

## Lanthanide and Actinide Contractions: Relativistic and Shell Structure Effects

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In the last decade superheavy element chemistry and physics has become an active and exciting field. Recent progress in the study of elements beyond  $Z = 103$  shows that these elements reveal some interesting and often unexpected chemistry.<sup>1</sup> Lifetimes of superheavy nuclei beyond  $Z = 109$  may be much higher than previously predicted,<sup>2–4</sup> opening the way for atom-at-a-time chemistry.<sup>1</sup> While the chemistry of element 104 has been studied in some detail,<sup>1,5</sup> the chemistry of the elements with nuclear charge greater than 105 is virtually unknown and only theoretical estimates of physical and chemical properties have been established from relativistic  $X\alpha$  calculations by Fricke et al.<sup>6</sup> Elements with nuclear charge greater than 111 have not definitely been identified so far (elements 110 and 111 have been announced just recently by the Darmstadt group of the Heavy Ion Research Centre).<sup>7</sup> It is therefore of interest to predict the chemical and physical properties of superheavy elements by accurate theoretical calculations.

It is well-known that the 5d transition metal atoms are of similar size compared to their 4d congeners. For instance, Ag and Au both have a metallic radius of ca. 1.44 Å.<sup>8</sup> The anomalously small size of the sixth-row transition elements and many other irregular features in the chemistry and physics of these elements are usually explained in two ways: (i) the diminished shielding of the nucleus due to the inclusion of the 4f electrons (f-shell effect) causing a contraction of the valence shells (the lanthanide contraction)<sup>8</sup> and (ii) The large relativistic effects present in the heavier atoms.<sup>9</sup> The effect of the filled 5f shell on the trans-actinides should be qualitatively similar to the 4f-shell effect on the sixth-row elements. However, relativistic effects in these superheavy elements are expected to be more important, thus suggesting the existence of a pronounced "actinide contraction". Early Dirac–Slater calcula-

tions on the elements 104–118 do indeed suggest the existence of such a contraction.<sup>6</sup>

To separate the relativistic effects from the f-shell contribution to the actinide contraction, we applied the method as formulated by Bagus et al.<sup>10</sup> and Pyykkö<sup>11</sup> performing numerical atomic Hartree–Fock (HF)<sup>12</sup> and Dirac–Fock (DF)<sup>13</sup> calculations with the 4f or 5f electrons removed (and therefore the nuclear charge reduced by 14). In contrast to the earlier work,<sup>10,11</sup> the pseudoatoms were treated at the relativistic (DF) as well as the nonrelativistic level (HF), to reveal whether relativistic and shell-structure contributions are strongly linked or essentially independent. The HF results for atoms with  $Z < 104$  were taken from ref 14, the DF atomic results were taken from ref 15 (except for elements 111 and 112), and the HF pseudoatom results for HF, Au, Hg, Tl, Pb, and Bi were taken from ref 10. All calculations on a particular atom or pseudoatom were carried out on a single nonrelativistic configuration averaged over all LS states and a finite extension of the nucleus in the relativistic case. For purposes of comparison between elements down four rows of the periodic table, the valence s-, p-, and d-shell occupations were kept constant throughout a group, even if the ground state configurations of some superheavy elements are predicted to differ from those of the lighter elements within the group, as is the case for elements 104<sup>16</sup> and 111.<sup>6,17</sup> The following configurations were chosen:  $6d^27s^2$  for element 104,  $6d^{10}7s^1$  for element 111,  $6d^{10}7s^2$  for element 112,  $7s^27p^1$  for element 113,  $7s^27p^2$  for element 114, and  $7s^27p^3$  for element 115. The numerical calculations for the superheavy elements were performed with a very tight point grid for the wave function (30 000 points).<sup>18</sup>

The calculations reveal that relativistic and shell-structure effects are not additive. For instance, the 4f-shell effect leads to a stabilization of the 6s electron in gold by 0.0303 au nonrelativistically, but if relativity is included the stabilization increases to 0.0707 au (Figures 1 and 2). It is well established<sup>9</sup> that relativity causes the s orbitals (and, to a lesser extent, the  $p_{1/2}$  orbitals) of an atom to contract (*direct relativistic orbital contraction*), resulting in a greater shielding of the nucleus. Consequently, the orbitals with higher angular quantum number become more diffuse (*indirect relativistic orbital expansion*).<sup>9</sup> Thus relativistic f orbitals are more diffuse than their nonrelativistic counterparts and the 4f-shell (5f-shell) effect is therefore relativistically enhanced! The 4f-shell (5f-shell) effect on the 6p electrons (7p electrons) is also enhanced by relativity (Figure 3), though less than for the 6s electrons (7s electrons).

The continuation of the data to include the post-actinide elements demonstrates that there will be an actinide contraction. As a peculiar result, element 111 is predicted to have a *smaller* atomic radius than copper, silver, or gold (!), Figure 2, in agreement with earlier estimates by Fricke et al.<sup>6</sup> This is also the case for the group 12 series of elements Zn, Cd, Hg, and 112 (but less dramatic compared to the group 11 elements). We mention that Fricke and Waber showed by  $X\alpha$  calculations

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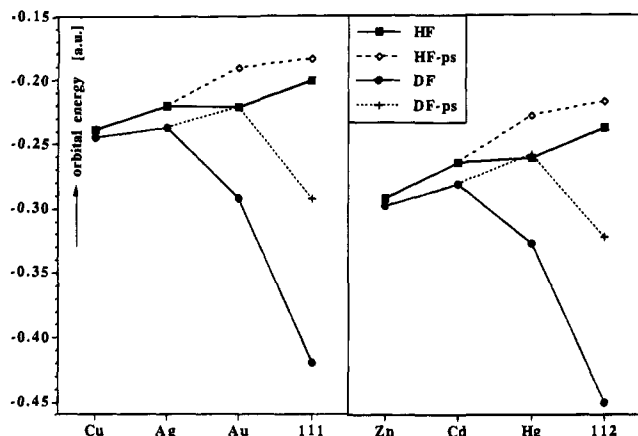
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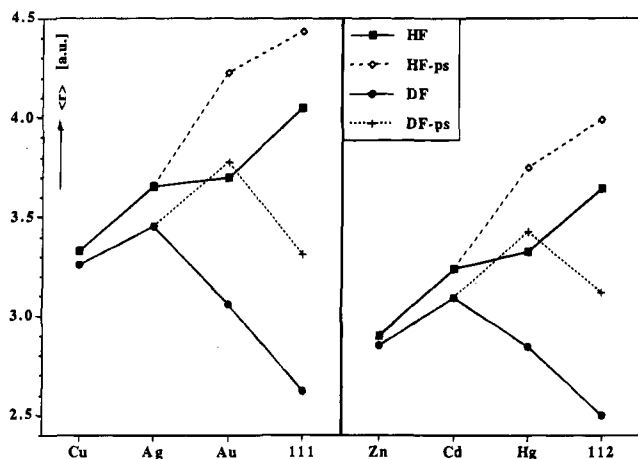
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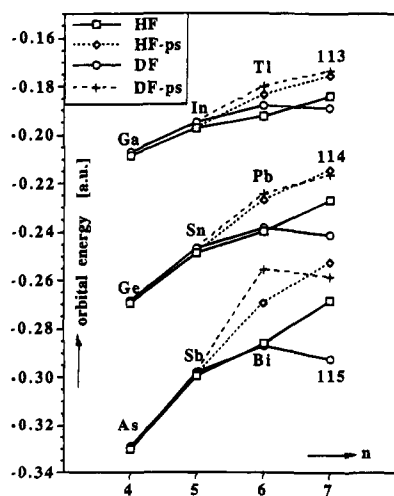
(18) The tight grid is necessary in order to obtain numerically stable total electronic energies.



**Figure 1.** Orbital energies of the valence  $ns$  electrons ( $n = 4-7$ ). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively.



**Figure 2.**  $\langle r \rangle$ -expectation value of the valence  $ns$  orbitals ( $n = 4-7$ ). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively.



**Figure 3.** Orbital energies of the valence  $np$  electrons ( $n = 4-7$ ). HF-ps and DF-ps indicate nonrelativistic and relativistic calculations for the pseudoatoms, respectively. DF and DF-ps results are the weighted averages of the  $p_{1/2}$  and  $p_{3/2}$  orbital energies.

that, within the alkaline series of elements, element 119 has a smaller atomic radius than Cs, and element 165 is even smaller than Rb.<sup>6</sup> In comparison, however, the shell-contraction effects are much smaller in the group 1 series of elements compared to the group 11, and we conclude that the so-called group 11 maximum of relativistic effects<sup>9</sup> is responsible for this unexpected feature. This suggests that compounds of the type (111)X (X electropositive ligand; see the discussion in ref 19)

could have smaller bond distances than the compounds of their lighter congeners MX ( $M = \text{Cu, Ag, or Au}$ ).<sup>20</sup> For example, relativistic calculations on  $\{111\}\text{H}$  using the pseudopotential technique including relativistic and electron correlation effects give the following sequence in bond distances along the group 11 hydrides:  $\text{CuH}$  (1.46 Å)<sup>21</sup> <  $\{111\}\text{H}$  (1.50 Å)<sup>20</sup> <  $\text{AuH}$  (1.52 Å)<sup>21</sup> <  $\text{AgH}$  (1.62 Å).<sup>21</sup> It is also apparent that, unlike the lanthanide contraction, the actinide contraction is caused mainly by relativity! As proposed by Bagus et al.,<sup>10</sup> the effect of the  $f$  shell remains almost constant at the nonrelativistic level when comparing sixth-row with seventh-row elements, but relativistic effects increase the actinide contraction substantially.

Relativistic effects are larger for the  $7p$  orbitals than for the corresponding  $6p$  orbitals of the sixth-row atoms. The  $7p$  orbital energies shown in Figure 3 are the  $j$  averages of the  $7p_{1/2}$  and the  $7p_{3/2}$  orbital energies. The unaveraged (spin-orbit coupled) orbital energies are not shown due to the large magnitude of the spin-orbit coupling (of the order of 0.2 au for element 115!). The  $f$ -shell effect stabilizes the  $7p_{1/2}$  orbitals, and the corresponding  $\langle r \rangle$ -expectation values are reduced by about 0.6 au. The  $7p_{3/2}$  orbitals are in fact destabilized by the  $f$ -shell effect, and their  $\langle r \rangle$ -expectation values are only about 0.2 au smaller. This is similar compared to the  $d$  shell as discussed below.

For comparison we discuss results for one of the  $6d$ -transition elements, 104. A comparison between the HF, DF, and pseudoatom results of the  $6d$  orbital energies or  $\langle r \rangle$ -expectation values shows that while the actinide contraction leads to the expected stabilization of the  $6d$  shell at the nonrelativistic level (*reduced screening* of the nucleus), relativistic effects overcompensate this by a large destabilization (*relativistically increased screening* of the nucleus). This effect is also evident for the  $6d$  shells of the other elements (111, 112, ...). It is interesting that the inclusion of the  $4f$  shell actually *destabilizes* the  $5d$  electrons in several sixth-row elements similar to the findings of Bagus et al.<sup>10</sup> However, the  $\langle r \rangle$ -expectation values are still larger in the pseudoatom compared with the atom including the  $4f$  shell. In a similar fashion, the  $5f$  shell destabilizes the  $6d$  electrons of some of the seventh-row elements, while the  $\langle r \rangle$ -expectation values are all larger in the pseudoatoms (see element 104, for example). A possible explanation of this unexpected feature is that the valence  $s$  shell, having large density in the near vicinity of the nucleus, undergoes a strong contraction due to inclusion of the  $f$  shell. This leads to an additional screening of the nucleus and thus to a destabilization of the  $d$  shell (*indirect actinidelanthanide expansion*).

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**Supplementary Material Available:** Tables SI–SIV, listing nonrelativistic and relativistic orbital energies and  $\langle r \rangle$ -expectation values of the elements Hf, Au, Hg, Tl, Pb, Bi, 104, 111, 112, 113, 114, and 115 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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