Beyond Oganesson: Relativistic Effects and the Next Row of the Periodic Table

There is no more ubiquitous—or more instantly recognizable—embodiment of modern chemistry than the periodic table of the elements. The number of chemical elements known has expanded enormously from the 11 of antiquity (C, S, Fe, Cu, As, Ag, Sn, Sb, Au, Hg, and Pb) to 118 today, with elements 119 and 120 having been reported but not yet confirmed unequivocally. Since the pioneering work of H. Moseley at the beginning of the 20th century, atomic number Z has been recognized as the table's fundamental "index" and lies at the heart of the periodic law: when the elements are arranged in order of increasing atomic number, those possessing similar properties appear at regular intervals. But will it always be so? Even as we celebrate the sesquicentennial of Dmitri Mendeleev's seminal contributions, theoretical predictions are converging to suggest that the enlarged periodic table of the not-too-distant future will look quite different.

Foundational to such predictions is (special) relativity. An electron in the vicinity of the nucleus is accelerated to a speed v ever nearer that of light as Z increases, which results in an effectively increased electron mass calculable in terms of the electron rest mass m_0 as

$$m' = \frac{m_0}{\sqrt{1-(v/c)^2}}.$$

The consequences of this relativistic mass increase are most easily appreciated *via* consideration of hydrogen-like species. For a one-electron system, the correspondingly modified Bohr radius

$$a_0' = \frac{4\pi\varepsilon_0\hbar^2}{m'Ze^2}$$

implies a relativistically contracted orbital.[1] The effect is most pronounced for *s* orbitals ($\ell = 0$) as only they give rise to nonvanishing electron density at the nucleus, at least in Schrödinger's treatment. Dirac's relativistic solution for the hydrogen atom indicates more profound changes, however. Most notably in the present context, n^{th}-shell orbitals with the same ℓ value are not necessarily degenerate; the related quantum number j (indicated by the notation $n\ell_j$) emerges as the arbiter of degeneracy instead as suggested in **Figure 1**. Furthermore, all orbitals are nodeless and the $p_{1/2}$ orbitals are remarkably "*s*-like" in that they possess spherical symmetry about the nucleus.[2,3] It is hardly surprising, then, that *p* orbitals (and particularly $p_{1/2}$ orbitals) are also found to contract in a relativistic treatment of the atom. For the multi-electron atoms of considerably greater interest to most chemists, these contractions of the *s* and *p* orbitals beget so-called indirect relativistic effects too: electrons populating these more compact orbitals are more effective in screening *d* and *f* electrons from the nuclear charge, which induces the expansion and energetic destabilization of *d* and *f* orbitals.

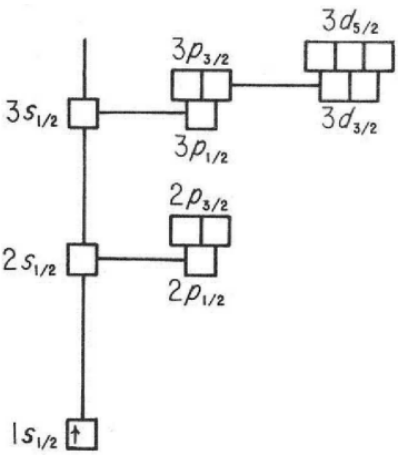

Figure 1. A (partial) aufbau-type diagram for the hydrogen atom according to the Dirac treatment.[2]

Such practical and readily observable properties as the color of gold and the room-temperature liquidity of mercury are now attributed principally to relativistic effects.[4] The "inert-pair effect" encompassing the reluctance of Tl, Pb, and Bi to achieve their respective maximum oxidation states of +3, +4, and +5 is likewise largely relativistic in origin, a consequence of the pro-

nounced stabilization of the 6*s* orbital. The superheavy elements ($Z \geq 104$) are so ephemeral that such bulk physical and chemical properties may never be established. Indeed, despite the formal completion of Period 7 with the 2016 addition of oganesson (Og) to the periodic table, flerovium is the heaviest element studied chemically to date. The half-lives of still heavier elements are too short for chemically relevant investigations even one atom at a time.[5] It falls to the theoretician, then, to examine such systems computationally and offer predictions of their behavior. The preeminence of relativistic effects in this elemental frontier all but ensures a number of distinctive features hitherto unknown as the eighth row of the periodic table is breached.

Oganesson itself poses a challenge to the current table in that its atomic number ($Z = 118$) necessitates its placement with the noble gases. Whether or not Og would actually be gaseous if it could be produced in macroscopic quantity is irrelevant to the table's utility, but chemically the element presents a thornier problem. Relativistic contraction and stabilization of the 8*s* orbital is computed to be so great that oganesson likely has a positive electron affinity, a unique feature among the members of Group 18 and one that would endow Og with decidedly uncharacteristic reactivity.[5,6] On the other hand, flerovium ($Z = 114$) effectively attains nobility earlier in Period 7

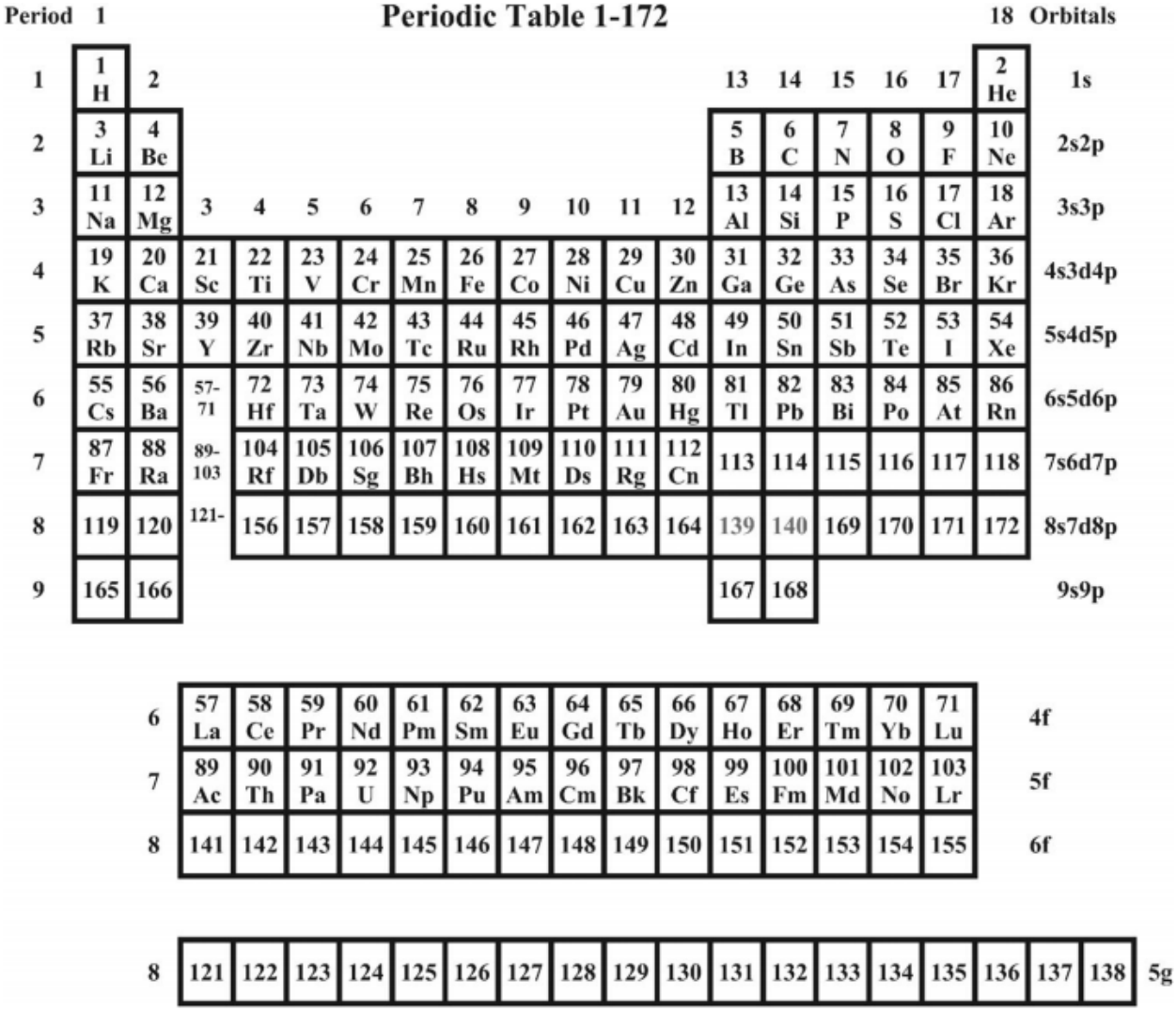

Figure 2. The periodic table extended through element 172 as proposed by P. Pyykkö on the basis of Extended Average Level (EAL) Dirac-Fock calculations.[8]

with the ground-state configuration [Rn]$7s^2 5f^{14} 6d^{10} 7p_{½}^2$; the $7p_{½}$ orbital is sufficiently stabilized relative to the other 7*p* orbitals that its filling amounts to achieving a closed shell.[7]

And what of the new period beckoning just beyond Og? The Finnish theoretical chemist Pekka Pyykkö has updated and expanded computational work dating from the 1970s to construct a recommended periodic table extending through element 172.[8] The predicted order of filling for the new orbitals is as follows:

$$8s < 5g \leq 8p_{1/2} < 6f < 7d < 9s < 9p_{1/2} < 8p_{3/2}.$$

Thus certain novel features manifesting in Period 8 are as anticipated on traditional grounds—the first 18-element *g* series complementing the *s*, *p*, *d*, and *f* blocks, for example. Others challenge the layout of the periodic table, however, as **Figure 2** on the previous page emphasizes. The sequence $8p_{1/2} < 6f < 7d$ mandates placement of elements 139 and 140 as shown therein if they are to be included in the *p* block, but this marks an obvious departure from the practice of displaying elements in order of monotonically increasing *Z*. Additionally, the splitting of the $8p_{1/2}$ and $8p_{3/2}$ orbitals is so large that occupancy of the latter is not expected until after the 9*s* and $9p_{1/2}$ orbitals have been filled. It then becomes necessary to position elements 165-168 in Period 9, deferring completion of Period 8 until element 172 is reached.

Some of Pyykkö's assertions have been questioned in light of more recent computational results—Eliav *et al.* reported that the 5*g* subshell likely won't begin to fill until *Z* = 122 with 5*g*, $8p_{1/2}$, and $7d_{3/2}$ orbitals all lying quite near each other energetically,[9] a situation reminiscent of that responsible for the "anomalous" ground-state configurations of several well-known transition metals. Nevertheless, the likelihood that the present scheme for organizing the periodic table will become untenable is high. Those inclined to dismiss such concerns as merely aesthetic are to be reminded that conformity of some eighth-period elements with their fellow group members will diminish as well. Flerovium's congener may be even less reactive than pseudo-noble flerovium itself, and it has been conjectured that the energetic proximity of multiple high-capacity subshells might give rise to exceptionally high oxidation states.[8] Thus it is fair to assert that, in this International Year of the Periodic Table, superheavy elements known and as-yet unknown are forcing us to confront the probable breakdown of the periodic law itself.

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