Chemistry of the 5g elements. Relativistic calculations on hexafluorides

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Abstract

A Periodic System was proposed for the elements 1-172 by Pyykkö (Phys. Chem. Chem. Phys. **2011**, *13*, 161) on the basis of atomic and ionic calculations. In it, the elements 121-138 were nominally assigned to a 5g row. We now perform molecular, relativistic four-component DFT calculations and find that the hexafluorides of the elements 125-129 indeed enjoy occupied 5g states.

Recent Dirac-Fock (DF) calculations on ions [1] led to a broad-brush assignment of the elements 121-138 as nominal 5g elements. A previous, Dirac-Slater (DS) study on the neutral atoms by Fricke et al. [2] reveals a growing 5g population for the neutral atoms 125-144. Already earlier, some 5g electrons were found from element 125 (E125) on by Waber et al.[3] at DS level, or at DF level by Mann and Waber[4].

Further atomic calculations by Umemoto and Saito [5] set the limit for 5g appearance at Z=126. Nefedov et al. [6] did Multiconfigurational Dirac-Fock (MCDF) calculations for the neutral atoms and found the g-shell filling up at E125-E145. Isoelectronic systems to Pyykkö's E140 atom are the cations $E143^{3+}$ to $E148^{8+}$ of Indelicato et al. [7]. They have the filled shells $8s^2(8p^*)^2 5g^{18}$ with no 6f nor 7d electrons.

For the monoatomic hexavalent ions $(E125)^{6+}$ to $(E136)^{6+}$ the DF electron configuration rises from $5g^1$ to $5g^{12}$ [1] suggesting that $(E125)^{VI}$ might form $5g^1$ compounds. Note here that E125 and Np both belong to Group 7 and Np^{VI} forms $5f^1$ compounds. Is this picture chemically relevant? Few molecular calculations exist for the elements E121-. Malli [8] treated at

Dirac-Fock (DF) level the diatomic (E126)F and found it to have an unspecified g-population. Malli [9] also reported DF-level results for (E126)X_6, X = F, Cl, O. His result of 201 pm for the E126-F distance of the hexafluoride is, however, far shorter than the present one. The g-population is said to be there but is not specified. Amador et al. [10] reported spectroscopic constants of diatomic (E121)F, obtained at 4-component all-electron CCSD(T) level including the Gaunt interaction. They found a strong and polarized bond between E121 and F (equilibrium distance r_e=217 pm). The outermost frontier molecular orbitals of (E121)F were fairly similar to the ones of (Ac)F and there was no evidence of g-population.

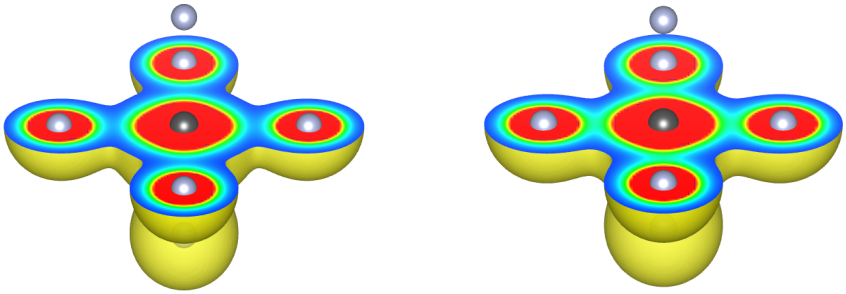
The radii of the 5g shell are small, even smaller than those of the radially equally nodeless, 4f shell [1]. Therefore this shell is not expected to directly participate in the chemical bonding. The true placement of the 5g elements in the Periodic Table (PT) can only be settled by chemical studies or molecular calculations. We start the story with the diatomic E125−F and continue with the possible existence of MF_6 (M=E125-E129). The intermediate oxidation states must be deferred to later study. We here choose the fully relativistic Dirac-Coulomb (DC) Hamiltonian as implemented [11] in the DIRAC program [12]. The necessary basis-sets are developed here with a Dirac-Fock approach to the problem (see supporting information for details). Although the DF lacks electron correlation, it is otherwise well-defined and fully consistent with building new basis sets. For the description of the electronic system E125−F and of MF_6 and its neighbours, we introduced correlation through density functional theory (DFT) using the long-range corrected hybrid CAM-B3LYP functional [13] as implemented [14] in the DIRAC program. Its can provide a significant improvement for long-range properties over conventional functionals. In addition, density or topological analyses as used below are fully consistent with the philosophy of DFT. As a first step, the M-F bond dissociation energy curves were computed at DC-DFT level for (E125)F (see supporting information for details), thereby obtaining equilibrium geometries and spectroscopic parameters given in Table 1.

Table 1: M−F stretch parameters from DC-DFT calculations. r_e is the equilibrium bond length (in pm), D_e the dissociation energy (in kJ/mol), expanding simultaneously the six M−F bonds for MF_6, ω_e the harmonic vibrational frequency (in cm^{-1}) and $\omega_e x_e$ the vibrational anharmonicity (in cm^{-1})

	(E125)F	(E125)F_6	(E126)F_6	(E127)F_6	(E128)F_6	(E129)F_6
r_e	198	275	269	253	252	246
D_e	607	192.3	175.8	314.2	455.5	740.7
ω_e	692	436	430	582	627	762
$\omega_e x_e$	2.4	3.0	3.2	3.2	2.6	2.3

If we compare the results obtained for (E125)F with the data from literature we find consistent values with those obtained by Amador et al. [10] for (E121)F (r_e=2.17 Å, D_e=759 kJ/mol, ω_e=519 cm^{-1}) and Malli [8] for (E126)F (r_e=2.03 Å, D_e=718 kJ/mol). The values are of the same order of magnitude taking into account the different basis sets and methods used. The valence molecular orbitals for (E125)F have similarities with the ones of (E121)F from Amador et al. [10]. The highest are non-bonding. A covalent bonding is observed with the mixing of 8p orbital from E125 and the 2p orbital from F. The interaction is mainly ionic with a significant covalent character. The ground state electronic configuration of E125 in (E125)F (from Mulliken population analysis [15]) is $8\,s^0\,5\,g^{0.9}\,6\,f^{1.9}\,7\,d^{2.0}\,8\,p^{0.1}$, suggesting a $5g^1$ compound. However, the 5g orbital is more contracted than a 6f or 7d orbital and does not participate in the bonding.

The situation looks quite different when we turn out to the hexafluoride compounds. The M−F bonds are lengthened with respect to the monofluoride complex. A contraction of 10% of the M-F bond length is observed as the atomic number of the metal increases. Simultaneously, the bond dissociation energy strongly increases from E125 to E129 following a change in the nature of the interactions. The hexafluoride of E125 and E126 are weakly bonded complexes with a low dissociation energy. This can be a consequence of predominant steric hindrance and electrostatic repulsion of the additional fluorine atoms. The Figure 1 reveals a local increase in the electron density between M and F along the series which suggests a fairly ionic character for E125-F bonds (Figure 1a) and the presence of some covalent character in the E129-F bonds (Figure 1b).



(a) $(E125)F_6$ (b) $(E129)F_6$

Figure 1: Electron density (0.01 a.u. isosurface with cut-plane) from DC-DFT calculations. Maximum density in red, zero value in blue.

Table 2 and Table 3 summarize the electron configurations for the ground state of M in the octahedral MF_6 complex.

Table 2: Orbital population of M in MF_6 and M effective charge from DC-DFT Mulliken population analysis. A is the atomic mass. See supporting information for details.

M	A(a.m.u.)	Population					Charge
E125	340.6	$8\,s^{0}$	$5\,g^{0.3}$	$6\,f^{3.7}$	$7\,d^{0.3}$	$8\,p^{2.6}$	0.9
E126	343.8	$8\,s^{0}$	$5\,g^{0.9}$	$6\,f^{4}$	$7\,d^{0.2}$	$8\,p^{2.2}$	1.3
E127	346.9	$8\,s^{0}$	$5\,g^{1.7}$	$6\,f^{4.2}$	$7\,d^{0}$	$8\,p^{1.9}$	1.6
E128	350.1	$8\,s^{0}$	$5\,g^{2.3}$	$6\,f^{4.6}$	$7\,d^{0}$	$8\,p^{1.3}$	2.3
E129	353.3	$8\,s^{0}$	$5\,g^{3.3}$	$6\,f^{4.4}$	$7\,d^{0}$	$8\,p^{1.6}$	2.5

Table 3: HOMO and LUMO character, HOMO-LUMO gap (eV) from DC-DFT calculations.

	E125	E126	E127	E128	E129
LUMO	5g	7d	5g	5g	8s
HOMO	7d	7d	5g	8p	8p
HOMO-LUMO gap	0.28	0.46	1.82	1.20	0.65

The electronic structure is very similar when moving across the series with a ground state characterized by a variable occupation of the 5g, 6f and 8p orbitals of M (see Table 2 and Figure 2). The 8s and 7d orbitals of the

metal remain empty except in the case of the 7d for the first two elements of the series where, however, the occupation remains low. The formation of the complex leads to a charge redistribution. Electron density from F^- is transferred to M^{6+} resulting in the effective charge given in Table 2 for M and the effective charge for F varies between -0.1 and +0.15 along the series.

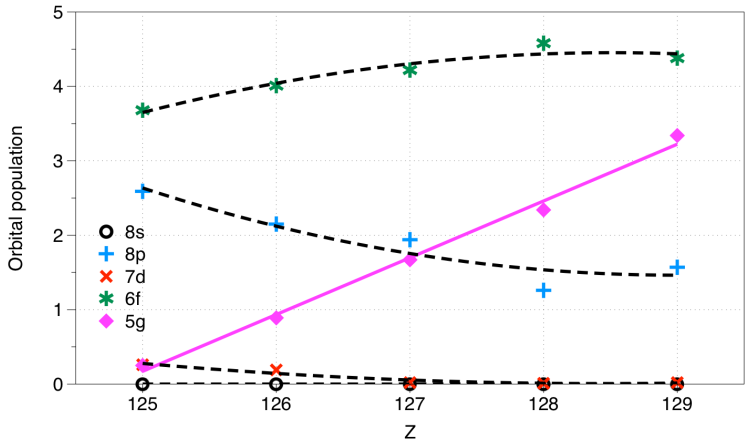


Figure 2: Electronic Mulliken occupation of the M valence orbitals in MF_6 from DC-DFT calculations. The increasing magenta line (diamonds) shows the charge of the 5g shell.

The linear trend in the population of the 5g orbital from E125 to E129 (Figure 2) clearly indicates its "non-bonding" character in the MF_6 complex. The 5g orbital does not participate in the bonding. The covalent bonding originates in the 8p orbital from M and the 2p orbital from F (Figure 3) whose mixing increases from E125 to E129.

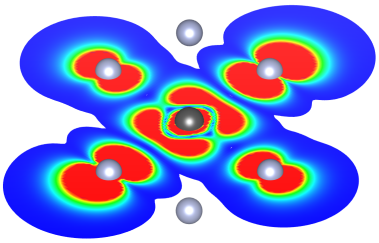
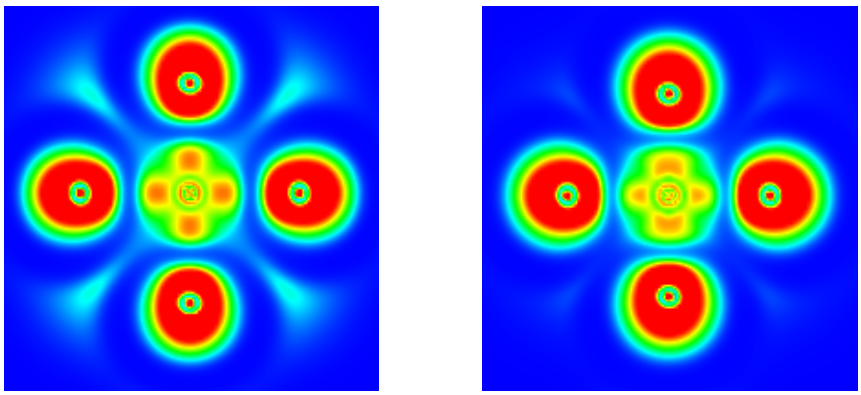


Figure 3: (E129)F_6 highest bonding molecular orbital (isosurface with cut-plane) involving 8p(E129) and 2p(F). Maximum density in red, zero value in blue.

This bonding picture is clearly different from an actinide hexafluoride. For example, the bonding in UF_6 is analyzed by Straka et al. [16] as a ionic and covalent character of U – F bonds the later arising from the overlap of 5f(U) and 6d(U) with the 2p(F) orbitals. This is in line with an analysis of the electron localization function (ELF) where for E125, the isosurfaces remain localized on individual atoms while the isosurfaces are deformed towards the bond between the atoms for E129. This modification of the ELF basins (see Figure 4) is the result of the mixing of the 8p(M) and 2p(F) orbitals driving the covalent bonding across the series.



(a) (E125)F_6 (b) (E129)F_6

Figure 4: Electron localization function (isosurface with cut-plane) from DC-DFT calculations. Maximum value in red, zero value in blue.

One can also ask in which order the 8s, 6f and 5g shells are occupied in (118 + 1)-electron systems of various nuclear charges[17]. The 118 first electrons fill a $7p^6$ core. The answer is that the 8s, 6f and 5g levels are preferred by the last electron for Z = 119-122, Z = 123-124 and $Z \geq 125$, respectively, according to DF-level calculations using the numerical MCDFGME code [18].

Concluding, we have studied the hexavalent fluorides of E125-E129, corresponding to oxidizing away all valence electrons of E124. We find that the occupation of the 5g shell indeed begins around Z=125, and increases linearly (see Figure 5). This allows a nominal assignment of the elements E121-E138 as "5g elements", just like the IUPAC Periodic Table calls the fifteen elements $_{89}$Ac - $_{103}$Lr "actinides", although the 5f electrons do not appear until the $^{231}_{91}$Pa atom or, to an extent, $^{232}_{90}$Th compounds.

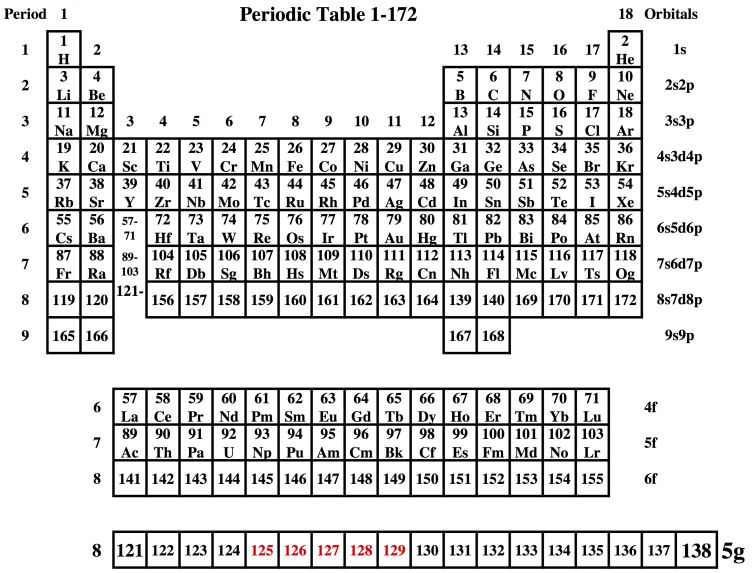


Figure 5: Periodic Table 1-172

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Graphical Abstract

Shape of the $5g$ atomic orbital ($m = 0 - 4$)