] R. M. Sternheimer, Phys. Rev. 164, 10 (1967); 146, 140 (1966).

[27] J. B. Mann, LASL Report No. LA-3691, 1968 (unpublished).

[28] R. M. Sternheimer (private communication).

PHYSICAL REVIEW A VOLUME 3, NUMBER 1 JANUARY 1971

LS-Term Dependence of Hyperfine-Interaction Parameters in d^2s Configurations*

M. Wilson†
Argonne National Laboratory, Argonne, Illinois 60439

(Received 24 August 1970)

Hartree-Fock calculations have been made for the configurations $3d^24s$ of Sc I and $5d^26s$, $5d6s^2$, and $5d^3$ of La I. Attention is drawn to the variation of atomic quantities which influence hyperfine structures owing to the LS-term dependence of the radial wave functions. Theoretical calculations of the level structure of $(5d+6s)^3$ of La I are also presented.

I. INTRODUCTION

The traditional Hamiltonian for the magnetic-dipole hyperfine interaction in a configuration of the type $l^N s$ is of the form[1]

$$H_{\mathrm{dip}} = \left[a_l \sum_{i=1}^{N} (l_i - \sqrt{10}\,(sC^{(2)})_i{}^{(1)}) + a_s s\right] I,$$

where

$$a_l = 2\mu_B \mu_N \mu_I \langle r^{-3}\rangle_l / I$$

and

$$a_s = 16\pi \mu_B \mu_N \mu_I \,|\,\psi(0)\,|^2 / 3I,$$

μ_B is the Bohr magneton, μ_N the nuclear magneton, and μ_I the nuclear magnetic-dipole moment in nuclear magnetons.

Matrix elements of this Hamiltonian are usually expressed in terms of products of reduced matrix elements and certain angular coefficients. The reduced matrix elements depend on the radial parts of the wave function and are often treated as adjustable parameters to be determined by fitting experimental hyperfine structure (hfs) data to the theoretical expressions. It is to be noted that a_l and a_s here are usually supposed constants for all the states of a given electron configuration.[2] This implies that the multiplet structure be ignored completely insofar as the radial functions are considered as being defined in terms of the occupation numbers of the various orbitals together with a single energy criterion.

Contributions to the hfs from the nuclear electric-quadrupole interaction serve to complicate further the interpretation of hfs splittings. Parametric treatments of this follow lines similar to those used for magnetic-dipole interaction in the use of a single parameter $b_l = e^2Q\langle r^{-3}\rangle_l$ in the traditional approach. Again, it is to be noted that b_l is usually supposed a constant for all states of a given electron configuration.[2]

In recent years a variation of this approach has been used with some success in attempts to accom-

TABLE I. HF results for $3d^24s$ of Sc I. Values of spin density $|\psi(0)|^2$ are in units of a_0^{-3}, expectation values $\langle r^{-3}\rangle$ and $\langle r\rangle$ in units of a_0^{-3}, and a_0, respectively, Slater integrals $F^2(dd)$, $F^4(dd)$, $G^2(ds)$, and ζ in cm^{-1}, and total binding energies E_{total} in a.u. (2Ry).

	^4F	^2F	^2D	^4P	^2G	^2P	^2S
$4\pi\|\psi(0)\|^2_{4s}$	17.7120	11.9062	16.5115	18.6272	16.9868	12.6512	19.2905
$\langle r^{-3}\rangle_{3d}$	1.063	1.158	1.043	0.997	1.012	1.096	0.892
$\langle r\rangle_{3d}$	2.0691	1.9244	2.1235	2.1998	2.1888	2.0317	2.5320
$\langle r\rangle_{4s}$	4.2014	4.7411	4.3024	4.1295	4.2637	4.6709	4.0894
$F^2(3d3d)$	43 533	47 301	42 350	40 650	40 965	44 553	35 068
$F^4(3d3d)$	26 560	29 015	25 789	24 694	24 894	27 220	21 115
$G^2(3d4s)$	12 239	8502	12 053	13 500	12 649	9655	14 820
ζ_{3d}	56.1	61.5	55.1	52.5	53.4	58.0	46.9
E_{total}	−759.6995	−759.6719	−759.6556	−759.6597	−759.6374	−759.6280	−759.5720

modate such effects as core-excitation perturbations. This procedure, originated by Harvey,[3] uses the notion of effective operators in that different $\langle r^{-3}\rangle$ parameters are introduced for different parts of the hfs operator in order to absorb the effects of configuration interactions and relativity.[4,5] The effective operators that arise in the case of the quadrupole interaction may either be determined separately by fitting them to experimental data or related to a single parameter by assumptions concerning the effective charge used in the simplified theory of spin-orbit coupling.

For a detailed example of the use of these parametric procedures, see Ref. 6.

This purely parametric approach has revealed some surprisingly large variations in $\langle r^{-3}\rangle$ values for the different parts of the hyperfine interaction operator and thus added to the procedural difficulties that arise in interpreting the hfs for the purposes of evaluating nuclear moments.

Explicit *ab initio* calculations of core-polarization effects for elements of the first short period[7] and the alkalis[8] have yielded reasonable values for spin densities and lend support to Harvey's work concerning the inadequacy of the use of a single value of $\langle r^{-3}\rangle$.

In recent years many accurate hfs data extending through numerous states belonging to low-lying configurations have been obtained by means of atomic-beam magnetic-resonance methods.[9] However, even after treating the $\langle r^{-3}\rangle$ terms as adjustable parameters and taking into account configuration mixing and breakdown of LS coupling, the best obtainable fit is still often poor.[10]

Thus, it is of interest to reexamine the adequacy of the assumptions usually made in such fitting procedures and in particular those concerning the constancy of the terms a_l, a_s, and b_l for the different LS states of a single configuration.

It is well known that single-configuration Hartree-Fock (HF) radial wave functions determined for open-shell configurations of atomic electrons differ somewhat according to the LS term of the configuration. For convenience we shall refer to these differences and their effects on atomic properties as those due to LS-term dependence. Such differences may be expected to be large in those regions of the Periodic Table where the onset of d- and f- shell collapse effects assume importance. Recent work[11] has revealed that these effects can be large enough in some instances to render inadequate the existing theoretical framework for performing atomic structure calculations owing to serious departures from the conditions under which the usual simplifying assumptions obtain.

In Sec. II we present the HF results for the LS

TABLE II. HF results for $5d^26s$ of La I. Values of spin density $|\psi(0)|^2$ are in units of a_0^{-3}, expectation values $\langle r^{-3}\rangle$ and $\langle r\rangle$ in units of a_0^{-3}, and a_0, respectively, Slater integrals $F^2(dd)$, $F^4(dd)$, $G^2(ds)$, and ζ in cm^{-1}, and total binding energies E_{total} in a.u. (2 Ry).

	^4F	^2F	^2D	^4P	^2G	^2P	^2S
$4\pi\|\psi(0)\|^2_{6s}$	39.5758	26.4928	36.3351	40.5726	36.8806	27.3791	39.8401
$\langle r^{-3}\rangle_{5d}$	1.944	2.137	1.956	1.878	1.924	2.076	1.775
$\langle r\rangle_{5d}$	2.9913	2.8445	3.0159	3.0755	3.0575	2.9127	3.3000
$\langle r\rangle_{6s}$	5.1337	5.8633	5.3059	5.0904	5.2814	5.8196	5.1534
$F^2(5d5d)$	33 825	36 007	33 428	32 641	32 850	34 922	29 842
$F^4(5d5d)$	21 984	23 573	21 686	21 122	21 266	22 773	19 103
$G^2(5d6s)$	11 943	7983	11 269	12 611	11 598	8604	13 088
ζ_{5d}	499	549	502	482	494	534	456
E_{total}	−8221.112	−8221.073	−8221.067	−8221.080	−8221.057	−8221.051	−8221.007

TABLE III. Calculated values of energy levels (in cm^{-1}), g values, and Slater integrals (in cm^{-1}) for $(5d+6s)^3$ of La I.

			Values calculated from set A			Values calculated from set B		
J		E_{obs}	E_{calc}	$(E_{\mathrm{calc}}-E_{\mathrm{obs}})$	g_{calc}	E_{calc}	$-(E_{\mathrm{calc}}-E_{\mathrm{obs}})$	g_{calc}
$\frac{1}{2}$	1	7231	7 238.4	−7.4	2.657 006	7230.1	0.9	2.656 340
	2	9044	9 048.7	−4.7	0.681 196	9056.4	−12.4	0.681 876
	3	• • •	17 029.4	• • •	2.650 838	16 537.2	• • •	2.651 360
	4	• • •	18 327.0	• • •	1.993 357	18 207.5	• • •	1.985 126
	5	• • •	21 510.0	• • •	0.692 767	20 715.7	• • •	0.700 463
$\frac{3}{2}$	1	0	−10.9	10.9	0.797 577	−31.9	31.9	0.797 487
	2	2668	2 661.6	6.4	0.404 722	2645.4	22.6	0.404 989
	3	7490	7 478.5	11.5	1.712 153	7478.5	11.5	1.711 758
	4	8446	8 549.3	−103.3	0.944 611	8569.8	−123.8	0.946 954
	5	9719	9771.4	−52.4	1.207 631	9784.9	−65.9	1.205 774
	6	12 430	12 429.2	0.8	0.403 927	12 470.8	−40.8	0.404 217
	7	• • •	17 157.6	• • •	1.718 999	16 657.8	• • •	1.718 611
	8	• • •	19 533.0	• • •	0.845 565	18 748.1	• • •	0.841 464
	9	• • •	22 121.4	• • •	1.298 627	21 272.3	• • •	1.302 535
	10	• • •	28 872.3	• • •	0.799 814	27 020.9	• • •	0.799 840
$\frac{5}{2}$	1	1053	1045.7	7.3	1.199 314	1061.3	−8.3	1.199 190
	2	3010	3011.7	−1.7	1.029 719	3004.8	5.2	1.029 821
	3	7011	7020.3	−9.3	0.894 517	7001.6	9.4	0.893 848
	4	7679	7675.3	3.7	1.521 618	7678.2	0.8	1.521 156
	5	9183	9241.3	−58.3	1.242 450	9271.6	−88.6	1.243 617
	6	12 787	12 782.2	4.8	1.029 502	12 801.4	−14.4	1.029 547
	7	• • •	17 515.7	• • •	1.597 244	16 987.4	• • •	1.597 002
	8	• • •	20 211.4	• • •	1.202 225	19 353.4	• • •	1.202 252
	9	• • •	23 477.7	• • •	0.861 578	22 170.5	• • •	0.861 828
	10	• • •	28 718.6	• • •	1.197 346	26 908.2	• • •	1.197 248
$\frac{7}{2}$	1	3494	3503.2	−9.2	1.237 823	3508.8	−14.8	1.237 783
	2	8052	7985.6	66.4	1.135 334	7985.0	67.	1.134 732
	3	9960	9873.5	86.5	0.897 500	9853.1	106.9	0.898 114
	4	13 238	13 233.1	4.9	1.236 891	13 220.9	17.1	1.236 692
	5	• • •	17 735.6	• • •	0.890 991	17 126.6	• • •	0.891 284
	6	• • •	23 372.1	• • •	1.142 385	22 079.9	• • •	1.142 318
$\frac{9}{2}$	1	4121	4 129.8	−8.8	1.333 000	4 151.5	−30.5	1.332 927
	2	9919	9 866.8	52.2	1.112 733	9 844.1	74.9	1.112 773
	3	13 747	13 747.6	−0.6	1.329 953	13 695.7	51.3	1.329 396
	4	• • •	17 820.9	• • •	1.037 605	17 165.8	• • •	1.028 490
	5	• • •	19 023.1	• • •	0.986 531	18 258.2	• • •	0.996 237
$\frac{11}{2}$	1	• • •	18 976.5	• • •	1.091 120	18 173.1	• • •	1.091 120
rms	error			±54			±66	
d^2s	$E(d^2s)$			7634.4 ± 19.1			7622.2 ± 23.2	
	$F^2(dd)$			20 605.5 ± 165.2			20 486.0 ± 199.4	
	$F^4(dd)$			12 865.3 ± 278.9			12 663.7 ± 338.6	
	ζ_d			415.2 ± 14.6			425.9 ± 13.7	
	$G^2(ds)$			7671.6 ± 97.6			7640.9 ± 118.9	
ds^2	$E(ds^2)$			1271.0 ± 73.5			1586.8 ± 81.0	
	ζ_d			480.2 ± 35.6			502.0 ± 16.1	
d^3	$E(d^3)$			18 474.8 ± 56.7			17 745.2 ± 61.0	
	$F^2(dd)$			20 605.5 ± 165.2			17 846.7 ± 173.2	
	$F^4(dd)$			12 865.3 ± 278.9			10 871.5 ± 290.0	
	ζ_d			374.5 ± 20.5			348.0 ± 11.2	
	$R^2(d^3\times d^2s)$			−10 345.9 ± 166.1			−9860.7 ± 192.2	
	$R^2(ds^2\times d^3)$			7671.6 ± 97.6			10 106.1 ± 156.9	
	$R^2(d^2s\times ds^2)$			−10 345.9 ± 166.1			−10 176.2 ± 198.7	

terms of the configurations $3d^24s$ of Sc I and $5d^26s$ of La I and discuss the relevance of these results in interpreting the hfs data.

In order to assist further the analysis of recent

TABLE IV. $(5d+6s)^3$ of La I. Eigenvector components of the eigenvalues given in Table III.

	$J=\frac{1}{2}$	$^2S(d^2s)$	$^2P(d^2s)$	$^4P(d^2s)$	$^2P(d^3)$	$^4P(d^3)$
1	A	0.0782	−0.0622	0.9946	−0.0289	0.0014
	B	0.0811	−0.0631	0.9943	−0.0300	0.0014
2	A	0.0490	−0.8709	−0.0724	−0.4828	0.0281
	B	0.0502	−0.8628	−0.0739	−0.4967	0.0287
3	A	−0.0305	0.0686	0.0033	−0.0693	0.9948
	B	−0.0246	0.0699	0.0030	−0.0669	0.9950
4	A	0.9914	0.0074	−0.0747	0.1006	0.0372
	B	0.9882	−0.0083	−0.0773	0.1279	0.0338
5	A	−0.0876	−0.4826	0.0018	0.8667	0.0910
	B	−0.1176	−0.4966	0.0038	0.8553	0.0895

	$J=\frac{3}{2}$	$^2P(d^2s)$	$^2D(d^2s)$	$^4P(d^2s)$	$^4F(d^2s)$	$^2D(ds^2)$	$^2P(d^3)$	$^2_1D(d^3)$	$^2_3D(d^3)$	$^4P(d^3)$	$^4F(d^3)$
1	A	0.0181	−0.3165	0.0100	−0.0749	−0.9335	0.0099	0.1349	−0.0631	−0.0023	−0.0088
	B	0.0186	−0.3167	0.0102	−0.0767	−0.9252	0.0109	0.1799	−0.0697	−0.0028	−0.0103
2	A	0.0046	−0.0679	0.0033	−0.9924	0.1021	0.0016	−0.0085	−0.0070	0.0001	0.0000
	B	0.0047	−0.0693	0.0034	−0.9920	0.1038	0.0015	−0.0145	−0.0061	0.0002	0.0004
3	A	−0.0268	−0.1396	0.9875	0.0188	0.0583	−0.0106	0.0053	−0.0257	0.0007	−0.0036
	B	−0.0273	−0.1408	0.9873	0.0194	0.0589	−0.0113	0.0012	−0.0254	0.0008	−0.0029
4	A	0.4416	−0.7791	−0.1192	0.0857	0.2873	0.2388	0.0536	−0.1798	−0.0217	−0.0343
	B	0.4423	−0.7770	−0.1195	0.0872	0.2894	0.2463	0.0324	−0.1790	−0.0216	−0.0289
5	A	0.7496	0.4634	0.1020	−0.0422	−0.1420	0.4267	−0.0199	0.0801	−0.0415	0.0213
	B	0.7386	0.4676	0.1037	−0.0435	−0.1431	0.4404	−0.0088	0.0805	−0.0432	0.0177
6	A	0.0059	−0.0636	−0.0030	0.0042	−0.0015	−0.0068	−0.0566	0.0758	0.0038	0.9934
	B	0.0071	−0.0588	−0.0028	0.0040	−0.0088	−0.0068	−0.0592	0.0815	0.0041	0.9931
7	A	−0.1145	0.0145	−0.0015	−0.0006	0.0078	0.1054	0.0521	−0.0592	−0.9844	0.0136
	B	−0.1169	0.0135	−0.0017	−0.0006	0.0121	0.1013	0.0531	−0.0619	−0.9843	0.0148
8	A	0.1456	−0.2112	−0.0024	0.0081	−0.0472	−0.2203	−0.4511	0.8095	−0.1180	−0.1030
	B	0.1429	−0.2094	−0.0027	0.0086	−0.0746	−0.2054	−0.4426	0.8162	−0.1187	−0.1084
9	A	−0.4557	−0.0696	−0.0060	0.0023	−0.0121	0.8372	−0.1386	0.2284	0.1202	−0.0219
	B	−0.4728	−0.0687	−0.0067	0.0024	−0.0182	0.8322	−0.1298	0.2171	0.1197	−0.0212
10	A	0.0025	0.0178	0.0002	−0.0004	−0.0979	−0.0060	−0.8659	−0.4898	−0.0180	−0.0110
	B	0.0030	0.0236	0.0003	−0.0006	−0.1396	−0.0061	−0.8644	−0.4818	−0.0189	−0.0118

	$J=\frac{5}{2}$	$^2D(d^2s)$	$^2F(d^2s)$	$^4P(d^2s)$	$^4F(d^2s)$	$^2D(ds^2)$	$^2_1D(d^3)$	$^2_3D(d^3)$	$^2F(d^3)$	$^4P(d^3)$	$^4F(d^3)$
1	A	0.3585	−0.0333	−0.0316	0.0818	0.9162	−0.1367	0.0670	0.0074	0.0048	0.0063
	B	0.3604	−0.0350	−0.0326	0.0855	0.9065	−0.1824	0.0731	0.0087	0.0062	0.0073
2	A	0.0364	−0.0773	−0.0045	0.9907	−0.1043	0.0110	0.0027	0.0105	−0.0004	−0.0005
	B	0.0364	−0.0793	−0.0046	0.9901	−0.1077	0.0176	0.0017	0.0108	−0.0007	−0.0007
3	A	−0.2072	0.9403	0.1478	0.0957	0.1166	0.0059	−0.0354	−0.1646	−0.0003	0.0028
	B	−0.2053	0.9397	0.1453	0.0983	0.1178	−0.0023	−0.0341	−0.1702	0.0001	0.0033
4	A	0.2872	0.2211	−0.9189	−0.0118	−0.1394	−0.0049	0.0534	−0.0407	0.0003	0.0060
	B	0.2908	0.2188	−0.9179	−0.0126	−0.1419	0.0052	0.0534	−0.0423	−0.0003	0.0050
5	A	0.8338	0.1722	0.3641	−0.0492	−0.3220	−0.0384	0.1818	−0.0354	0.0027	0.0259
	B	0.8324	0.1705	0.3676	−0.0501	−0.3237	−0.0140	0.1829	−0.0380	0.0010	0.0221
6	A	−0.0398	−0.0115	−0.0049	0.0014	−0.0007	−0.0345	0.0498	−0.0147	0.0042	0.9972
	B	−0.0372	−0.0114	−0.0047	0.0013	−0.0054	−0.0357	0.0534	−0.0156	0.0045	0.9970
7	A	0.0229	−0.0008	0.0014	−0.0007	0.0122	0.0781	−0.0576	−0.0068	−0.9949	0.0106
	B	0.0218	−0.0010	0.0015	−0.0007	0.0189	0.0792	−0.0596	−0.0073	−0.9946	0.0114
8	A	0.2169	−0.0022	0.0106	−0.0055	0.0404	0.4083	−0.8775	−0.0463	0.0894	0.0656
	B	0.2164	−0.0020	0.0116	−0.0059	−0.0645	0.3935	−0.8824	−0.0480	0.0913	0.0686
9	A	0.0149	0.1730	0.0006	0.0023	−0.0131	−0.0777	−0.0845	0.9778	−0.0076	0.0186
	B	0.0173	0.1792	0.0007	0.0026	−0.0188	−0.0794	−0.0854	0.9763	−0.0083	0.0197
10	A	−0.0082	0.0139	−0.0002	0.0003	0.1053	0.8942	0.4188	0.1064	0.0465	0.0113
	B	−0.0135	0.0147	−0.0004	0.0004	0.1514	0.8930	0.4060	0.1088	0.0487	0.0122

	$J=\frac{7}{2}$	$^2F(d^2s)$	$^2G(d^2s)$	$^4F(d^2s)$	$^2F(d^3)$	$^2G(d^3)$	$^4F(d^3)$
1	A	0.0751	0.0274	−0.9967	−0.0110	−0.0045	0.0004
	B	0.0769	0.0281	−0.9966	−0.0115	−0.0046	0.0004
2	A	0.9641	−0.1777	0.0696	−0.1816	0.0332	0.0060
	B	0.9613	−0.1840	0.0710	−0.1890	0.0353	0.0058
3	A	0.1717	0.9436	0.0407	−0.0454	−0.2750	0.0272
	B	0.1773	0.9397	0.0421	−0.0493	−0.2838	0.0261

TABLE IV (*continued*).

	$J=\frac{5}{2}$	${}^2D(d^2s)$	${}^2F(d^2s)$	${}^4P(d^2s)$	${}^4F(d^2s)$	${}^2D(ds^2)$	${}^2_1D(d^3)$	${}^2_3D(d^3)$	${}^2F(d^3)$	${}^4P(d^3)$	${}^4F(d^3)$
4	A	−0.0161	−0.0427	−0.0015	−0.0212	−0.0548	0.9972				
	B	−0.0165	−0.0435	−0.0016	−0.0226	−0.0589	0.9969				
5	A	−0.0264	−0.2746	−0.0047	−0.0508	−0.9576	−0.0659				
	B	−0.0287	−0.2834	−0.0052	−0.0523	−0.9545	−0.0705				
6	A	−0.1856	0.0041	−0.0033	−0.9807	0.0574	−0.0205				
	B	−0.1934	0.0040	−0.0038	−0.9790	0.0598	−0.0217				

	$J=\frac{9}{2}$	${}^2G(d^2s)$	${}^4F(d^2s)$	${}^2G(d^3)$	${}^2H(d^3)$	${}^4F(d^3)$
1	A	−0.0696	0.9975	0.0108	−0.0005	−0.0007
	B	−0.0718	0.9974	0.0112	−0.0005	−0.0006
2	A	0.9613	0.0699	−0.2629	0.0184	0.0394
	B	0.9588	0.0721	−0.2713	0.0193	0.0381
3	A	−0.0719	−0.0031	−0.1143	0.0144	0.9907
	B	−0.0741	−0.0033	−0.1229	0.0170	0.9895
4	A	−0.2123	−0.0065	−0.7514	0.6147	−0.1111
	B	−0.2115	−0.0069	−0.7193	0.6513	−0.1164
5	A	−0.1444	−0.0040	−0.5942	−0.7884	−0.0676
	B	−0.1588	−0.0048	−0.6275	−0.7584	−0.0768

	$J=\frac{11}{2}$	${}^2H(d^3)$
1	A	1.0000
	B	1.0000

hfs studies[6] in La I, a theoretical calculation of the level structure of $(5d+6s)^3$ has been made, the results of which are presented in the Appendix.

II. RESULTS AND DISCUSSION

Closed expressions for the open-shell average of configuration HF equations are given by Slater[12] and form the basis for the procedure used here. HF solutions for specific LS terms of such open-shell configurations are obtained by minimizing the energy formed by adding to the average total binding energy of the configuration energy expressions, which, for the d^2s configuration, take the form

$$\left.\begin{matrix} H({}^4F) \\ H({}^2F) \end{matrix}\right\} = -\frac{58}{441}\,F^2(dd)+\frac{5}{441}\,F^4(dd)\;\begin{cases} -\frac{1}{5}\,G^2(ds), \\ +\frac{2}{5}\,G^2(ds) \end{cases}$$

$$\left.\begin{matrix} H({}^4P) \\ H({}^2P) \end{matrix}\right\} = +\frac{77}{441}\,F^2(dd)-\frac{70}{441}\,F^4(dd)\;\begin{cases} -\frac{1}{5}\,G^2(ds), \\ +\frac{2}{5}\,G^2(ds) \end{cases}$$

$$H({}^2G) = +(50/441)\;F^2(dd)+(15/441)\;F^4(dd),$$

$$H({}^2D) = -(13/441)\;F^2(dd)+(50/441)\;F^4(dd),$$

$$H({}^2S) = +(140/441)\;F^2(dd)+(140/441)\;F^4(dd).$$

Adopting the HF procedure developed by Froese,[13] single-configuration HF calculations were made for all of the LS terms of the configurations $3d^24s$ of Sc I and $5d^26s$ of La I. The values of various atomic quantities calculated from these HF solutions are given in Tables I and II.

Let us draw attention to the unexpectedly large variations in those atomic quantities that may be expected to reveal themselves by means of studies of hyperfine interactions and, to a lesser extent, isotope shifts.

The values of spin density $|\psi(0)|_s^2$ due to the outermost s electron indicate that the contact terms a_s are expected to vary considerably from one term to another, being smallest for the ${}^2F$ and largest for the ${}^4P$. The over-all change is ~56% for Sc and ~53% for La. The values for the neighboring terms ${}^4F$ and ${}^2F$ in both Sc and La differ by ~49%. It should be noted that these are variations in the spin density due to the outermost s electron alone and the effects of core polarization are not included.

In parametrizing this spin-density factor, approximate groupings of the contact terms could perhaps be made to test the validity of the indicated behavior, viz.,

$$a_s({}^2F)\approx a_s({}^2P)<a_s({}^2D)\approx a_s({}^2G)<a_s({}^4F)\approx a_s({}^4P)\approx a_s({}^2S).$$

The values of $\langle r^{-3}\rangle_d$ also exhibit variations consistent in behavior with those of the contact terms.

It is clear that such effects may well help in accounting for certain anomalies observed in the parametric approach and failure to take them into account, when present, might result in substantial error.

ACKNOWLEDGMENTS

The author would like to express his thanks to Professor Charlotte Froese Fischer, Mrs. Cynthia Chamot, and Dr. M. Fred for helpful advice concerning the use of their computer codes, and to Dr. W. J. Childs and Dr. L. S. Goodman for both drawing

his attention to their interest in obtaining the results presented here and for helpful discussions.

APPENDIX: MIXED-CONFIGURATION EIGENVALUES AND EIGENVECTORS FOR $(5d+6s)^3$ OF La I

Progress towards a detailed understanding of the low even configurations of La I was made after Stein[14] found the ^4F term of $5d^3$. This enabled the major effects of $5d^3$ to be taken into account in a theoretical study of $(5d+6s)^3$.

Several fittings of the LS matrices of electrostatic and spin-orbit interaction to the observed energy levels have been made in order to obtain calculated values for levels, g values, and eigenvector components. Since the number of known electrostatic terms is smaller than the total number of electrostatic parameters,[15] constraints on the latter must be introduced. The results of adopting two different sets of constraints are given in Tables III and IV.

In set A we have adopted constraints similar to those used by Stein, i.e., $F^2(dd)$ and $F^4(dd)$ take identical values in d^2s and d^3 and $G^2(ds)$ of d^2s takes the same value as $R^2(ds^2\times d^3)$. However, we did not impose that the ζ_d values obey a linear progression.

In order to obtain physically reasonable eigenvectors, several points must be borne in mind. In calculations of physical quantities which involve the use of mixed-configuration eigenvectors, care must be taken that the signs of off-diagonal matrix elements are calculated in a consistent fashion. We have taken care to ensure that the phases of the off-diagonal R^k integrals used here were those obtained from the HF results, i.e., $R^2(d^2s\times d^3)$ and $R^2(ds^2\times d^2s)$ are both negative while $R^2(ds^2\times d^3)$ is positive.

In addition, it was thought worthwhile to investigate the effects of an attempt to make the constraints on the parameters more physically plausible than those of set A. Thus, in set B, we have forced the parameters (i) $F^2(dd)$ and $F^4(dd)$ in d^2s and d^3, (ii) $G^2(ds)$ and $R^2(ds^2\times d^3)$, (iii) $R^2(d^3\times d^2)$ and $R^2(d^2s\times ds^2)$, and (iv) the ζ_d's of d^3, d^2s, and s^2d to retain their HF ratios.

The deviations between the calculated and observed values for energies and g values[6] show similar qualitative features for the two sets although the differences between the two for the remaining levels, as yet unobserved, becomes increasingly large with increase in energy.

---

*Work performed in part under the auspices of the U. S. Atomic Energy Commission.

†Permanent address: Physics Department, Chelsea College, University of London, Pulton Place, London, S.W.6., England.

[1] R. E. Trees, Phys. Rev. 92, 308 (1953).

[2] See, e.g., B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Interscience, New York, 1965), Chap. 5.

[3] J. S. M. Harvey, Proc. Roy. Soc. (London) A285, 581 (1965).

[4] P. G. H. Sandars and J. Beck, Proc. Roy. Soc. (London) A289, 97 (1965).

[5] G. K. Woodgate, Proc. Roy. Soc. (London) A293, 117 (1966).

[6] W. J. Childs and L. S. Goodman, preceding paper, Phys. Rev. A 3, 25 (1971).

[7] H. P. Schaefer III, R. A. Klemm, and F. E. Harris, Phys. Rev. 176, 49 (1968).

[8] L. Tterlikkis, S. D. Mahanki, and T. P. Das, Phys. Rev. 176, 10 (1968); W. A. Goddard III, *ibid.* 176, 106 (1968).

[9] W. J. Childs and L. S. Goodman, Phys. Rev. 170, 50 (1968); 170, 136 (1968); Y. W. Chan, W. J. Childs, and L. S. Goodman, *ibid.* 173, 107 (1968).

[10] W. J. Childs (private communication).

[11] M. Wilson and M. Fred, J. Opt. Soc. Am. 59, 827 (1969).

[12] See, e.g., J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Chap. 17.

[13] C. Froese, J. Chem. Phys. 45, 1417 (1966).

[14] J. Stein, J. Opt. Soc. Am. 57, 333 (1967).

[15] The usual linear and nonlinear distortion parameters were omitted because of their lack of reliable estimates and insufficient data concerning d^3.