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New Relativistic Atomic Natural Orbital Basis Sets for Lanthanide Atoms with Applications to the Ce Diatom and LuF_3

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New basis sets of the atomic natural orbital (ANO) type have been developed for the lanthanide atoms La−Lu. The ANOs have been obtained from the average density matrix of the ground and lowest excited states of the atom, the positive ions, and the atom in an electric field. Scalar relativistic effects are included through the use of a Douglas−Kroll−Hess Hamiltonian. Multiconfigurational wave functions have been used with dynamic correlation included using second-order perturbation theory (CASSCF/CASPT2). The basis sets are applied in calculations of ionization energies and some excitation energies. Computed ionization energies have an accuracy better than 0.1 eV in most cases. Two molecular applications are inluded as illustration: the cerium diatom and the LuF_3 molecule. In both cases it is shown that 4f orbitals are not involved in the chemical bond in contrast to an earlier claim for the latter molecule.

1. Introduction

This work is the final step in an effort to develop a new set of atomic orbital basis sets for molecular calculations. The aim has been to cover the entire periodic table with basis sets of the same quality. We have previously presented results for the group Ia (Li−Fr) and group IIa (Be−Ra) elements,[1] the main group (IIIa−VIIa) and rare gas elements (VIIIa),[2] and recently also for the transition metal atoms[3] and the actinide atoms.[4] The basis sets are of the atomic natural orbital (ANO) type as was originally suggested by Almlöf and Taylor in 1987.[5] They can be considered as extensions of the ANO-L basis sets developed by Widmark and co-workers[6−8] for the first- and second-row atoms and the first-row transition metals. These ANO-RCC basis sets were developed using average density matrices obtained from configuration interaction calculations on ground and excited states of the atom, the positive and negative ions, and the atom in an electric field (to obtain functions that describe the polarizability of the atoms). In this paper we fill the last hole and complete the ANO-RCC basis sets by adding the lanthanide atoms La−Lu (the acronym RCC stands for relativistic and (semi-)core correlation).

The basis sets are intended for relativistic one- or two-component calculations where scalar relativistic effects are included using the Douglas−Kroll−Hess (DKH) Hamiltonian.[9,10] Thus, this Hamiltonian is used in the basis set generation. The nonscalar part of the DKH Hamiltonian (spin−orbit coupling) is included a posteriori and does not affect the generation of the ANO basis set. Another feature that needs to be included for heavier elements is correlation of the semicore electrons. For the lanthanides we add the 5s and 5p electrons in the correlation treatment, and ANOs that include such effects are generated. Because the basis set is generated with a relativistic Hamiltonian, it cannot and should not be used in nonrelativistic calculations.

Multiconfigurational wave functions have been used (CASSCF) with the most important orbitals in the active space and dynamic correlation treated using second-order perturbation theory (CASPT2).[11−13] This approach was used because it is general and can be applied to all electronic states without loss of accuracy. The experience gained also shows that the approach works well and generates ANOs that are well suited for correlated calculations in the relativistic regime. The generation of the basis sets has been carried out without taking spin−orbit coupling into account. Some test calculations on spectroscopic parameters have been performed that include these effects, and the results will be presented below. A variation-perturbation approach, the RAS state interaction (RASSI-SO) method, was used.[14] It has been described in detail in a recent review.[15]

Below, we shall present the general features of the new basis sets and some results obtained for the atoms with emphasis on spectroscopic data. Two molecular applications are also included: the cerium diatom and the molecule LuF_3. The basis sets are available in the MOLCAS basis set library under the heading ANO-RCC (for directions go to http://www.teokem.lu.se/MOLCAS).

2. Primitive Basis Sets and Density Averaging

The sets of primitive Gaussian functions were generated starting from the primitive set published by Faegri,[16] which were extended with 2 primitive s-type functions, 3 p-type, 1 d-type, and 2 f-type functions, in all cases using a scale factor of 0.4. The exponents for a set of 4 g-type functions were optimized at the CASPT2 level. Two h-type functions were added with exponents 1.2 times the most important g-type functions. The final primitive basis set has the size: 25s, 22p, 15d, 11f, 4g, 2h (a slightly smaller primitive basis set was used for the La atom: 24s, 21p, 15d, 11f, 4g).

Calculations with the primitive basis set were performed for each atom in its ground state, one excited state, and the positive ion. In addition, calculations were performed for the atom in

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TABLE 1: The Ground-State Electronic Configuration for the Lanthanide Atoms and the 1+ Ions

		Neutral Atoms		
La: d^1s^2 (^{2}D)	Ce: $f^1d^1s^2$ (^{1}G)	Pr: f^3s^2 (^{4}I)	Nd: f^4s^2, (^{5}I)	Pm: f^5s^2 (^{6}H)
Sm: f^6s^2 (^{7}F)	Eu: f^7s^2 (^{8}S)	Gd: $f^7d^1s^2$ (^{9}D)	Tb: f^9s^2 (^{6}H)	Dy: $f^{10}s^2$ (^{5}I)
Ho: $f^{11}s^2$ (^{4}I)	Er: $f^{12}s^2$ (^{3}H)	Tm: $f^{13}s^2$ (^{2}F)	Yb: $f^{14}s^2$ (^{1}S)	Lu: $f^{14}d^1s^2$ (^{2}D)
		Positive Ions		
La: s^2 (^{1}S)	Ce: f^1d^2 (^{4}I)	Pr: f^3s^1 (^{5}I)	Nd: f^4s^1, (^{6}I)	Pm: f^5s^1 (^{7}H)
Sm: f^6s^1 (^{8}F)	Eu: f^7s^1 (^{9}S)	Gd: $f^7d^1s^1$ (^{10}D)	Tb: f^9s^1 (^{7}H)	Dy: $f^{10}s^1$ (^{6}I)
Ho: $f^{11}s^1$ (^{5}I)	Er: $f^{12}s^1$ (^{4}H)	Tm: $f^{13}s^1$ (^{3}F)	Yb: $f^{14}s^1$ (^{2}S)	Lu: $f^{14}s^2$ ^{1}S)

an electric field of strength 0.01 au. An average density matrix was constructed as:

$$\rho_{\text{av}} = \sum_i \omega_i \rho_i \tag{1}$$

where ρ_i values are the density matrices obtained from the different CASPT2 wave functions. Equal weights, ω_i, were used for all states. The final ANOs were obtained as the eigenfunctions of ρ_{av}. All orbitals with occupation number larger than about 10^{-6} were kept in the final basis set, resulting in a maximum basis set of the size 12s, 11p, 8d, 7f, 4g, 2h (11s, 10p, 8d, 5f, 3g for La). These calculations were performed using the GENANO utility of the MOLCAS program system.[17]

The 5s, 5p semicore electrons were correlated. Because the basis sets have been constructed including these correlation effects, they should also be included when the basis sets are used. Other core electrons are described with minimal basis set quality and should not be included in any correlation treatment, since that could cause large basis set superposition errors.

The active space comprised the 4f, 5d, and 6s shells (13 orbitals). In some cases the 6p orbitals were also included. The CASSCF/CASPT2 calculations were performed in D_{2h} symmetry, and the orbital rotations were restricted such that mixing between different angular momenta did not occur. This does not completely ensure spherical symmetry because orbitals in different irreps may have different radial shape, but the deviations are small. Separate calculations were in most cases made for each of the electronic states. In some cases this was not possible because the two states have components in the same irreps and have the same spin. State average calculations were then made. The CASPT2 calculations used the new level shift technique (IPEA) that shifts active orbital energies in order to simulate ionization energies for orbitals excited out of and electron affinities for orbitals excited into. This technique has recently been shown to reduce the systematic error in the CASPT2 approach for processes where the number closed shell electron pairs changes.[18] The accuracy in the IPs computed here is another illustration of this approach.

3. Results

We present in this section the results obtained for ionization energies (IP) and some excitation energies. Some of the calculations have been performed with spin−orbit coupling (SOC) in order to make comparison to experimental data more straightforward. All results presented have been obtained with the primitive basis set. Contracted basis sets of QZP quality give results that differ by less than 0.1 eV from results obtained with the primitive basis.

3.1. Ionization Energies. The ground-state electronic configurations for the atoms and their positive ions are presented in Table 1.

Inspection of the table shows that for all atoms except two, it is the 6s electron that is removed in the ionization process. For the atoms La and Lu it is instead the 5d electron. The cerium atom is a special case. It has the ground state $f^1d^1s^2$ ^{1}G, while the lowest state of the positive ion is f^1d^2 ^{4} I. Thus both 6s electrons are removed and the number of 5d electrons is increased by one. The ground state of cerium is ^{1}G in conflict with Hund's rules. We shall not discuss this interesting property of the 4f5d shell further here but refer to a detailed analysis of the "unnatural parity states" carried out by Morgan and Kutzelnigg.[19]

TABLE 2: Atomic Ionization Energies (in eV)[a]

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
CASPT2	5.52	5.68	5.35	5.46	5.49	5.54	5.68	5.92
expt	5.58	5.54	5.47	5.53	5.58	5.64	5.67	6.15

	Tb	Dy	Ho	Er	Tm	Yb	Lu
CASPT2	5.86	5.93	6.01	6.08	6.17	6.21	5.28
expt	5.86	5.94	6.02	6.11	6.18	6.25	5.43

[a] Experimental data are for the lowest multiplets. Experimental data from the NIST tables.[31] *J*-averaged values for Ce and Lu are 5.87 and 5.28 eV, respectively.

Computed ionization energies are presented in Table 2. Comparison is made between CASPT2 energies (no spin−orbit coupling) and experimental IPs. The effect of spin−orbit coupling is small when a 6s electron is removed, but larger for La, Ce, and Lu. The agreement between computed and experimental values is also in general good with differences around 0.1 eV. The effect of spin−orbit coupling was studied for Ce. The calculations used the variation-perturbation method, RASSI-SO described in ref 15. For the neutral atom, state average CASSCF/CASPT2 calculations were performed including all singlet and triplet terms arising from the configuration $(4f)^1(5d)^1(6s)^2$. For the ion, all quartet terms from the configuration $(4f)^1(5d)^2$ were included. The resulting IP was 5.53 eV to be compared to the experimental value 5.54 eV.

3.2. Excitation Energies. The lowest excited state has been included in the density averaging for the construction of the ANOs. No SOC was included, so direct comparison with experimental spectral data is difficult. Because of its special nature, it was decided to compute the electronic spectrum for the Ce atom including SOC. The results for the lowest states are presented in Table 4. These states have excitation energies up to about 1 eV and are dominated by the electronic configurations $(4f)^1(5d)^1(6s)^2$ and $(4f)^1(5d)^2(6s)^1$. The difference between computed and experimental energies is for most levels less than 0.1 eV. The ^{5}I-derived levels are an exception. Here the errors are 0.2−0.3 eV with the computed levels systematically too large. We have at present no explanation for this discrepancy.

Finally, we present in Table 3 the effect of contraction on computed total and relative energies for two atoms, Ce and Lu. We notice that the relative energies are converged to within 0.1 eV at the TZP level of accuracy. This is a general observation. At this level of contraction, the total energy converged to within a few hundreds of an atomic unit. Corresponding tables for all the atoms of the periodic system can be found in the basis set library: http://www.teokem.lu.se/MOLCAS.

4. The Cerium Diatom

As a first example of the use of the new basis set, we shall consider the cerium diatom. Cerium is the first of the lanthanides and therefore has the most diffuse 4f orbitals. Involvement of

TABLE 3: Effect of Contracting the Basis Set on the Total Energy, the IP, and One Excitation Energy for the atoms Ce and Lu (total energy in au, relative energies in eV)[a]

	Ce			Lu		
contraction	CASPT2 energy[b]	^{3}F	IP	CASPT2 energy[b]	^{4}F	IP
MB:6s5p3d1f	−8853.388548	0.20	5.85	−14549.601253	1.88	4.76
DZP:7s6p3d2f1g	−8853.557383	0.24	5.66	−14550.266774	2.05	4.93
TZP:8s7p4d3f2g1h	−8853.597199	0.27	5.71	−14550.399914	2.11	5.18
QZP:9s8p5d4f3g2h	−8853.620641	0.23	5.71	−14550.449138	2.13	5.25
large:12s11p8d7f4g2h	−8853.627545	0.22	5.73	−14550.468850	2.13	5.28
primitive:	−8853.631215	0.27	5.73	−14550.470489	2.13	5.28
expt (J averaged)		0.24	5.78		2.38	5.28

[a] Experimental data have been J-averaged. Experimental data from the NIST tables.[31] [b] For the ^{1}G and ^{2}D ground states, respectively.

TABLE 4: The Electronic Spectrum of the Cerium Atom Computed Including Spin−Orbit Coupling[a]

level	calcd	exptl	level	calcd	exptl
$^1G_4$[b]	0.000	0.000	$^5H_3$[c]	0.299	0.293
$^3F_2$[b]	0.076	0.028	$^5H_4$[c]	0.340	0.302
$^3F_3$[b]	0.197	0.206	$^5H_5$[c]	0.437	
$^3F_4$[b]	0.397	0.384	$^5H_6$[c]	0.631	0.588
$^3H_4$[b]	0.188	0.158	$^5H_7$[c]	0.752	0.719
$^3H_5$[b]	0.305	0.273	$^5I_4$[c]	0.602	0.396
$^3H_6$[b]	0.539	0.492	$^5I_5$[c]	0.690	0.466
$^3G_3$[b]	0.227	0.172	$^5I_6$[c]	0.797	0.552
$^3G_4$[b]	0.425		$^5I_7$[c]	0.921	0.659
$^3G_5$[b]	0.521	0.520	$^5I_8$[c]	1.066	0.844
$^3D_2$[b]	0.338	0.294	$^3G_3$[c]	0.527	0.515
$^3D_1$[b]	0.517	0.460	$^3G_4$[c]	0.547	0.517
$^3D_2$[b]	0.657	0.590	$^3G_5$[c]	0.586	0.547

[a] Experimental data from the NIST tables.[31] [b] Dominant electronic configuration 4f5d6s^2. [c] Dominant electronic configuration 4f5d^{2}6s.

these orbitals in chemical bonding should therefore be most clearly seen for bonds involving this atom.

Not much is known experimentally about the cerium diatom. Its resonance Raman spectra were studied by Shen et al.[20] A single progression gave an ω_e value of 245.4 ± 4.2 cm^{-1}. They also give an estimate of the dissociation energy to 2.57 eV using the "Third Law". Cao and Dolg carried out extensive CASSCF and MRCI calculations using a small core pseudopotential for Ce.[21] They suggest as possible candidates for the ground state $^1\Sigma_g^+$, $^1\Sigma_u^-$, $^3\Sigma_g^-$, $^3\Sigma_u^+$, ^16_g and ^36_u. Further studies with extended basis sets gave the following spectroscopic constants for a possible $^1\Sigma_g^+$ or $^3\Sigma_u^+$ ground state: $R_e = 2.62 \pm 0.02$ Å, $D_e = 1.60 \pm 0.41$ eV, and $\omega_e = 210 \pm 13$ cm^{-1}. No detailed discussion is given in the paper concerning the nature of the ground state and the type of chemical bonding.

The ground-state electronic configuration of the Ce atom is $(4f)^1(5d)^1(6s)^2$, ^{1}G. The promotion energy to the lowest term in the configuration $(4f)^1(5d)^2(6s)^1$, ^{5}H is, however, only 0.29 eV (see Table 4 for details). If twice this promotion energy can be overcome, the Ce diatom can form at least a triple bond involving the 5d and 6s orbitals and six electrons: $(6s\sigma_g)^2(5d\pi_u)^4$ coupled as $^1\Sigma_g^+$. These orbitals together with their antibonding counterparts are shown in Figure 1. The question is now what happens to the two 4f electrons. There is a competition between the nonbonded situation where a high angular momentum coupling (4fϕ) would be preferred and a possible bond involving 4f orbitals with lower angular quantum numbers.

In the present study we used a basis set of VQZP quality: 9s8p6d5f2g1h. The active space included the 6s, 5d, and a selection of 4f orbitals, in all 20 orbitals with 8 active electrons. The 4f orbitals were varied in these exploratory CASSCF/CASPT2 calculations. They showed that the most stable electronic states are found with the two extra electrons in atomic 4fϕ orbitals. They can couple to form the following molecular configurations: $(4f\phi_g)^2$, $(4f\phi_g)(4f\phi_u)$, and $(4f\phi_u)^2$. Coupling to the $^1\Sigma_g^+$ of the triple bound, one arrives at a large number of almost degenerate electronic states with angular momenta 0 or 6. We could conclude that the 4f electrons do not contribute directly to the bonding but remain atomic in character. The cerium diatom is formed as a triple bond bond between two Ce atoms in a $(4f)^1(5d)^2(6s)^1$ valence state. Further evidence for this can be found in the Mulliken populations, which are 0.89, 0.42, and 1.66 for the 6s, 6p, and 5d orbitals on each Ce atom, adding up to a total of 2.97 electrons in the orbitals shown in Figure 1. The remaining electron is in a 4fϕ localized on the Ce atom.

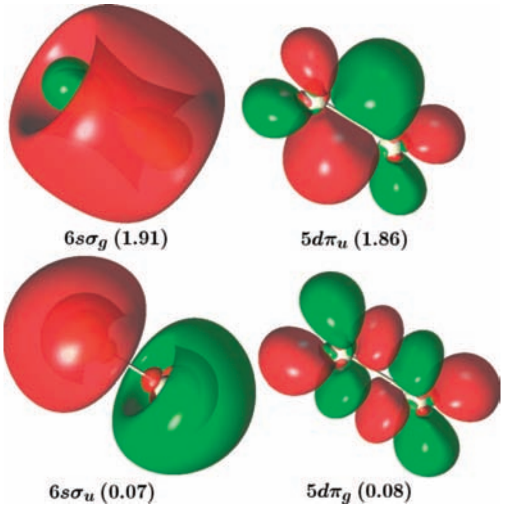

Figure 1. The σ and π bonding orbitals in the cerium diatom and their antibonding counterparts. A 0.05 au^{-3} level set surface was used. Natural orbital occupation numbers are shown within parentheses.

The active space was now reduced to 8 electrons in 16 orbitals (5d, 6s, and 4fϕ). Potential curves were generated for the electronic states described above (12 singlet and 14 triplet states). The calculations were performed in C_{2h} symmetry. The Ce 5s and 5p orbitals were correlated at the CASPT2 level of theory.

Resulting spectroscopic constants are presented in Table 5 for the six lowest electronic states. These results have been obtained at the CASPT2 level of theory and do not include spin−orbit coupling. We find the six electronic states within an energy range of about 400 cm^{-1}. The potential curves are almost parallel with a bond distance that varies between 2.63 and 2.66 Å, a little longer than the 2.62 Å reported by Cao and Dolg.[21] The computed vibrational frequency is also somewhat smaller than their value, $\omega_e = 210 \pm 13$ cm^{-1}. Both these results are smaller than the experimental estimate 245.4 ± 4.2 cm^{-1}. At present we have no explanation for this discrepancy, but we

TABLE 5: Spectroscopic Constants for the Lower Electronic States of the Ce_2 Diatom at the CASPT2 Level of Theory

state	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	T_e (cm^{-1})
$^1\Sigma_u^-$	2.664	2.68	186	
$^3\Sigma_g^-$	2.664	2.67	166	182
$^1\Sigma_g^+$	2.633	2.62	189	245
^16_g	2.632	2.62	189	251
$^3\Sigma_u^+$	2.629	2.61	184	403
^36_u	2.630	2.61	184	415
expt[a]		2.57	245	

[a] Experimental data from ref 20.

TABLE 6: Spectroscopic Constant for the Three Lowest Electronic States of the Ce Diatom at the RASSI-SO Level of Theory

Ω	R_e (Å)	ω_e (cm^{-1})	T_e (cm^{-1})	composition
0	2.649	175		49% $^1\Sigma_g^+$ + 51% $^3\Sigma_g^-$
0	2.652	177	65	55% $^1\Sigma_u^-$ + 45% $^3\Sigma_u^+$
5	2.630	184	176	^36_u

do not think that further extended calculations would change the present theoretical estimate with as much as 40 cm^{-1}.

Finally, we present in Table 6 the results obtained when we allow these electronic states to mix under the influence of a spin−orbit Hamiltonian. The RASSI-SO method of MOLCAS has been used in these calculations.[14] Spin−orbit coupling has only small effects on the computed properties. The dissociation energy has not been computed, but it should be smaller than the CASPT2 value. Assuming only a small effect in the 0_g^+ state of the molecule, we can estimate the decrease from the SO stabilization of the ground state of the Ce atom, which has been computed to be 0.083 eV. For two atoms this gives 0.17 eV and an estimated bond energy of 2.51 eV in surprisingly good agreement with the "Third law" estimate.[20] Cao and Dolg obtained a much lower dissociation energy, 1.60 eV. This is most likely due to the use of a smaller basis set and a less extensive treatment of electron correlation.

5. The LuF $_3$ molecule

In a recent paper Clavaguéra et al. have presented a study of the structure and properties of the LuF_3 molecule, which contains a number of unexpected results.[22] ZORA/DFT calculations were performed, and it was concluded that the 4f orbitals are involved in the bonding between Lu and F. This is a very unexpected result. It has generally been believed that 4f orbitals do not play any role in bonding between the lanthanide atoms (or ions) and the ligands. Instead they represent an inert core. It would be even more surprising to find an exception to this rule at the end of the series where the contraction of these orbitals is largest. It is further claimed that "The strong lanthanide contraction of the bond length finds its origin in the Lu(4f)−F(2p) hybridization". A Lu(5p) hole of about 0.2e is also found and is said to be due to "hybridization" with F(2s). A similar claim had already earlier been made by Tatewaki and Matsuoka, based on Dirac−Hartree−Fock−Roothaan calculations on GdF.[23] It was rebutted in an article by Dolg et al. on a series of gadolinium diatomics.[24] Tatewaki and Matsuoka also claimed that the 4f orbitals were involved in the bonding between Gd and F in the GdF diatom. Also this claim was shown by Dolg et al. to be wrong. The electronic structure of the lanthanide trihalides has also been discussed by Hargittai,[25] Kovacs and Konings,[26] and Lanza et al.[27] None of these authors believe that the 4f orbitals are involved in the bonding. Because we found the results Clavaguéra et al. for LuF_3 quite unexpected, it was decided to study this molecule using the CASSCF/CASPT2 method in combination with the new Lu basis set.

CASSCF/CASPT2 calculations were performed on the ground state using an active space comprising the nine F 2p orbitals together with six Lu orbitals (corresponding to the 5d and 6s orbitals, which could be expected to play a dominant role in the chemical bonds) with 18 active electrons. ANO-RCC basis sets were used. For Lu 8s7p5d3f2g1h basis functions were used, and for F the 4s3p2d1f ANO-RCC basis set. Thus, scalar relativistic corrections are included at all levels of theory. Studies including spin−orbit coupling were not found necessary for this

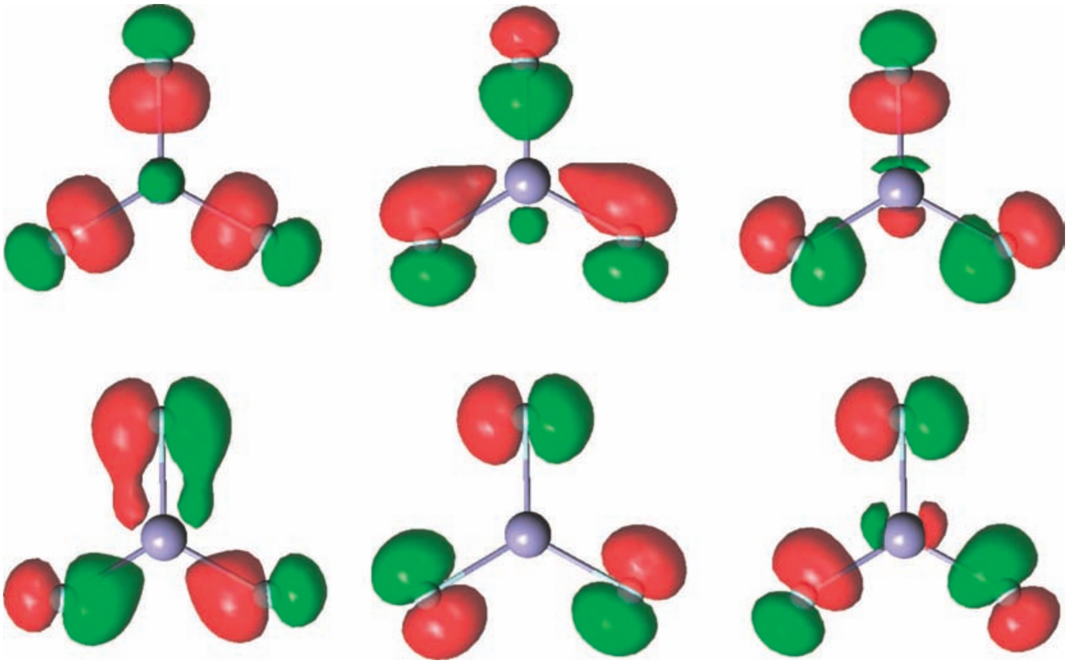

Figure 2. The six in-plane strongly occupied molecular orbitals for LuF_3.

closed shell system. The geometry was optimized at the CASPT2 level of theory using a numerical grid.

The molecule was found to be planar with an Lu−F distance of 1.961 Å, quite close to the value reported by Clavaguéra et al., 1.969 Å. They, however, found the molecule to be pyramidal with an F−Lu−F bond angle of 101.4° in contrast to the other Lu trihalides LuX_3 (X = Cl, Br, I) which were found to be planar. Relativistic DFT/B3LYP calculations with the same ANO-RCC basis set also yield a planar molecule with a bond distance of 1.985 Å.

We present in Figure 2 the six in-plane strongly occupied molecular orbitals. They have occupation numbers in the range 1.98−2.00 showing that the wave function is dominated by a single configuration. We can see some delocalization of the electron density from F to Lu. A closer analysis shows that this is due mainly to interaction with the Lu 5d orbitals, which achieve a total occupation of 0.56 electrons. There is also a slight participation of 6s: 0.04 electrons. This gives a total charge on Lu of +2.4. The 4f shell is completely inert and filled with 14 electrons. It does not participate in the bonding at all. The same is of course true for the 5p shell.

If there are any holes in the 4f and 5p shell as claimed in the article cited above, this must be due to transfer of electrons to the valence shell, the 5d and 6s orbitals. A small calculation was therefore performed on the Lu^{3+} ion with the 5p, 4f, 5d, and 6s orbitals active (20 active electrons). No such excitations were, however, found. The 5p and 4f shells remained doubly occupied.

Finally, it was claimed in ref 22 that the unusually large electric field gradient (EFG) found for LuF_3 was due to the “hole” in the 5p shell. We therefore computed this quantity at the equilibrium geometry. Third-order DKH and picture change corrections were included in the calculation.[28] A value of 8.39 au was found to be compared to values ranging from 6.92 to 7.72 obtained using the ZORA/DFT approach. The large EFG is thus not due to any local holes on Lu but to the strongly ionic character of the bond, as expected.

To summarize, we have not been able to confirm any of the unexpected results found the paper by Clavaguéra et al. On the contrary, we find LuF_3 to be a normal closed shell molecule with strongly ionic bonds, with some participation of the Lu 5d orbitals and an inert $(5p)^6(4f)^{14}$ core. The atomization energy was computed at the CASPT2 level and was found to be 473.3 kcal/mol or 157.8 kcal/mol per bond, characteristic for a strong ionic bond.

6. Conclusions

The present article concludes the work on the ANO-RCC basis sets, which are now available for all atoms in the range H−Cm. The basis sets are accurate and therefore large. Still, they can be used for large molecules, especially in combination with the Cholesky decomposition technique for the two-electron integrals. Recent applications include studies of transition metal complexes with up to about 80 atoms and close to 1000 basis functions (B. O. Roos, private communications, see also refs 29 and 30).

Scalar relativistic effects are automatically included in these calculations as well as dynamic correlation effects including the semicore electrons. The ANO-RCC basis sets are today well established and have been used in a large number of applications involving heavy elements such as second- and third-row transition metals and actinides. With the present work, the lanthanides can also be added to the list.

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