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PAPER

# A suggested periodic table up to $Z \leq 172$ , based on Dirac–Fock calculations on atoms and ions

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Extended Average Level (EAL) Dirac–Fock calculations on atoms and ions agree with earlier work in that a rough shell-filling order for the elements 119–172 is  $8s < 5g \leq 8p_{1/2} < 6f < 7d < 9s < 9p_{1/2} < 8p_{3/2}$ . The present Periodic Table develops further that of Fricke, Greiner and Waber [*Theor. Chim. Acta* 1971, **21**, 235] by formally assigning the elements 121–164 to  $(nlj)$  slots on the basis of the electron configurations of their ions. Simple estimates are made for likely maximum oxidation states,  $i$ , of these elements M in their  $MX_i$  compounds, such as  $i = 6$  for  $UF_6$ . Particularly high  $i$  are predicted for the  $6f$  elements.

## 1. Introduction

The Periodic Table (PT) is a compact, approximate way to summarise both the electronic shell structure of individual atoms, or their ions, and chosen aspects of the chemical behaviour of the elements. The history of the PT was recently discussed by Kaji,<sup>1</sup> Gordin<sup>2</sup> and Scerri.<sup>3</sup> We also quote the study on certain  $(n, l)$  ('Madelung') rules by Ostrovsky<sup>4</sup> and the attempts at a group-theoretical classification of the elements by Kibler.<sup>5</sup> The underlying electronic principles were discussed by Schwarz *et al.*<sup>6–8</sup>

A modern, 18-column, shape of the PT is shown in Fig. 1. The latest two essential additions were the addition of the  $5f$  or actinide elements by Seaborg (see ref. 10) and the now completed transactinide series up to  $Z = 118$ . The last of them was the case  $Z = 117$ , reported in 2010 by Oganessian *et al.*<sup>11</sup> One often speaks of 'Superheavy Elements (SHE)'. Chemically speaking, decades of both experimental<sup>12–14</sup> and theoretical<sup>15,16</sup> work give good reason to regard at least the elements 104–109 as a fourth,  $6d$  transition-metal series. A drastic change of the covalent radii may occur from E110 (Darmstadtium, Ds) onwards, see Fig. 2. The experimental chemical studies on the elements  $Z \leq 118$ , and maybe beyond, are of the type 'one atom at a time'. In cases where the nuclear lifetimes now are too short for chemical studies, new, more neutron-rich isotopes may help. Studies on the bulk chemistry are expected to remain computational, only.

The values  $l = 0, 1, 2, 3, 4$  are denoted by the symbols  $s, p, d, f, g$  respectively. When necessary, the lower spin–orbit (SO) split component  $j = l - \frac{1}{2}$  is denoted by a star, e.g.  $p^* = p_{1/2}$ . The principal quantum number  $n$  of the  $s$  and  $p$  shells coincides with the number of the period in Fig. 1. It should be stressed

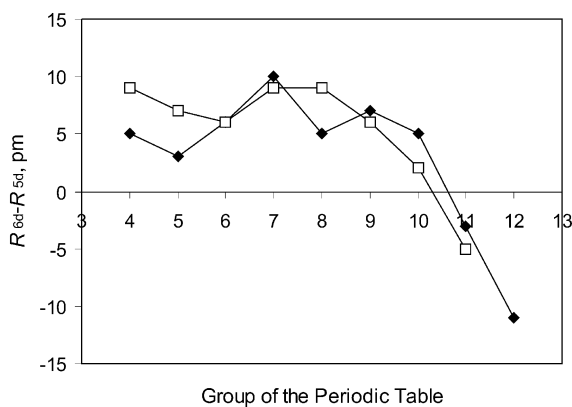
that, while nuclear charges are well defined, the concept of an electron configuration, both for atoms and molecules, is only approximate. For both systems, the true many-electron wave function can be a superposition of a large number of effective electron configurations. This aspect especially affects the transition metals.

The filling of such shells up to  $Z = 172$  was studied using Dirac–Slater (DS) theory by Fricke *et al.*<sup>19,20</sup> for single,  $jj$ -coupled electron configurations in this approximate form of density functional theory (DFT). It was found that, approximately for  $Z = 121$ –143,  $8p_{1/2}$  and  $5g$  shells become occupied in neutral atoms. The full  $6f$  and  $7d$  series are completed around  $Z = 144$ –154 and 155–164, respectively. The following row contained the  $9s, 9p_{1/2}$  and  $8p_{3/2}$  elements 165–166, 167–168 and 169–172, respectively, see Fig. 10 of ref. 19. The heaviest atom treated seems to be E184.<sup>21</sup> The primary, numerical DS data are listed in ref. 22.

Period	1	Periodic Table 1–118																18	Orbitals						
1	1 H	2																13	14	15	16	17	18 He	1s	
2	3 Li	4 Be																5	6	7	8	9	10 Ne	2s2p	
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar							3s3p
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr							4s3d4p
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe							5s4d5p
6	55 Cs	56 Ba	57–71 La Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn							6s5d6p
7	87 Fr	88 Ra	89–103 Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118							7s6d7p
6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu										4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr										5f

Fig. 1 The Periodic Table of the 118 experimentally known elements. The numbers  $g = 1$ –18 are the Groups. The IUPAC PT<sup>9</sup> coincides with this table, but so far only includes the elements, up to Rg.

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**Fig. 2** The collapse after Group 10 of the 7th Period ('6d') covalent radii, compared to 6th-Period ('5d') ones. Black diamonds: Single-bond radii.<sup>17</sup> Open squares: Triple-bond radii.<sup>18</sup>

Already slightly earlier, Waber<sup>23,24</sup> found 5g electrons in the atomic ground state from E125 on. Lu *et al.*<sup>25</sup> also provided DS data up to  $Z = 126$ . At Dirac-Fock (DF) level, Mann<sup>26</sup> noticed the particular stability of the  $8p^*$  shell and Mann and Waber<sup>27</sup> reported results for E118–E131. The general conclusion is that, around E121–131, both  $8p$ ,  $7d$ ,  $6f$  and  $5g$  orbitals may enter the atomic ground states.

At this point one should point out that a realistic finite nuclear size keeps the lowest ( $1s$ ) eigenvalue within the normally allowed range  $\epsilon > -2mc^2$  (a free electron being taken as  $\epsilon = 0$ ). For the  $1s$  state of a one-electron atom, and the available nuclear models, the critical limit,  $Z_{cr}$  has been put at  $Z = 175$ ,<sup>28</sup>  $> 170$ <sup>29</sup> or  $171.5$ .<sup>30</sup> The screening from the other electrons should raise that limit.

Zel'dovich and Popov<sup>31,32</sup> actually point out that the electron wave functions remain localized beyond  $Z_{cr}$  but this behaviour has not been implemented in any atomic codes yet.

It is not obvious how to treat the quantum electrodynamical (QED) effects in the supercritical domain  $Z > 137$ . Here they are hence simply dropped out. In the range  $Z = 50$ – $100$ , they are typically  $-1\%$  of the one-electron, Dirac-level relativistic effects,<sup>33–35</sup> on the valence  $ns$  orbital binding energies of neutral or nearly neutral atoms. For a recent summary on the QED aspects, see Indelicato *et al.*<sup>36</sup> Because their sign on  $s$  levels is repulsive, they should also increase  $Z_{cr}$ .

Average-of-configurations Dirac-Fock (DF) calculations for the elements 1–120 were reported by Desclaux.<sup>37</sup> Umemoto and Saito<sup>38</sup> also found 5g electrons to appear at E126 at DS level. Very precise relativistic coupled-cluster calculations were reported by the group of Kaldor on individual atoms and their ions, such as E122.<sup>39</sup> Multiconfiguration, MCDF-level calculations on the atomic ground configurations for elements 119–164 were reported by Nefedov *et al.*<sup>40</sup> who, however, do not specify the exact computational method used, nor the value of the total atomic angular momentum,  $J$ .

Little molecular work has been done on superheavy elements beyond the rare gas E118 (which has an electron affinity<sup>41,42</sup>). The exceptions comprise an MS X $\alpha$  study of  $5g^1$  complexes of E125<sup>43</sup> (entirely supporting the present PT), a single-configuration DF study on diatomic (E126)F<sup>44</sup> and a study on (E119)H and (E120)H<sup>+</sup>.<sup>45</sup>

**Table 1** Comparisons of the present EAL results against literature. PW = present work

$Z$	$q$	El. conf.	$2J$	$I/a.u.$	Reference
121	0	$8p^1$	1	0.113	PW
				0.1634	47
	+1	$8s^2$	0	0.423	PW
				0.4652	47
	+2	$8s^1$	1	0.653	PW
			0.6854	47	
	+3	$8s^0$	0	1.627	PW
	+4	$7p^{-1}$			PW
122	0	$8s^2 8p 7d$	4	0.206	39
	+1	$8s^2 7d$	3	0.415	39
	+2	$8s^2$	0	0.704	PW
				0.749	39
	+3	$8s^1$	1	0.961	PW
			0.997	39	

The purpose of present work is to extend the previous work on neutral atoms to chemically plausible ions, fully realising the difference between free ions and ions in chemical compounds, at a—still approximate—but realistic DF level, in order to see how a 21st-Century Periodic Table could possibly be shaped in its most compact, approximate form.†

## 2. Methods

The calculations were performed using the latest version of the MCDF program of Desclaux and Indelicato,<sup>46</sup> at the Extended Average Level (EAL) level. Because many atomic levels can be mixed in chemical-bond formation, as emphasized by Schwarz and coworkers,<sup>6</sup> this may actually be a desirable approximation. The EAL is useful, as long as the spin-orbit (SO) effects are not excessive, or can be separately checked.

The nuclear charge distribution was taken as a Fermi one with the parameters

$$\rho(r) = \rho_0/[1 + \exp((r - c)(4 \ln 3)/t)], \quad (1)$$

where  $\rho_0$  is a normalization constant to obtain a charge  $Z$  and the surface thickness  $t = 2.3$  fm (Fermi) for  $Z > 45$ . Using

$$A = 0.00733Z^2 + 1.3Z + 63.6. \quad (2)$$

for the atomic mass, the RMS nuclear radius  $c$  (in fm) is extrapolated in the program from known values of  $c$  as a function of  $A(Z)$  for large  $Z$ . We have not studied here the chemical effects of varying the nuclear size.

Some calibration results are compared to earlier ones in the Table 1.

## 3. Results

### 3.1 A broad mapping

A compact, very schematic grouping of the elements up to  $Z = 172$  is shown in Fig. 3. The underlying atomic results are shown in Tables 2–4.

† The present work was done in preparation for a lecture at the 150th Anniversary Congress of "Weltkongress Chemie" in 1860 at Karlsruhe on 3–4 September, 2010.

Period	Periodic Table 1-172																18 Orbitals						
1	1 H	2															13	14	15	16	17	2 He	1s
2	3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p				
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s3d4p				
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p				
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p				
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p				
8	119	120	121-	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p				
9	165	166											167	168					9s9p				

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g
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**Fig. 3** The new, compact Periodic Table for elements 1–172. The numbers 1–18 are the Groups. For Periods 8 and 9, the Groups 13–14 are interpreted as  $p^*$  ( $p_{1/2}$ ) states and the Groups 15–18 as  $p$  ( $p_{3/2}$ ) states. Please note that, in this most compact version and respecting the ‘Orbitals’ assignment in the right-hand marginal, the Z values do not increase systematically. An alternative were to break present Period 8 into the pieces 8a (119–120), 8b (139–140) and 8c (156–164, 169–172).

### 3.2 Elements 119–126 and the beginning of a 5g series

As discussed before, elements 119 and 120 are  $8s^1$  and  $8s^2$ , and thus belong to Groups 1 and 2, respectively.<sup>19,37,48,49</sup> For neutral E121, the present EAL calculations prefer  $8p$ , with  $7d$  only slightly above. The one-electron ions  $E123^{4+}$  and  $E124^{5+}$  switch the  $8s$  ground state for a  $6f$ . From  $E125^{6+}$  onwards, a  $5g^1$  state is preferred, as seen in Table 2. The one-electron ions  $E125^{6+}$  and  $E126^{7+}$  being clearly  $5g^1$ , this motivates placing these elements in Groups 7 and 8, of a beginning  $5g$  row, respectively. A chemical example on the former would be the  $(E125)F_6$  of Makhyoun.<sup>43</sup> For the next element, the  $(E126)F_6$  are then expected to be  $5g^2$  systems. An analog for the one-electron ion is  $Ce^{3+}$ ,  $4f^1$ , placed in Group 4. Further analogs are  $U^{5+}$  and  $Np^{6+}$ , both  $5f^1$ , placed in Groups 6 and 7, respectively. There is room for 18 elements E121–E138 on this  $5g$  row. We repeat that we do not mind if

other orbitals, such as  $8p^*$ ,  $7d$ , or  $6f$  ones could be occupied in some early members of a row, or in low oxidation states of these elements. They are nevertheless counted as members of the  $5g$  series.

Note that, depending on the oxidation state, the  $8s$  occupation may vary from 0 to 2. In this sense the  $8s$  and  $5g$  levels cross. Concerning the filling of the  $5g$  shell, in the neutral-atom calculations, this does not occur until E144.<sup>19</sup>

The size of the  $5g$  orbitals being very small (see Section 4), their direct involvement in chemical bonding is unlikely, just as in the case of the  $4f$  orbitals of the lanthanides.

### 3.3 The $8p^*$ shell

Mann and Waber<sup>26,27</sup> found in their single-configuration  $jj$ -coupled DF calculations that, in the neutral atoms, one  $8p^*$  electron appeared at E121–E125, and two at E126-. In the

**Table 2** Calculated electron configurations for nuclear charge  $Z$  and ionicity  $q$  for  $Z \leq 140$ . The post-E118 electron configuration is shown. The quantity  $I$  is the energy of the next ionization. Further data for E121 and E122 are given in Table 1. An 'r' in the last column indicates that the corresponding  $r_{\max}$  was included in Fig. 4 below

$Z$	$q$	El. conf.	$I/\text{a.u.}$	Exc. en.	
119	0	$8s^1$			r
120	0	$8s^2$			r
121	0	$8s^2 8p^1$	0.113		r
		$8s^2 7d^1$		+0.0042	r
	+1	$8s^2$			
123	+4	$6f^1$	1.374		r
124	+5	$6f^1$	1.918		r
		$5g^1$		+0.0948	r
125	+6	$5g^1$	2.721		r
	+7	$5g^0$			
126	+6	$5g^2$	2.714		r
		$6f^1 5g^1$		+0.2091	r
	+7	$5g^1$	3.677		r
133	+6	$5g^0$			r
136	+2	$8s^2 6f^3 5g^{11}$			
	+6	$5g^{12}$			
138	+5	$8s^2 5g^{13}$	2.089		
		$8s^1 5g^{14}$		+0.0977	
		$6f^2 5g^{13}$		+0.2146	
		$6f^1 5g^{14}$		+0.2923	
		$6f^3 5g^{12}$		+0.3779	
		$8p^1 5g^{14}$		+0.7159	
	+6	$8s^1 5g^{13}$			r
		$6f^1 5g^{13}$		+0.0225	
		$5g^{14}$		+0.0360	
		$6f^2 5g^{12}$		+0.2509	
		$8p^1 5g^{13}$		+0.7033	
140	+2	$8s^2 5g^{16} 8p^2$			
		$8s^2 5g^{17} 8p^1$		+0.2921	
	+4	$8s^2 6f^2 5g^{14}$			
	+6	$6f^1 5g^{15}$	2.428		r
		$8s^2 5g^{13}$		+0.6637	
	+7	$5g^{14}$			

**Table 3** Calculated electron configurations for nuclear charge  $Z$  and ionicity  $q$  for  $Z = 143$ –149. The quantity  $I$  is the energy of the next ionization

$Z$	$q$	El. conf.	$I/\text{a.u.}$	Exc. en.
143	+6	$8s^1 5g^{18}$	2.652	
		$6f^1 5g^{18}$		+0.2473
	+7	$5g^{18}$		
144	+5	$8s^2 6f^1 5g^{18}$	2.139	
	+6	$8s^2 5g^{18}$	2.760	
	+7	$8s^1 5g^{18}$	3.185	
		$6f^1 5g^{18}$		+0.1269
	+8	$5g^{18}$		
		$6f^1 5g^{17}$		+0.4306
		$8s^1 5g^{17}$		+0.4908
		$7d^1 5g^{17}$		+1.0658
		$6f^1 5g^{17}$		+1.5227
145	+6	$5g^{18} 8s^2 6f^1$	2.783	
		$5g^{18} 8s^1 6f^2$		+0.1737
	+7	$5g^{18} 8s^2$	3.303	
		$5g^{18} 8s^1 6f^1$		+0.0443
		$5g^{18} 6f^2$		+0.1755
	+8	$5g^{18} 6f^1$	3.755	
		$5g^{18} 8s^1$		+0.0025
	+9	$5g^{18}$		
146	+8	$5g^{18} 8s^1 6f^1$	3.836	
		$5g^{18} 6f^2$		+0.0031
		$5g^{18} 8s^2$		+0.0887
	+9	$5g^{18} 6f^1$	4.494	
		$5g^{18} 8s^1$		+0.1388
	+10	$5g^{18}$		
147	+10	$5g^{18} 6f^1$	5.272	
		$5g^{18} 8s^1$		+0.2800
148	+11	$5g^{18} 6f^1$	6.088	
149	+12	$5g^{18} 6f^1$	6.940	

we expect an E118 core + a  $5g^{18} 8s^2$  semicore + the remaining electrons, going to the  $6f^k$  shell with

$$k = Z - 138 - i, \quad (3)$$

where  $i$  is the ionic charge. For the heavier  $6f$  elements, see Table 4. As another example, the trivalent E155 will correspond to a  $6f^{14}$  closed-shell configuration, like its analogs Lu and Lr in the suggested PT, Fig. 3. Note that the  $8p$  shell still remains above  $6f$  in our EAL total-energy calculations. The  $8p^* = 8p_{1/2}$  eigenvalue is comparable with the  $6f$  ones at E155 $^{3+}$ .

For the  $6f$  series we also have the higher oxidation state, such as E144 $^{8+}$ , where the  $8s$  shell is ionized away. In fact, as the last electron above a  $5g^{18}$  core, the  $6f$  replaces the  $8s$  starting from E145 $^{8+}$ . The E146 $^{8+}$  has one of each, an  $8s^1 6f^1$  configuration in the EAL model. This underlines the similar binding energies of the  $8s$  and  $6f$  electrons in this neighbourhood.

This situation may create for the  $6f$  elements a large range of high oxidation states, as discussed in Chapter 5. This is also a bit analogous with the Groups 13–15 of Period 6, with the choice between Tl(I,III), Pb(II,IV) or Bi(III,V).

As seen from Table 4, at E153 $^{3+}$  the  $8s$  shell is already clearly under the  $6f$ . Similarly, in the pentavalent state, E155 $^{5+}$ , the  $8s$  electrons are kept but the  $6f$  shell is ionized to  $6f^{12}$ .

For the higher oxidation state, the number of  $6f$  electrons is

$$k = Z - 136 - i, \quad (4)$$

DS calculations of Fricke *et al.*<sup>19</sup> the limits were E121–E126 and E127-, respectively.

For our electron book-keeping, we put the  $8p^*$  shell at E139 and E140. As seen in Table 2 for the previous element, E138 $^{5+, 6+}$ , the available electrons will be placed in a full,  $8s^2$  shell, the rest going to the  $5g$  shell, and none yet to the  $8p$  shell. This supports the present placement.

### 3.4 The $6f$ series

We here have a choice of keeping the  $8s^2$  shell, or ionizing it away. If we keep it, we can place the 15 following elements E141–E155 below the actinides Ac–Lr. (Note that in the upper part of the PT, there is a slot at Group 3, and Ac,  $7s^2 6d^1$ , is usually included on the actinide row, giving fifteen items. In contrast to the actinides, which lose their  $7s$  electrons in compounds, the present series, in their lower oxidation states, keep their  $8s^2$  but formally lose the  $(8p^*)^2$  electrons.

Taking as example the system E144 $^{+5}$  (see Table 3), it has an  $8s^2 6f^1 5g^{18}$  configuration, and belongs in this sense to a  $6f$  series. As its analog U $^{5+}$  ( $5f^1$ ), E144 in its lower oxidation state hence does belong to Group 6 on the  $6f$  row of Period 8. More generally, for the lower oxidation state of the  $6f$  series,

**Table 4** Calculated electron configurations for nuclear charge  $Z$  and ionicity  $q$  for  $Z \geq 153$ . The quantity  $I$  is the energy of the next ionization

$Z$	$q$	El. conf.	$I/\text{a.u.}$	Exc. en.
153	+1	$8s^2 6f^{14}$	0.380	
	+2	$8s^2 6f^{13}$	0.872	
	+3	$8s^2 6f^{12}$	1.415	
		$8s^1 6f^{13}$		+0.5810
		$6f^{14}$		+1.2253
	+4	$8s^2 6f^{11}$	1.999	
	+5	$8s^2 6f^{10}$	2.619	
155	+6	$8s^2 6f^9$	3.270	$r$
	+7	$8s^2 6f^8$		
	+3	$8s^2 6f^{14}$	1.484	
	+4	$8s^2 6f^{13}$	2.084	
	+5	$8s^2 6f^{12}$	2.720	$r$
		$8s^1 6f^{13}$		+0.4201
		$6f^{14}$		+0.9189
156	+6	$8s^2 6f^{11}$		
	+3	$8p^1$	1.177	
		$7d^1$		+0.0538
	+4	$8s^2$	2.126	
	+5	$8s^2 6f^{13}$	2.770	$r$
158	+6	$8s^1 6f^{14}$		+0.4434
	+6	$8s^2 6f^{12}$		
	+3	$7d^1 8p^2$		
	+1	$7d^9 8s^2 8p^2$	0.888	
			0.600 <sup>a</sup>	
164	+2	$7d^8 8s^2 8p^2$	1.300	$r$
	+3	$7d^7 8s^2 8p^2$	1.741	
	+4	$7d^6 8s^2 8p^2$		
	+2	$7d^{10} 8p^2$		+0.5826
166		$9s^1 7d^9 8p^2$		+1.2594
		$9s^2 7d^8 8p^2$		
	+2	$8p^4$		+1.0742
168		$9s^1 8p^3$		+2.2027
		$9s^2 8p^2$		

<sup>a</sup> Single-configuration *jj*-coupled DF, ref. 50.

### 3.5 The 7d series

After the 6f series, we assign the nine elements E156–E164 formally to a 7d series in Groups 4–12.

Table 3 suggest 8p to lie slightly below 7d for E156<sup>3+</sup>. The 8p\* eigenvalue of  $-1.91$  au is clearly below the SO-averaged 7d one of  $-1.14$  au. Note that trivalent Ti, Zr and Hf are  $d^1$  while E156<sup>3+</sup> is  $p^1$  but has a low-lying  $d^1$  state.

As seen from Table 4, E156<sup>4+</sup> is  $8s^2 6f^{14}$ . If ionized further to 5+ or 6+, the electrons are taken from the 6f, not from the 8s.

At the end of the series, the chemical properties of eka-copernicium, E164, were discussed by Penneman *et al.*<sup>50</sup> It was mainly predicted to be divalent, but oxidation states +IV and +VI were also expected. The calculated  $I_i$  for  $i = 2-4$  in Table 3 lie above the limiting line in Fig. 6, suggesting at most borderline chemical stability. Notice that, unlike Zn–Hg, but like Cn,<sup>51</sup> the ions of E164 keep both 8s electrons but remove 7d ones, which lie clearly higher. The  $8s^2 7d^{10}$  ground-state configuration of E164 is analogous to all of Zn–Cn, which motivates keeping E164 in Group 12 of Period 8. This also fixes the positions of the preceding 7d elements.

### 3.6 The last main-group elements

The 9s<sup>1</sup> and 9s<sup>2</sup> elements E165 and E166 are now in Groups 1 and 2, respectively. Unlike the ns elements of Periods 3–8, which have an underlying  $np^6$  core, the E165 and E166,

however, have an underlying  $7d^{10}$  core. In that sense, they would have a chance of rather being analogs to Au and Hg, or to Rg and Cn, and being members of Groups 11–12 of the Period 9, next to E167.

As seen from Table 3, the dication E166<sup>2+</sup> strongly prefers a  $7d^{10} 9s^0$  configuration to the alternatives  $7d^9 9s^1$  or  $7d^8 9s^2$ . We recall here that Rg (E111) prefers a  $6d^9 8s^2$  ground state.<sup>52</sup> Due to this orbital order  $7d < 9s$ , we therefore let E165 and E166 stay in Groups 1 and 2, as done by Fricke *et al.*<sup>19</sup>

For the elements E167–E172 we likewise follow them in taking the energetic order as  $9s < 9p_{1/2} < 8p_{3/2}$ . Note that the SO splittings are so large that they are making two SO-split suborbitals with different  $n$  nearly degenerate.

## 4. Orbital radii

### 4.1 The nodeless 5g orbital

It is well-known that the first orbital with every  $l$  (1s, 2p, 3d, 4f, 5g, ...) is much more compact than the following orbitals with the same  $l$ . This was noticed for 3d and 4f orbitals by Jørgensen,<sup>53</sup> who related it to the number of radial nodes (actually ‘maxima’, see his p. 46). Similar later arguments exist for the shells  $2p$ <sup>54,55</sup> and  $1s$ .<sup>56</sup> Also Slater<sup>57</sup> comments that the  $r_{\text{max}}$  of the 3d shells of Sc–Ni, given earlier by himself,<sup>58</sup> are ‘much smaller than those for the 4s, even though the energies are about the same’. He mentions their ‘different shapes’. Qualitatively one could say that the higher levels with the same  $l$  feel a *primogenie repulsion*<sup>59</sup> from the first, nodeless orbital. For a recent review on this problem, see Kaupp.<sup>60</sup>

How compact is the 5g shell, compared with its counterparts? We show in Table 5 typical radii,  $\langle r \rangle$ , for the four series. The 5g shell is compact, but rather comparable with the other three series.

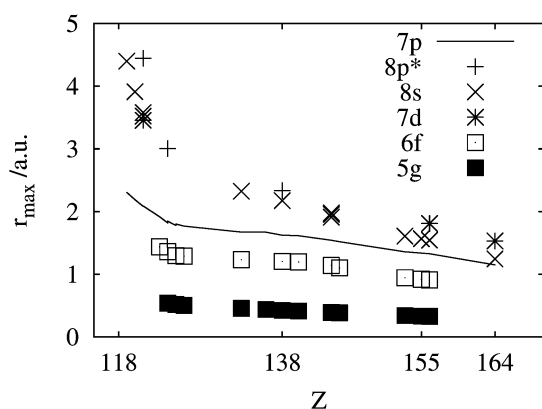
Estimates for the ionic radii of E104–E120 and E156–E172 were provided by Fricke and Waber<sup>61</sup> as the  $r_{\text{max}}$  of the outermost occupied orbital. The neutral atom  $r_{\text{max}}$  of Waber *et al.*<sup>24</sup> for the 6f and 5g shells from E124 to E132 are comparable with the present values for their ions in Fig. 4.

Because of the small size of the 5g shell, the 5g elements may rather chemically form a group of *superlanthanides*, in the sense of systematic magnetic behaviour, and non-participation of the ‘label orbital’ 5g in the formation of bonds. The difference is that the lanthanides use 6s and 5d in their covalent bonds, but the 5g series has the panoply of 8s, 8p\*, 7d and 6f for the purpose. For factors determining the ionic radii, see the subsection on  $7p_{3/2}$  orbitals.

### 4.2 Magic numbers

The Lewis octets, corresponding to a formally filled  $ns^2 np^6$  electron configuration, are well-known. Likewise, the 18-electron rule with a formal  $ns^2 np^6 (n-1)d^{10}$ -like configuration at the central atom is well-known; for its history and actual interpretation, see ref. 62. The next step is a 32-electron closed-shell structure around a central atom. Recently, both the predicted Pu@Pb<sub>12</sub><sup>63</sup> or Pu@Sn<sub>12</sub><sup>64</sup> and the experimentally observed U@C<sub>28</sub><sup>65</sup> isoelectronic series were found to form good examples on such 32-electron systems.

To obtain the next, 50-electron magic number, the first chance would be the 6g shell which, however, remains outside the elemental range, studied here.



**Fig. 4** The distances for maximum electron density for the orbitals 7p, 8s, 8p\*, 7d, 6f and 5g for the systems indicated by an 'r' in Tables 2–4. Note that 7p (given by the line) remains the outermost core orbital until about E153.

**Table 5** The decrease of the average radius  $\langle r \rangle$  for the nodeless atomic orbitals from DF calculations. Desclaux's tables for neutral atoms<sup>37</sup> are used for the 1s, 2p, 3d and 4f series. Present data for the 5g examples

Series	Beginning		End	
	Atom	$\langle r \rangle$	Atom	$\langle r \rangle$
1s	H	1.5	He	0.927
2p	B	2.205	Ne	0.964
3d	Sc	1.692	Cu	0.998
4f	Ce	1.041	Lu	0.702
5g	E124 <sup>5+</sup>	0.756	E140 <sup>6+</sup>	0.593

### 4.3 The 7p<sub>3/2</sub> semicore orbital

In the PT, the 5p orbital is filled at Xe and becomes the core orbital of the lanthanides. Similarly, the 6p orbital is filled at Rn and becomes the semicore orbital of the actinides. Although so far not formally oxidized, it can strongly hybridize with the valence orbitals in systems like uranyl or UF<sub>6</sub> (for some references, see ref. 66). We now notice that the 7p<sub>3/2</sub> orbital, filled at E118, remains the largest core orbital up to about E164. It is only slightly more compact than the 8s one, when this becomes permanently occupied around E153. The  $r_{\max}$  values are shown in Fig. 4.

## 5. Ionization potentials and oxidation states

Concerning the possible SHE oxidation states, Jørgensen<sup>67</sup> guessed for E126 an oxidation state of +IV (5g<sup>4</sup>), while

**Table 6** Successive ionization potentials,  $I_n$  (in au) for certain elements. 'Chemically unknown' ionizations are given in italics

Atom	$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$	$I_7$	$I_8$	Source
La	0.20495	0.4064	0.7047	<i>1.836</i>					76
Hf	0.2508	0.55	0.856	1.225					77
Ta	0.290	0.569	0.872	1.36	1.774				78
W	0.2890	0.589	0.950	1.396	1.884	2.377			79
Re							3.0395		80
Os								3.7493	80
Th	0.2318	0.437	0.735	1.058					77
U	0.233	0.411	0.707	1.171	1.711	2.274	3.268		81

Fricke *et al.*<sup>19</sup> thought its normal oxidation state could be as high as +8. Along the series, they expected a reduction to +6 at E132, and to +3 or +4 around E144.

As well-known in the chemical literature (*e.g.* ref. 68 and 69), for electrons removed from the same atomic shell, the ionization potentials  $I_n$  systematically increase. Pyper and Grant<sup>70,71</sup> rationalized this observation considering the atomic integrals involved.

How far along the atomic  $I_n$  sequence can we go in chemical compounds, assuming that the sum of the ionization energies is paid back by combined interionic Coulomb attractions and covalent bonding? Moreover it should be noticed that *e.g.* the Mulliken charges of the central atom can be roughly half of the formal oxidation state. An early example on this rule of thumb were the XeF<sub>*n*</sub>;  $n = 2-6$ , (see ref. 66, Fig. 4).

Experimentally, oxidation states up to +VIII are now known in oxides and fluorides.<sup>72</sup> Himmel *et al.*,<sup>73</sup> suggest gas-phase IrO<sub>4</sub><sup>+</sup> as a possible chemical system with oxidation state +IX. Parenthetically, the octahedral UO<sub>6</sub> has been predicted to exist as a local high-energy minimum.<sup>74,75</sup> It is not really a U(XII) compound, in the sense of oxidizing the 6p semicore levels, and has, moreover, lower-lying peroxido and superoxido isomers.

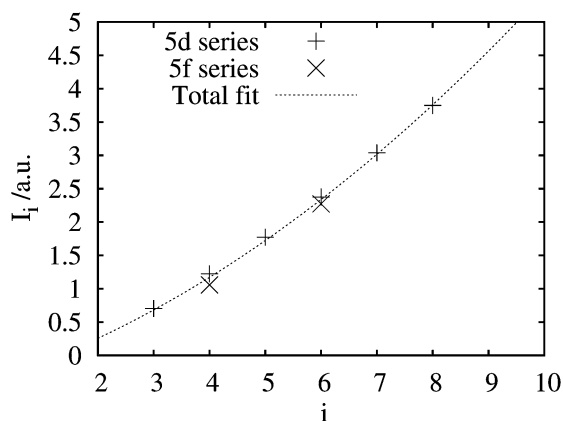
Can we relate the ionization energies,  $I_i$  of the free ions to the maximum oxidation states in compounds? Certain  $I_i$  values are shown in Table 6 and a correlation between the two numbers is shown in Fig. 5. This, rather Gordian, empirical attempt may give some idea of the possible oxidation states, if the  $I_i$  is known.

We then compare some calculated ionization energies for the present SHE in Fig. 6. For the nominal 5g series, the last valence electron is 8s, 6f and 5g for E121–122, E123–124 and E125–126, respectively. The values reach the line of Fig. 5 at  $I_8$ . A further ionization, leading to a 7p<sup>5</sup> configuration, would have a much higher ionization energy, *e.g.* an  $I_7$  of 3.184 au for E124.

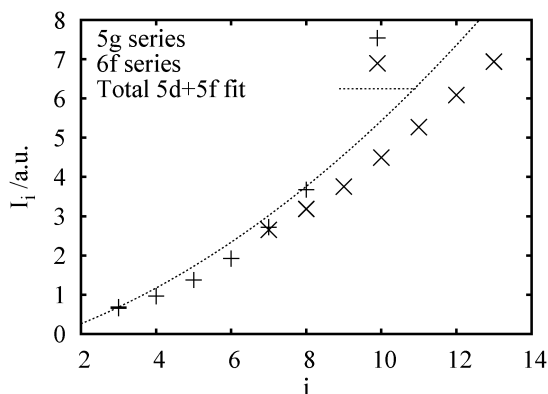
The curve for the higher oxidation state of the 6f series lies below the experimentally known cases, making them also plausible, possibly to some very high  $i$  values, such as  $i = 12$  for the hypothetical (E148)O<sub>6</sub>. A further study would require molecular calculations.

## 6. Multi-shell transition metals?

Taking an example, it is known that the Gd atom ground state is 6s<sup>2</sup>5d<sup>1</sup>4f<sup>7</sup>, with open 5d and 4f shells. For neutral or nearly neutral SHE this also is a common occurrence. Could this occur in compounds, or the present highly-charged ions?



**Fig. 5** The correlation between the free-ion last ionization energies,  $I_i$ , and the maximum known oxidation state,  $i$  for certain  $5d$  and  $5f$  elements. The data are taken from Table 6.



**Fig. 6** A comparison of some present calculated ionization energies with the fit to experimentally known maximum ones in Fig. 5. The '6f' series corresponds to the higher oxidation state.

**Table 7** Some possible molecules, containing the  $5g$ ,  $6f$  and  $7d$  elements E121–E164. X is a halogen, O oxygen

Class	Molecules	Analogues
$8s^0 5g^0$	(E121)X <sub>3</sub> (E122)X <sub>4</sub> (E123)X <sub>5</sub> (E124)X <sub>6</sub> ...	LaX <sub>3</sub> <sup>82</sup>
$8s^0 5g^1$	(E126)O <sub>4</sub> (E125)X <sub>6</sub> <sup>a</sup>	
$8s^2(8p^*)^0 6f^0 5g^{18}$	(E142)X <sub>4</sub> (E144)X <sub>6</sub> (E144)O <sub>2</sub> <sup>2+</sup>	ThF <sub>4</sub> UF <sub>6</sub> UO <sub>2</sub> <sup>2+</sup>
$8s^0(8p^*)^0 6f^0 5g^{18}$	(E144)F <sub>8</sub> (E144)O <sub>4</sub> (E148)O <sub>6</sub> (E142)X <sub>6</sub>	PuF <sub>8</sub> <sup>83</sup> PuO <sub>4</sub> <sup>83</sup> UO <sub>6</sub> <sup>74,75</sup>
$8s^2(8p^*)^0 7d^0 6f^{14} 5g^{18}$	(E158)X <sub>6</sub> (E160)O <sub>4</sub>	WF <sub>6</sub> , SgF <sub>6</sub> OsO <sub>4</sub> , HsO <sub>4</sub>
$8s^0(8p^*)^0 7d^0 6f^{14} 5g^{18}$	(E158)X <sub>8</sub> (E158)O <sub>4</sub>	
$8s^2(8p^*)^0 7d^{10} 6f^{14} 5g^{18}$	(E164)X <sub>2</sub>	HgX <sub>2</sub> <sup>84</sup>
$8s^2(8p^*)^0 7d^8 6f^{14} 5g^{18}$	(E164)X <sub>4</sub>	HgF <sub>4</sub> <sup>84</sup>

<sup>a</sup> Done in ref. 43.

Table 2 has E138<sup>+6</sup> with a low-lying  $6f^1 5g^{13}$  configuration. E140<sup>+6</sup> has a  $6f^1 5g^{15}$  ground state. Thus some  $6f$ – $5g$  overlap may occur in this neighbourhood.

## 7. Possible new molecules

Some characteristic molecules for the presently studied  $5g$ ,  $6f$  and  $7d$  elements are given in Table 7. Their theoretical verification must be left to future quantum chemical studies. The  $5g^0$  cases in the beginning are analogs of lanthanides in the sense of having a compact, inner shell, being filled.

## 8. Conclusions

Based on the present ionic calculations, we have found a way to split the very long row E121–E164 of Fricke *et al.*<sup>19</sup> to the suggested  $5g$ ,  $6f$  and  $7d$  segments, used in the present Fig. 3. Especially the  $6f$  series may possess some very high oxidation states.

While most experimental verifications may take a while, relativistic quantum chemistry could be used to show that *e.g.* (E125)F<sub>6</sub> is indeed  $5g^1$ , as calculated by Makhyoun.<sup>43</sup> It is similarly expected that (E143)F<sub>6</sub> and/or (E145)F<sub>6</sub> would be  $6f^1$  systems, and so on.

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