Inorganica Chimica Acta, *119* (1986) 99–105

Relativistically Parameterized Extended Hückel Calculations. 10. Lanthanide Trihalides

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(Received February 25, 1986; revised May 26, 1986)

Abstract

The REX relativistically parameterized extended Hückel method is used to study the electronic structure of lanthanide trihalide molecules. All valence orbitals are described in terms of double-zeta Slater functions, with the atomic orbital parameters being determined by a least-squares fitting to published relativistic (Dirac–Fock) radial densities. Comparisons of orbital energies to experimental values are made and various trends are discussed. *Ab initio* all-electron calculations at the self-consistent field level and as a function of molecular geometry are reported for LaH_3, LaF_3, and $LaCl_3$. While LaH_3 and LaF_3 are calculated to be pyramidal, $LaCl_3$ is calculated to be planar.

I. Introduction

The gaseous lanthanide trihalides have been the subject of numerous experimental and theoretical investigations. The experimental investigations have included electric-field deflection [1], electron diffraction [2], and photoelectron spectroscopy (PES) [3–5], with related PES studies [6–8] having been carried out for the solid trifluorides. The theoretical investigations have included calculations at the extended Hückel (EH) [9–10], INDO [11], multiple-scattering Xα(MS-Xα) [12, 13] and relativistic discrete variational Xα(DVM) [5] levels. We earlier published [14] relativistic extended Hückel results (REX) for LaI_3, GdI_3 and LuI_3 with the focus being upon the equilibrium geometry of these molecules. The best of the theoretical studies is the relativistic DVM study [5] based on assumed structures (mostly planar). In order to explore further not only the structural question but also the spin–orbit splittings of the occupied valence and core levels, we present here some further REX results augmented by selected non-relativistic all-electron *ab initio* results. The REX method [15–16] has been used in describing [18–25] various properties, including nuclear spin–spin couplings, of heavy-element compounds.

II. Double-zeta Atomic Functions

Slater-type radial wave functions are widely used in semi-empirical quantum chemical calculations, with double-zeta functions generally providing more satisfactory results than single-zeta functions. Earlier papers in this series [17, 22–23] have reported double-zeta parameters for halogens and actinides. These parameters were typically obtained by a fitting of the radial density to that calculated by Desclaux [26] using numerical Hartree–Fock (HF) or Direc–Fock (DF) procedures. Single-zeta exponents for the lanthanides have been obtained from atomic self-consistent field (SCF) calculations by Clementi *et al.* [27] and from fits to HF or DF radial expectation values by Li *et al.* [11] and by us [15, 16]. Double-zeta parameters for transition metals have recently been reported by Fitzpatrick and Murphy [28].

In our present study we have obtained double-zeta parameters for the 6s, $5p_{1/2}$, $5p_{3/2}$, $5d_{3/2}$, $5d_{5/2}$, $4f_{5/2}$, and $4f_{7/2}$ shells of the elements La through Lu. Again these have been based on Desclaux' numerical DF atomic wave functions, but rather than a fitting to the radial density, a least-squares fitting to DF radial expectation values was employed. We have also obtained by this procedure a new set of double-zeta parameters for the ns, $np_{1/2}$, and $np_{3/2}$ shells of the halogens F ($n = 2$) through I ($n = 5$). Our earlier experience was that such a procedure occasionally produced unstable fittings, but our present procedure is more satisfactory. A double-zeta function of given principal quantum number contains two exponents and two linear coefficients. In the first stage of our fittings, we take these as four independent parameters to be adjusted by a least-squares procedure to fit the set of four DF radial expectation values $\langle r^k \rangle$, $k = 2, 1, 0$ and -1. Thus the norma-

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0020-1693/86/$3.50

TABLE I. Double-zeta Parameters and Energy Parameters for Selected Lanthanides[a,b,c]

Atom	Atomic orbital	C_1	ζ_1	C_2	ζ_2	$-E$ (eV)
La	6s	0.554609	1.953578	0.589752	1.042466	4.89
	5p	0.476821	5.014282	0.682859	2.370811	27.78
	5p*	0.522058	4.933225	0.631565	2.402945	30.51
	5d	0.572423	2.922350	0.600120	1.357840	6.35
	5d*	0.596218	2.901245	0.575124	1.352633	6.48
	(4f)	0.473645	8.700132	0.733310	3.215338	9.42
Nd	6s	0.535387	1.969653	0.609236	1.043426	4.74
	5p	0.476821	5.014282	0.682859	2.370811	26.89
	5p*	0.562016	4.867585	0.583374	2.436657	30.14
	(5d)	0.767605	2.776867	0.377059	1.303870	(6.30, 6.46)
	4f	0.458016	8.643562	0.745092	3.202980	12.67
	4f*	0.469666	8.599291	0.733399	3.214391	13.04
Gd	6s	0.694744	1.973528	0.448731	1.027802	5.44
	5p	0.611170	4.795486	0.520638	2.486839	32.70
	5p*	0.673131	4.711819	0.436953	2.562657	37.34
	5d	0.721038	2.806742	0.461175	1.229689	5.97
	5d*	0.827562	2.734545	0.360506	1.069351	6.14
	4f	0.636189	8.031788	0.533169	3.451086	14.95
	4f*	0.645464	8.003089	0.520126	3.470138	15.71
Lu	6s	0.817347	2.008402	0.323628	0.968808	6.00
	5p	0.719122	4.656918	0.371444	2.639202	36.95
	5p*	0.848037	4.518940	0.192191	2.848987	44.24
	5d	0.750661	2.786901	0.450971	1.141330	5.04
	5d*	0.800069	2.755971	0.396519	1.090771	5.21
	4f	0.779192	7.632421	0.313140	3.883810	16.02
	4f*	0.787354	7.581198	0.283276	3.871316	17.77

[a] For $l \neq 0$, nl denotes $j = l + \frac{1}{2}$, while nl^* denotes $j = l - \frac{1}{2}$. [b] The notation (nl) denotes use of the same parameters for $j = l + \frac{1}{2}$ and $j = l - \frac{1}{2}$; where two values of $-E$ are given, the first is for nl, the second for nl^*. [c] For all 15 elements La through Lu, see 'Supplementary Material'.

lization condition $\langle r^0 \rangle = 1$ is implicitly rather than explicitly incorporated. The use of four parameters with four conditions implies that an exact fitting is possible. However, the final stages of convergence are slow, so that after a reasonably satisfactory fit has been found, typically after 5 to 10 cycles, the least-squares process is stopped and the linear coefficients are adjusted to give an exactly normalized function. These final adjustments are small, as the sum of the squares of the differences between the input and calculated values of the $\langle r^k \rangle$ is typically 0.01 at this point, with distances in atomic units (a.u.) or Bohr.

In Fig. 1 we compare the radial density calculated from our double-zeta function for the 7s orbital of U to that calculated from Pyykkö and Laaksonen's (P–L) double-zeta function [23] and to that calculated from a single-zeta function fitted to the mean value of r ($\zeta(7s) = 1.728$). We note that our double-zeta function is somewhat more contracted than the P–L function as compared to the single-zeta function, but the difference does not appear significant for our semi-quantitative purposes.

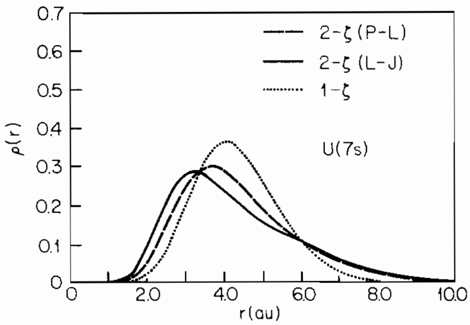

Fig. 1. Comparison of radial densities $\rho(r) = r^2 R^2(r)$ for U(7s) as obtained from our double-zeta function (———), the Pyykkö-Laaksonen (ref. 23) double-zeta function (– – –), and a single-zeta function (· · · · ·) with $\zeta = 1.728$. Distance is in atomic units (a.u.) (Bohr).

We list in Tables I and II the double-zeta coefficients and exponents thereby obtained for the lantha-

TABLE II. Double zeta Parameters and Energy Parameters[a] for Halogens

Atom	Atomic orbital	C_1	ζ_1	C_2	ζ_2	$-E$ (eV)
F	2s	0.642565	2.616176	0.357451	2.589120	34.89
	2p	0.525985	2.632205	0.487474	1.959236	13.83
	2p*	0.523319	2.642499	0.490315	1.963235	13.90
Cl	3s	0.772504	2.524923	0.252063	1.698524	23.38
	3p	0.688138	2.222300	0.354653	1.379071	11.72
	3p*	0.683790	2.233997	0.358314	1.393848	11.86
Br	4s	0.685466	3.156290	0.373837	1.925222	23.78
	4p	0.576701	3.089149	0.547709	1.532434	11.23
	4p*	0.635842	3.025343	0.487968	1.491662	11.79
I	5s	0.542381	4.313218	0.619170	2.060634	20.86
	5p	0.435694	3.774910	0.723409	1.755239	9.58
	5p*	0.484959	3.704515	0.669183	1.785650	10.72

[a] For $l = 1$, np denotes $j = 3/2$, while np* denotes $j = ½$.

nides La, Nd, Gd, and Lu and for the halides. Also listed are the orbital energy parameters as used in our REX calculations. See also 'Supplementary Material'. The energy parameters are basically Desclaux' DF orbital energies [26], but have been shifted by the following amounts in eV: Ce(4f), +4; Pr(4f) through Eu(4f), −3; Gd(4f), +4.4; Tb(4f) through Yb(4f), −3; Lu(4f), +5.5; F(2s), +8; F(2p) and Cl(3s), +6; Cl(3p), +2; Br(4s), +4; Br(4p), +1; I(5s), +3; and I(5p), +1. In each case both j-levels for a given n and l were given the same shift. The basic direction of these shifts were chosen to raise the halogen levels and lower the Ln(4f) levels; the Ce, Gd, and Lu DF atomic eigenvalues were already very low (negative) and were raised, giving 4f values varying smoothly (Fig. 2) with atomic number Z. The La(4f) value was obtained as −9.42 eV by extrapolation and used for both $4f_{5/2}$ and $4f_{7/2}$. A key feature of these parameters is that the Ln(4f) levels lie at least 1 eV below the X(np) levels for Pr to Lu for X = I, Nd to Lu for X = Br or Cl, and Eu to Lu for X = F, so that in these cases the 4f levels may be considered to be core-like. Only for LaF_3 to NdF_3, $LaCl_3$, $LaBr_3$, $CeCl_3$, and $CeBr_3$ are the 4f levels appreciably above the X(np) levels.

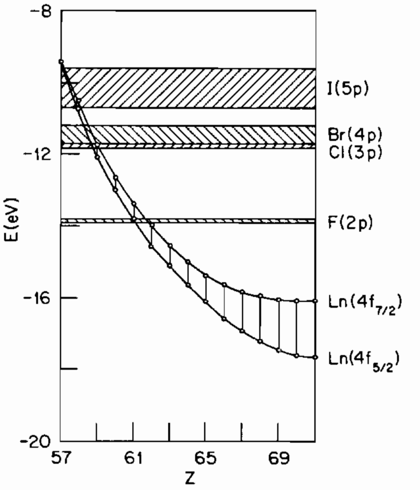

Fig. 2. Orbital energies in eV for Ln(4f) and X(np) levels. The width of the shaded band for each X(np) level denotes the separation betweeen X($np_{3/2}$) and X($np_{1/2}$). The energies are the neutral atom Dirac–Fock values of Desclaux (ref. 26), but shifted as described in the text.

III. REX Orbital Energies for LnX_3

We have carried out REX calculations for all 60 of the molecules LnX_3, with Ln = La to Lu and X = F to Cl, assuming for the halides of La, Ce, Nd, Gd, Er, and Lu the same geometries (Table III) as used by Ruščić *et al.* [5] in their relativistic Xα studies. These geometries are planar (D_{3h}), except for $LaCl_3$, $CeCl_3$, $LuCl_3$, $CeBr_3$, $NdBr_3$, $GdBr_3$, and $LuBr_3$, which are pyramidal (C_{3v}). The fluorides and iodides of the remaining lanthanides were assumed to be planar, while the chlorides and bromides were assumed to be pyramidal. We seriously doubt the correctness of many of these structural assignments, but

TABLE III LnX_3 Geometries[a] used in REX Calculations

	La	Nd	Gd	Lu
F	2.22	2.15	2.10	2.02
	120	120	120	120
Cl	2.587	2.545	2.489	2.417
	112.5	120	120	111.5
Br	2.741	2.689	2.640	2.56
	120	111	113.8	114
I	2.946	2.894	2.845	2.766
	120	120	120	120

[a] Bond lengths in Å and bond angles in degrees from ref. 5.

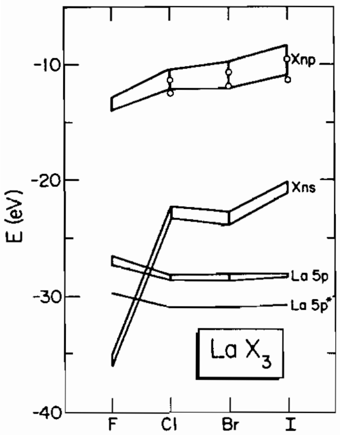

Fig. 3. REX orbital energies in eV for LaX_3 using parameters from Tables I and II and geometries from Table III (ref. 5). The levels are labeled by the atomic orbital (AO) which is the principal component of each MO. Only the highest and lowest energy are shown for each group of levels. Circled points are experimental PES values (refs. 3–5). The notation nl^* and nl for Ln denote $j = 1 - ½$ and $j = l + ½$, respectively.

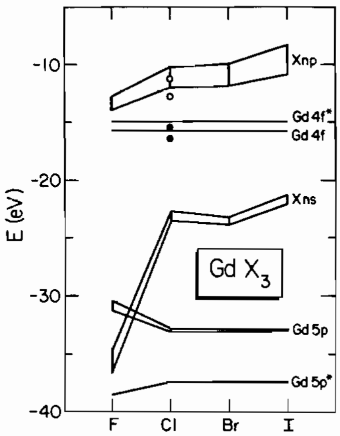

Fig. 4. As in Fig. 3, but for NdX_3. The open (○) and closed (●) circled points denote experimental PES values (refs. 3–5) assigned to X(np) and Ln(4f) levels, respectively.

they do facilitate comparisons between the REX and Xα results. In Figs. 3–6 we present the results for the halides of La, Nd, Gd, and Lu; experimental PES [3–5] data are also shown as available.

We show the REX orbital energies for the X(np), X(ns), Ln(5p), and Ln(4f) (if occupied) levels. For X(np) and X(ns) we show only the highest and lowest energy levels of each group of levels, thus defining a 'band width'. For Ln(5p) we show the $p_{1/2}$ (denoted p*) and the crystal-field split $p_{3/2}$ (denoted p) levels. For Ln(4f) we show the $f_{5/2}$ (denoted f*) and $f_{7/2}$ levels (denoted f), but typically do not show the very small crystal-field splittings of each of these j levels. Several features are common to all of the LnX_3 results. The X(np) levels rise in energy (a reflection of the input atomic energies) and increase in band width (a consequence of spin–orbit splitting and intramolecular interaction) for F to I. Specifically, the width increases from approximately 1.2 eV to 2.8 eV, matching well the observed increases for La, Gd, and Lu. At the single-zeta level the widths are smaller than at the double-zeta level, an example being 1.65 *vs.* 2.34 eV for LuI_3. The X(ns) levels are narrow in width, typically 0.25 to 1.0 eV. An exception is GdF_3, as in our parameterization the F(2s) atomic level at −34.89 eV is nearly degenerate with the Gd($5p_{1/2}$) and ($5p_{3/2}$) levels at −37.34 and −32.70 eV, respectively. As a consequence the predominantly F(2s) band shows (Fig. 5) a width of approximately 2.0 eV. The Ln($5p_{3/2}$) level shows a crystal-field splitting that is small (0.25 to 0.75 eV) compared to the $p_{3/2}$–$p_{1/2}$ spin–orbit splitting of 2.73 (La) to 7.29 eV (Lu) and that typically decreases in going from F to I and in going from La to Lu. The Ln($5p_{1/2}$) and ($p_{3/2}$) levels become increasingly core-like as Z increases, with energy lowerings in our input parameters of 13.73 and 9.13 eV, respectively, in going from La to Lu.

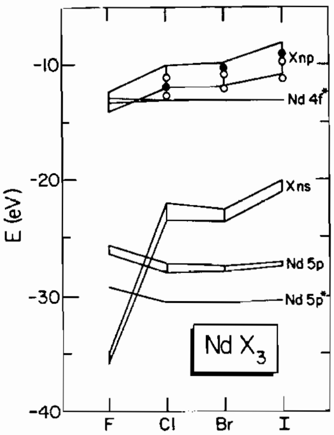

Fig. 5. As in Fig. 4, but for GdX_3.

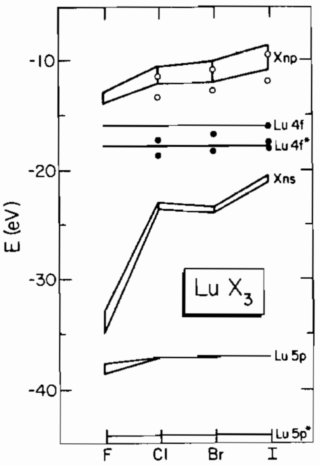

Fig. 6. As in Fig. 4, but for LuX_3.

The $Ln(4f_{7/2})$ and $(f_{5/2})$ levels have from our parameterization a spin orbit separation that agrees well with that observed for GdX_3 and LuX_3 (Figs. 5 and 6) The absolute position of these levels is largely determined by the assumed shifts of the atomic DF values as described at the end of 'Section II'. An interesting experimental result that we cannot reproduce with the present non-iterative (no charge self-consistency) version of REX is the rise in the 4f levels of approximately 0.5 to 0.75 eV in going from Cl to Br or Br to I. As the 4f levels are core-like in their radial distribution even when their energy is high; this rise is best interpreted as a binding energy chemical shift Thus it reflects the change in the electrostatic potential at or near the Ln nucleus accompanying a change of X, and in no way indicates 4f covalency. We can easily change the input 4f energies to fit the observed ionization energies for any given LnX_3, but any particular choice does not fit for all X. We do note that our computed Mulliken charges on Ln decrease in going from F to I, an example being LuX_3 for which the charges are 2.82, 2.37, 2.31, and 2.01 for X = F, Cl Br, and I, respectively These changes are in the direction which would produce rises in the 4f energies (decreases in the ionization energies) and reflect increased occupancy of the 6s and 5d levels of Lu. Specifically the Mulliken orbital charges for LuX_3, X = F, Cl, Br, and I, are 0.029, 0.156, 0.168, and 0.245 for 6s, 0.070, 0.196, 0.220, and 0.326 for $5d_{3/2}$, and 0.090, 0.284, 0.307, and 0.424 for $5d_{5/2}$

IV. *Ab Initio* Calculations for LaH_3, LaF_3, and $LaCl_3$

In order to explore further the question of the equilibrium geometry of LnX_3 molecules we carried out geometry optimizations for LaH_3, LaF_3, and $LaCl_3$ using analytical energy gradients and the *ab initio* GAUSSIAN 82 program [29]. The calculations were made at the single-determinantal (self-consistent field or SCF) level and employed for La a minimal (3G) basis set published by Huzinaga [30] for the shells 1s to 6s 2p to 5p and 3d to 4d. We augmented this set with single Gaussian basis functions for the 5d and 6p shells, with exponents of 0.2725 and 0.05, respectively. As the 5d function is expected to be particularly important in describing La compounds its exponent was chosen by minimization of the energy of LaF_3 (D_{3h}) with La–F = 2.20 Å The exponent for the less important 6p function was simply selected to be approximately one-half of the smallest p-exponent in the minimal basis set For each of the three d-shells only the set of five true d functions were employed. For H we employed the split-valence 31G basis commonly used with 6-31G basis sets [31] for main-group elements, while for F and Cl we employed the minimal 3G basis sets of Huzinaga. Optimizations were carried out with D_{3h} and with C_{3v} symmetry constraints.

TABLE IV. *Ab Initio* Equilibrium Geometries and Relative Energies

Molecule	Symmetry	MX[a]	XMX[b]	ΔE[c]
LaH_3	C_{3v}	2.129	114.7	0
	D_{3h}[d]	2.137	120.0	239
LaF_3	C_{3v}	2.080	112.0	0
	D_{3h}[d]	2.089	120.0	921
$LaCl_3$	D_{3h}	2.623	120.0	0
	C_{3v}[e]	2.613	112.0	381[f]

[a] Bond length M–X in Å. [b] Bond angle X–M–X in deg. [c] $E(D_{3h}) - E(C_{3v})$ in cm^{-1} except for $LaCl_3$. [d] Unstable with respect to out-of-plane deformation. [e] Non-equilibrium structure with bond angle assumed to be the same as that computed for LaF_3. [f] $E(C_{3v}) - E(D_{3h})$.

We find (Table IV) the pyramidal C_{3v} structure found to be favored for LaH_3 and LaF_3, although by only 239 cm^{-1} for LaH_3. By contrast we find the planar D_{3h} form of $LaCl_3$ to be stable with respect to the out-of-plane deformation. The computed La–H bond length is approximately 0.05 Å longer than the La–F length, a result consistent with a mostly ionic description of the bonding. Interestingly our computed distances of 2.129 and 2.080 Å for LaH_3 and LaF_3, respectively, are similar to the observed [32] distances of 2.110 and 2.097 Å for the $^1\pi$ states of the corresponding diatomics LaH and LaF. The gaseous Cs diatomics show an even greater difference between bond lengths to H and to F, namely observed [32] distances of 2.4938 and 2.3454 Å for CsH and CsF, respectively. The Mulliken charges on La are similar for all three molecules, namely +1.62 and +1.66 for the C_{3v} forms of LaH_3 and LaF_3, respctively, and +1.75 for the D_{3h} form of $LaCl_3$. We also note that the calculated La–F and La–Cl bond lengths are considerably shorter than the distances observed [33, 34] in the crystalline trihalides; 2.08 *vs.* 2.36 Å for LaF_3 and 2.62 *vs.* 2.95 Å for $LaCl_3$. Although our computed distances may be too short, we do believe the trend to be correct. For example, observed distances for CsF are 2.3454 and 3.005 Å in the molecule [32] and in the solid [33], respectively, with the corresponding distances for other alkali halides also showing a significant contraction in going from the solid to the molecule. As our *ab initio* results are based on the use of small basis sets and do not incorporate either correlation or zero-point energy corrections, we attach to them only semi-quantitative significance. They do offer some support to the expectation of a non-planar equilibrium geomtry for at least some of the LnX_3 molecules.

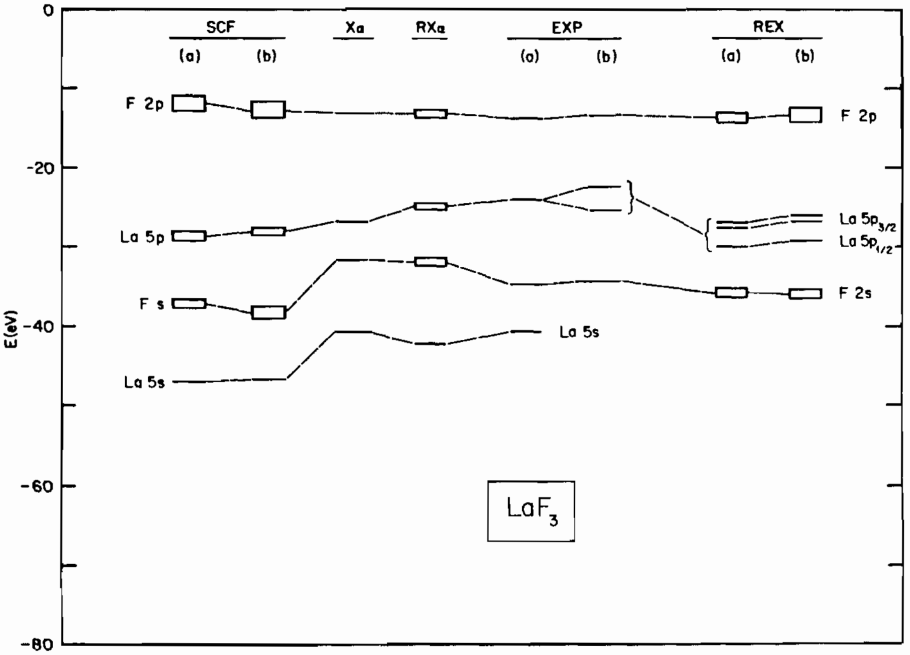

Fig. 7. Orbital energies for LaF_3 at various levels. SCF denotes *ab initio* values obtained using an augmented STO-3G basis for optimized structures obtained for assumed (a) D_{3h} and (b) C_{3v} structures. REX denotes relativistically parameterized extended Hückel values at the SCF (a) D_{3h} and (b) C_{3v} geometries. Xα and RXα denote the non-relativisitic and relativistic Xα calculations or Weber *et al.* (ref. 12) and of Ruščić *et al.* (ref. 5), respectively. The experimental (EXP) values are from (a) Weber *et al.* and (b) Wertheim *et al.* (ref. 6), both sets being for the solid state. With the exception of the REX La(5p) levels only band widths rather than individual levels are shown.

The experimental situation with respect to the structural question is not conclusive. From electric-field deflection studies [1], Kaiser *et al.* concluded that the fluorides of La, Gd, and Lu were polar and therefore pyramidal, those of Tm, Ce, and Er were probably polar, and those of Nd, Pr, Tb, Dy, and Ho were non-polar and therefore planar; no conclusions could be drawn about the fluorides of Sm, Eu, and Yb. Electron diffraction data have suggested [2] pyramidal structures for the iodides of Pr, Nd, Gd, and Lu.

In Fig. 7 we summarize our findings for the orbital energies of LaF_3. Shown are the SCF *ab initio* and REX values, with both being for the (a) D_{3h} and (b) C_{3v} SCF geometries given in Table IV. We note that both the SCF and REX values are rather insensitive to the geometry change as compared to the relatively large energy separations between the energy 'bands'. Also shown are the non-relativistic and relativistic Xα values of Weber *et al.* [12] and Ruščić *et al.* [5], respectively. The experimental values shown are from the solid-state data of Weber *et al.* [12] and Wertheim *et al.* [6]. Overall there is general agreement among the various computational levels and between computation and experiment. The SCF La(5s) and (5p) energies are too low, probably reflecting an excessively ionic description arising in part from the SCF approximation and in part from basis set inadequacies. The fine-structure obtained at the REX level for the La(5p) levels is shown in detail; the overall band width matches the observed width better than does the relativistic Xα width, although the absolute REX energies are approximately 4 eV too low.

V. Conclusion

We have obtained a set of double-zeta Slater-type atomic functions for lanthanide orbitals and used these in REX calculations to study the electronic structure of the lanthanide halide molecules. Comparisons of calculated orbital energies to observed ionization energies indicate that the REX method gives a good description of the levels which are mostly ligand X(*n*p) in composition. Spin–orbit and crystal-field splittings of the Ln (5p) and (4f) levels are discussed. The question of planar *vs.* non-planar geometries for the LnX_3 molecules is approached with the aid of *ab initio* calculations at the SCF level. Although LaH_3 and LaF_3 are calculated to be non-planar, the inversion barriers for LaH_3 and LaF_3 (239 and 921 cm^{-1}, respectively) are small, as is the energy required (approximately 380 cm^{-1}) to distort planar $LaCl_3$ to the same bond angle as computed for LaF_3 (112°).

Supplementary Material

A table of parameters for all 15 elements La through Lu may be obtained from the authors on request.

Acknowledgements

The authors wish to thank the University of Michigan Computing Center for the use of its facilities and the Academia Sinica of China for fellowship support for Y. Q. Jia.

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