

## Elemental Radii

## Atomic and Ionic Radii of Elements 1–96

Martin Rahm,<sup>\*,[a]</sup> Roald Hoffmann,<sup>\*,[a]</sup> and N. W. Ashcroft<sup>[b]</sup>

**Abstract:** Atomic and cationic radii have been calculated for the first 96 elements, together with selected anionic radii. The metric adopted is the average distance from the nucleus where the electron density falls to 0.001 electrons per bohr<sup>3</sup>, following earlier work by Boyd. Our radii are derived using relativistic all-electron density functional theory calculations, close to the basis set limit. They offer a systematic quantita-

tive measure of the sizes of non-interacting atoms, commonly invoked in the rationalization of chemical bonding, structure, and different properties. Remarkably, the atomic radii as defined in this way correlate well with van der Waals radii derived from crystal structures. A rationalization for trends and exceptions in those correlations is provided.

## Introduction

What is the size of an atom or an ion? This question has been a natural one to ask over the century that we have had good experimental metric information on atoms in every form of matter, and (more recently) reliable theory for these same atoms. And the moment one asks this question one knows that there is no unique answer. An atom or ion coursing down a molecular beam is different from the “same” atom or ion in a molecule, or a molecular crystal, or an ionic salt, or a metal.

So long as we are aware of this inherent ambiguity in the concept of “size” of an atom, we can proceed. In doing so we use a method (and associate numerical techniques) as described in the summary at the end of the article. In this work we present atomic radii calculated for elements 1–96. The radii we compute are clearly specified in terms of the electron density. We define (as best as our calculations allow, and quite arbitrarily, even as we offer a rationale) a radius as that average distance from the nucleus where the electron density falls to 0.001 electrons per bohr<sup>3</sup> (0.00675 eÅ<sup>-3</sup>). The criterion is not original with us; the presented data is a revisiting of earlier work by Boyd,<sup>[1]</sup> as will be detailed below.

The definition and estimate of radii which we will use here focuses on the electron density of isolated atoms and ions. We are well aware that the orbital configuration of a free atom may not reflect well the configuration it takes up in a mole-

cule,<sup>[2]</sup> but we prefer to follow through with a consistent picture, one of gauging the density in the atomic ground state.

The attractiveness of defining radii from the electron density is that a) the electron density is, at least in principle, an experimental observable, and b) it is the electron density at the outermost regions of a system that determines Pauli/exchange/same-spin repulsions, or attractive bonding interactions, with a chemical surrounding. We are also interested in a consistent density-dependent set of radii, for the systematic introduction of pressure on small systems by the XP-PCM method,<sup>[3]</sup> which we will report on in the near future. Our aim there is to provide a consistent account of electronegativity under compression.

## History

As we implied, the size of individual atoms or ions is a long-standing issue, with many approaches to their estimation. Eugen Schwarz reminded us that Loschmidt was the first to calculate the diameter of a molecule,<sup>[4]</sup> Experimental estimates of atomic radii began with Lothar Meyer’s periodic curve of atomic volumes,<sup>[5]</sup> followed by early X-ray structure work by Bragg<sup>[6]</sup> and Pauling,<sup>[7]</sup> the atomic volumes derived by Biltz,<sup>[8]</sup> the Wigner–Seitz radius, the Bondi radii (a refinement of Pauling’s values),<sup>[9]</sup> the extensive compilation of Batsanov,<sup>[10]</sup> empirically function-fitted radii,<sup>[11]</sup> and more recently, van der Waals radii obtained from a remarkable statistical analysis of the Cambridge Structural Database (CSD) by Alvarez,<sup>[12]</sup> Islam and Ghosh have also calculated radii based on spectroscopic evaluation of ionization potentials.<sup>[13]</sup>

Theoretical estimates of atomic radii began, to the best of our knowledge, with Slater,<sup>[14]</sup> who, followed by many others, devised sets of radii calculated from the maximum radial density of the outermost single-particle wavefunction, or from the radial expectation values of individual orbitals.<sup>[15–17]</sup> Other approaches use radii defined using potential minima (orbital nodes),<sup>[18]</sup> radii calculated from the gradients of the Thomas–

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Fermi kinetic energy functional and the exchange correlation energy,<sup>[19]</sup> and a DFT–electronegativity-based formulation.<sup>[20]</sup> Calculations invoking a simulated noble gas probe have been used to refine the Bondi radii of main-group elements,<sup>[21]</sup> and to calculate atomic and ionic radii for elements 1–18.<sup>[22]</sup> Calculations of the electronic second moment,<sup>[23]</sup> and periodic trends<sup>[11]</sup> are other ways for the estimation of the size of atoms and molecules.

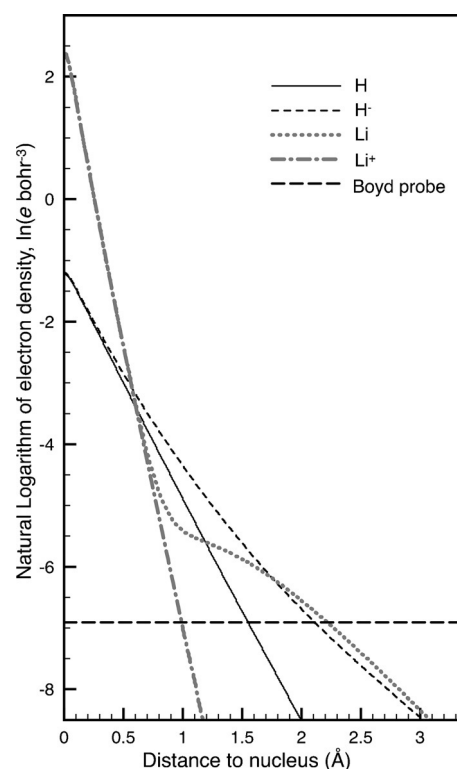
It may be noted that our estimates of radii are very different from average values of powers of  $r$  (such as those tabulated for atoms in the Desclaux tables),<sup>[16]</sup> or from maxima in the radial density distribution. The latter are understandably smaller than those defined by a density cutoff. Each indicator has good reasons for its use, and the various radii complement each other. The ones we discuss clearly address the (in a way, primitive) question of the size of an atom or ion.

In general there are multiple uses for radii in chemistry and physics. Van der Waals surfaces (based on radii) are commonly invoked, together with weak intra- and supra-molecular interactions, for explaining crystalline packing and structure.<sup>[24,25]</sup> Van der Waals surfaces and radii can also be useful descriptors when rationalizing material properties, such as melting points,<sup>[26]</sup> porosity,<sup>[27]</sup> electrical conductivity,<sup>[28]</sup> and catalysis.<sup>[29]</sup> We also have covalent and ionic radii, sometimes differentiated by their coordination number.<sup>[30,31]</sup>

## A density metric for atomic radii

So many radii. Clearly radii for atoms, however defined, are useful. And just as clearly, all such definitions are human constructs, as noted above. We present a set of computed radii for isolated atoms based on a density metric. Because of steady advancement in electronic structure theory over the last 39 years, our radii are markedly different from those originally calculated by Boyd in 1977.<sup>[1]</sup> A further advantage of this set of radii is that they are available for 96 elements; we also complement the radii for neutral atoms with cationic radii and a selection of anionic radii.

Bader et al. were first to propose an electron density cutoff of  $0.002 \text{ ebohr}^{-3}$  as the van der Waals boundary of molecules,<sup>[32]</sup> A limiting electron density value of  $0.001 \text{ ebohr}^{-3}$  was later motivated by Boyd, who showed that the relative radii of different atoms are nearly invariant with further reduction of the cutoff density.<sup>[1]</sup> Figure 1 shows the motivation clearly in another way—it illustrates the computed density (actually its natural logarithm) for some strictly spherical atoms as a function of distance. There are variations to be avoided (see the Li curve) until the density settles down to its expected exponential falloff. The Boyd density cutoff has been used as a practical outer boundary for quantum chemical topology domains.<sup>[33,34]</sup> Other limiting values have been proposed,<sup>[35]</sup> and variable iso-density surfaces have been used for the construction of solvation spheres in implicit solvation models.<sup>[36]</sup>



**Figure 1.** Radial decay of the natural logarithm of the electron density in selected atoms and singly charged ions. The dashed horizontal line marks a density of  $0.001 \text{ ebohr}^{-3}$ .

## The radii

Our calculated radii for the ground state atoms ( $Z=1-96$ ) are shown in two ways. In Figure 2 they are displayed on the periodic table, and in Figure 3 as a plot versus atomic number. Figure 3 also shows the cation radii, which we will discuss in due course.

If we are concerned with quantifying the sizes of non-interacting atoms, one of few relevant experimental comparisons available is with the noble-gas elements. Figure 4 shows how our radii agree with Alvarez's experimental radii obtained from a statistical analysis of 1925 noble-gas containing structures reported in the Cambridge Structural (CSD), Inorganic Crystal Structure (ICSD) and the molecular gas phase documentation (MOGADOC) databases.<sup>[37]</sup> The experimental van der Waals radii for the noble gas elements are a further refinement of Alvarez's original set.<sup>[12]</sup>

The dashed line in Figure 4, of slope 1 and 0 intercept is a pretty good fit.<sup>[38]</sup> Thus the density cutoff criterion choice ( $0.001 \text{ ebohr}^{-3}$ ) is a reasonable one for a situation of little interaction. We might have expected deviations from this line as the atomic numbers of the noble gas elements increase (and the strength of dispersion interactions grow), but only a small deviation—in the expected direction—is seen for Ar, Kr, Xe and Rn.

The radii we present are based on free atom densities. In contrast, most experimentally motivated radii in the literature are based on atoms in a molecular or extended structure,

## Radii of the Elements

Density cutoff is 0.001 e Bohr<sup>-3</sup>  
Radii given in Ångström (1 Å = 1.8897 Bohr)

1																	18	
1	H 1s <sup>1</sup> 1.54															He 1s <sup>2</sup> 1.34		
2	Li 2s <sup>1</sup> 2.20	Be 2s <sup>2</sup> 2.19	<b>Radii of the Elements</b>										B 2s <sup>2</sup> 2p <sup>1</sup> 2.05	C 2s <sup>2</sup> 2p <sup>2</sup> 1.90	N 2s <sup>2</sup> 2p <sup>3</sup> 1.79	O 2s <sup>2</sup> 2p <sup>4</sup> 1.71	F 2s <sup>2</sup> 2p <sup>5</sup> 1.63	Ne 2s <sup>2</sup> 2p <sup>6</sup> 1.56
3	Na 3s <sup>1</sup> 2.25	Mg 3s <sup>2</sup> 2.40											Al 3s <sup>2</sup> 3p <sup>1</sup> 2.39	Si 3s <sup>2</sup> 3p <sup>2</sup> 2.32	P 3s <sup>2</sup> 3p <sup>3</sup> 2.23	S 3s <sup>2</sup> 3p <sup>4</sup> 2.14	Cl 3s <sup>2</sup> 3p <sup>5</sup> 2.06	Ar 3s <sup>2</sup> 3p <sup>6</sup> 1.97
4	K 4s <sup>1</sup> 2.34	Ca 4s <sup>2</sup> 2.70	Sc 4s <sup>2</sup> 3d <sup>1</sup> 2.63	Ti 4s <sup>2</sup> 3d <sup>2</sup> 2.57	V 4s <sup>2</sup> 3d <sup>3</sup> 2.52	Cr 4s <sup>1</sup> 3d <sup>5</sup> 2.33	Mn 4s <sup>2</sup> 3d <sup>5</sup> 2.42	Fe 4s <sup>2</sup> 3d <sup>6</sup> 2.26	Co 4s <sup>2</sup> 3d <sup>7</sup> 2.22	Ni 4s <sup>2</sup> 3d <sup>8</sup> 2.19	Cu 4s <sup>1</sup> 3d <sup>10</sup> 2.17	Zn 4s <sup>2</sup> 3d <sup>10</sup> 2.22	Ga 4s <sup>2</sup> 4p <sup>1</sup> 2.33	Ge 4s <sup>2</sup> 4p <sup>2</sup> 2.34	As 4s <sup>2</sup> 4p <sup>3</sup> 2.31	Se 4s <sup>2</sup> 4p <sup>4</sup> 2.24	Br 4s <sup>2</sup> 4p <sup>5</sup> 2.19	Kr 4s <sup>2</sup> 4p <sup>6</sup> 2.12
5	Rb 5s <sup>1</sup> 2.40	Sr 5s <sup>2</sup> 2.79	Y 5s <sup>2</sup> 4d <sup>1</sup> 2.74	Zr 5s <sup>2</sup> 4d <sup>2</sup> 2.68	Nb 5s <sup>1</sup> 4d <sup>4</sup> 2.51	Mo 5s <sup>1</sup> 4d <sup>5</sup> 2.44	Tc 5s <sup>2</sup> 4d <sup>5</sup> 2.41	Ru 5s <sup>1</sup> 4d <sup>7</sup> 2.37	Rh 5s <sup>1</sup> 4d <sup>8</sup> 2.33	Pd 4d <sup>10</sup> 2.15	Ag 5s <sup>1</sup> 4d <sup>10</sup> 2.25	Cd 5s <sup>2</sup> 4d <sup>10</sup> 2.38	In 5s <sup>2</sup> 5p <sup>1</sup> 2.46	Sn 5s <sup>2</sup> 5p <sup>2</sup> 2.48	Sb 5s <sup>2</sup> 5p <sup>3</sup> 2.46	Te 5s <sup>2</sup> 5p <sup>4</sup> 2.42	I 5s <sup>2</sup> 5p <sup>5</sup> 2.38	Xe 5s <sup>2</sup> 5p <sup>6</sup> 2.32
6	Cs 6s <sup>1</sup> 2.49	Ba 6s <sup>2</sup> 2.93	Lu 6s <sup>2</sup> 5d <sup>1</sup> 2.70	Hf 6s <sup>2</sup> 5d <sup>2</sup> 2.64	Ta 6s <sup>2</sup> 5d <sup>3</sup> 2.58	W 6s <sup>2</sup> 5d <sup>4</sup> 2.53	Re 6s <sup>2</sup> 5d <sup>5</sup> 2.49	Os 6s <sup>2</sup> 5d <sup>6</sup> 2.44	Ir 6s <sup>2</sup> 5d <sup>7</sup> 2.33	Pt 6s <sup>1</sup> 5d <sup>9</sup> 2.30	Au 6s <sup>1</sup> 5d <sup>10</sup> 2.26	Hg 6s <sup>2</sup> 5d <sup>10</sup> 2.29	Tl 6s <sup>2</sup> 6p <sup>1</sup> 2.42	Pb 6s <sup>2</sup> 6p <sup>2</sup> 2.49	Bi 6s <sup>2</sup> 6p <sup>3</sup> 2.50	Po 6s <sup>2</sup> 6p <sup>4</sup> 2.50	At 6s <sup>2</sup> 6p <sup>5</sup> 2.47	Rn 6s <sup>2</sup> 6p <sup>6</sup> 2.43
7	Fr 7s <sup>1</sup> 2.58	Ra 7s <sup>2</sup> 2.92																
6	La 6s <sup>2</sup> 5d <sup>1</sup> 2.84	Ce 6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup> 2.82	Pr 6s <sup>2</sup> 4f <sup>3</sup> 2.86	Nd 6s <sup>2</sup> 4f <sup>4</sup> 2.84	Pm 6s <sup>2</sup> 4f <sup>5</sup> 2.83	Sm 6s <sup>2</sup> 4f <sup>6</sup> 2.80	Eu 6s <sup>2</sup> 4f <sup>7</sup> 2.80	Gd 6s <sup>2</sup> 4f <sup>7</sup> 5d <sup>1</sup> 2.77	Tb 6s <sup>2</sup> 4f <sup>9</sup> 2.76	Dy 6s <sup>2</sup> 4f <sup>10</sup> 2.75	Ho 6s <sup>2</sup> 4f <sup>11</sup> 2.73	Er 6s <sup>2</sup> 4f <sup>12</sup> 2.72	Tm 6s <sup>2</sup> 4f <sup>13</sup> 2.71	Yb 6s <sup>2</sup> 4f <sup>14</sup> 2.77	<b>Element</b> ground state atom configuration <b>Radius</b>			
7	Ac 7s <sup>2</sup> 6d <sup>1</sup> 2.93	Th 7s <sup>2</sup> 6d <sup>2</sup> 2.89	Pa 7s <sup>2</sup> 5f <sup>2</sup> 6d <sup>1</sup> 2.85	U 7s <sup>2</sup> 5f <sup>3</sup> 6d <sup>1</sup> 2.83	Np 7s <sup>2</sup> 5f <sup>4</sup> 6d <sup>1</sup> 2.80	Pu 7s <sup>2</sup> 5f <sup>6</sup> 2.78	Am 7s <sup>2</sup> 5f <sup>7</sup> 2.76	Cm 7s <sup>2</sup> 5f <sup>7</sup> 6d <sup>1</sup> 2.64										

Figure 2. Calculated radii of elements 1–96. The ground state configurations of the atoms are shown in small print.

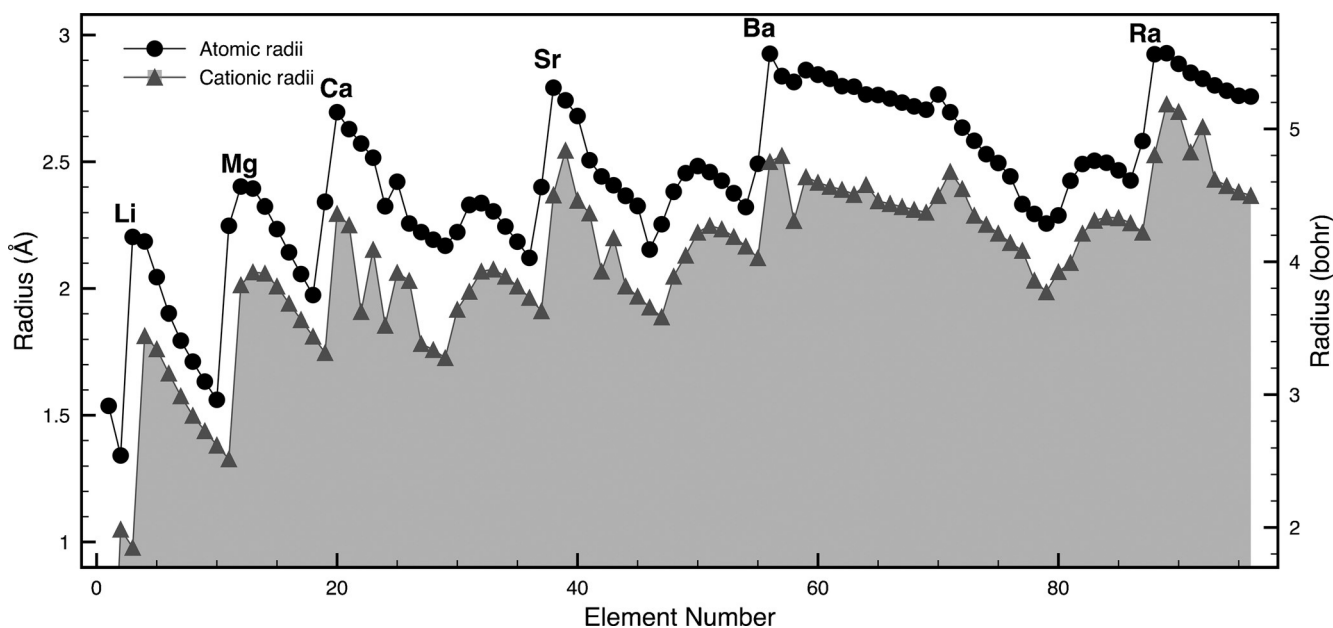
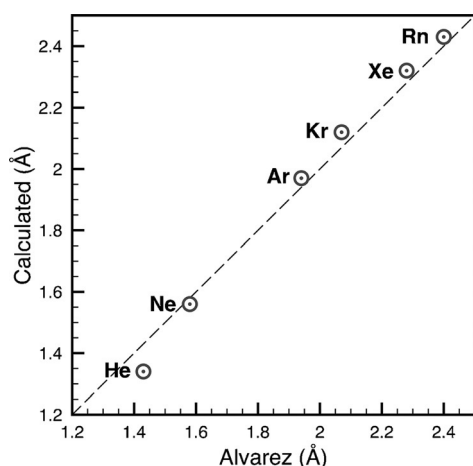


Figure 3. Atomic and mono-cationic radii versus element number.

often in a crystal. Brought up to another atom, even one as innocent of interacting as He or Ne, our reference atom will experience attractive interactions, at the very least those due to dispersion. If the atom has electrons available for covalent bonding, that bonding, of course, will bring it closer to other atoms. If already bonded to another atom, the electron density on the reference atom may be enhanced or reduced by bond polarity, and so an ionic component may enter to reduce its distance to other atoms. These modifications to the radii will

be explored. Thus, in a chemical environment, for most other situations aside from the noble gas elements, we expect smaller interatomic distances than those shown in Figure 2, due either to binding, ionicity, or dispersion interactions.

Graphite is one of many telling examples of how the distances in real materials may deviate from those implied by the atomic radii calculated here: The intersheet separation between individual graphene layers is 3.35 Å, leading to an experimental van der Waals radius of 1.68 Å, in excellent agree-



**Figure 4.** Comparison between experimentally obtained van der Waals radii of the noble-gas elements and those as calculated here. Alvarez's radius for Rn is an empirical estimate. Dashed line shows  $y=x$ . To convert to bohr,  $1 \text{ \AA} = 1.8897 \text{ bohr}$ .

ment with the Alvarez radius of carbon (1.67 Å). Considering that the exfoliation energy of graphite has been experimentally estimated as  $52 \pm 5 \text{ meV/atom}$ <sup>[39]</sup> and calculated as  $66 \text{ meV/atom}$ <sup>[40]</sup> we know that the radius of 1.68 Å, half the spacing between graphite layers, is the consequence of significant dispersion interactions. Our calculated radius for carbon, 1.90 Å, compares better with half the inter-sheet distance in graphite if dispersion interactions were omitted, that is, if the sheets truly were non-interacting. When crystalline graphite is calculated using DFT with and without a dispersion correction, PBE + B3(BJ), half the distance between sheets comes out as 1.68 and 2.11 Å, respectively, illustrating the effect of dispersion.

## Comparison with van der Waals radii based on structures

The correspondence of the atomic radii emerging from this simple density criterion with noble gas crystal structures make it evident that for other elements we should look for a correlation with van der Waals radii, and not the much smaller cationic crystal radii, or covalent, or metallic radii. The calculated radii of the neutral atomic elements show a good linear correlation with the 61 crystallographic van der Waals radii compiled by Batsanov.<sup>[10]</sup> The coefficient of determination ( $r^2$ ) is 0.876, provided that Li, Na, K, Rb, and Cs are omitted (see the Supporting Information). Our radii are, on average, 28% larger than those reported by Batsanov.

The agreement with the more comprehensive list of 89 van der Waals radii derived by Alvarez is good (see the Supporting Information);  $r^2$  is 0.769 when all of Alvarez's elements are considered, and 0.856, if the alkali metals are omitted. The absolute average deviation between our calculated radii and the crystallographic radii of Alvarez is negligible; our radii are on average smaller by 0.01 Å (Supporting Information, Figure S1), which corresponds to an average difference of only 0.5% overall. The corresponding standard deviation is +0.21, or 0.16 Å if Group 1 elements are omitted. Slightly larger relative radii

(compared to crystallographic ones) are calculated here for lighter p-block elements, and some deviations are seen in the d-blocks where a few elements show dramatic changes in atomic valence orbital occupation, which affects the radii (Supporting Information, Figure S1).

The relative size given by our radii for Group 1 and 2 atoms is at variance with the Batsanov and Alvarez orderings, which lists alkali metal atoms as larger. Furthermore, in almost all crystal structures studied, Group 16 and 17 atoms are anionic, and Group 1 and 2 atoms are positively charged, both trends a consequence of electronegativity. Even though we are not dealing with ionic radii, but with van der Waals ones, we expected the deviations from the correlation of our radii with those extracted from crystal structures to be in the direction that for Group 1 and 2 our radii would be "too big", and for Groups 16 and 17 "too small". As Figure S1 in the Supporting Information shows, this is the opposite of what happens.

With the exception of Li and Be, predicted to be roughly the same size, our computed Group 1 radii consistently come out smaller than those of the neighboring Group 2 atoms.

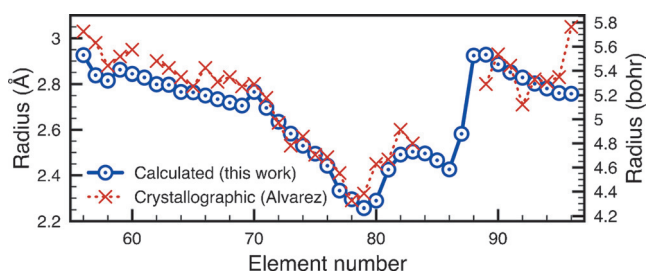
There is a possibility that by relying solely on the density we are, in fact, underestimating the Group 1 atom radii. The reason that the outermost electron density can be assumed a good measure of the size of an atom is because it relates<sup>[41]</sup> to the Pauli (or same-spin) repulsion that the density feels in proximity to other atoms (with electrons of same and opposite spin). The electron density in the tail of Group 1 atoms is special in this sense, because it arises from only one s-electron, which is isolated or separate relative to same spin-counterparts. Same-spin loneliness is one measure of electron localization,<sup>[34]</sup> and can be viewed as the primary cause behind steric strain in and between molecules. This qualitatively explains how a given outer electron density in Group 1 atoms can generate a larger repulsion toward the electrons of neighboring atom, compared to the same (mixed-spin) density of other atoms. The difference in the density cutoff required for the same Pauli repulsion translates to an underestimation of Group 1 radii by the criterion we adopted.

The variations that we have just focused on are, in a balanced analysis, minor ones. The remarkable fact remains in that atomic radii estimated by a simple density fall-off criterion, and that assumed to be the same for all elements, correlate very well with experimental estimates on van der Waals radii. For example calculated radii of the heavier elements, including all f-block elements, show an overall excellent agreement with Alvarez's van der Waals radii obtained from crystal structures (Figure 5 for  $Z=56-96$ ). Our radii can therefore offer a complement to experiment, for elements where no data is currently available.

## Trends and partial explanations

The well-known contraction of the d- and f-block element atoms is clearly seen (Figure 2 and 3). So is a relative contraction, equally expected with increase in the nuclear charge, that is, poorer shielding, as one moves across the main group; the noble-gas elements, followed by the halogens, are the smallest





**Figure 5.** Comparison with Alvarez crystallographic van der Waals radii for the heavier elements 56–96.

p-elements of each row. Distinct contractions of Cr and Pd atoms, relative to their respective nearest neighbors, are also seen. A sharp decline in radii from Hf, Ta→W marks the onset of record mass densities, and a linear correlation between radii and densities is seen for Hf→Os ( $r^2=0.983$ ).

The Group 2 atoms all have large radii, and largest of all elements is Ba. Its radius of 2.93 Å is a consequence of a diffuse outer  $6s^2$  shell exceedingly well screened by the [Xe] core below. The radii of the Ba, Sr, and Ra atoms, are, in fact, larger than any of the anion radii we have considered (see next section), such as  $I^-$  (2.59 Å) or  $Au^-$  (2.55 Å). Relativistic effects are partially responsible for certain decreases in radii when going down the periodic table, for example in comparing Ba (2.93 Å) with Ra (2.92 Å), and Cd (2.38 Å) with Hg (2.29 Å).

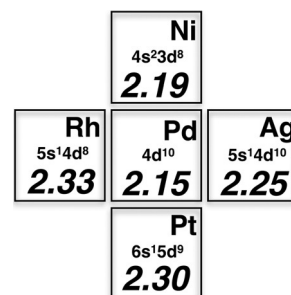
In addition to the contraction of d- and f-elements arising from relativistic effects, overall trends in our radii, including apparent anomalies, can be rationalized from a simple rule of thumb: Frontier levels corresponding to lower azimuthal quantum numbers ( $l=s < p < d < f$ ) exhibit slower radial decays at long distances from the nucleus. In other words, occupied s-levels have a greater spatial extent (measured by a density fall-off, not by radial maxima) than comparable p-levels, which have a slower radial decay than d-levels, and so on. This is certainly so for hydrogenic wavefunctions, and has been emphasized in previous work.<sup>[42,2]</sup>

One simple way to think about this  $l$ -dependence is to note that for a given principal quantum number  $n$ , the highest  $l$  ( $=n-1$ ) orbital has no inner levels of same  $l$  to remain orthogonal to, the next lower  $l$  value ( $l=n-2$ ) has one core level to remain orthogonal to. And so on. The net result is that the electron density in the low  $l$  level (for a given  $n$ ) is “forced” further out from the nucleus. Because valence levels of lower  $l$  are important, but not completely determining, in governing the outermost density, a relative increase in the number of electrons corresponding to the highest  $l$  value, everything else being equal, decreases the radius of an atom.

By way of example, a relative decrease of s-occupation helps to explain the successive contraction in the first rows of the main group: for example, Be( $[He]s^2p^0$ ), that is, 2.19 Å→Ne( $[He]s^2p^6$ ), that is, 1.56 Å. In each case (Be vs. Ne), the “outermost” atomic density is of 2s-type. But in Ne there is a larger effective nuclear charge acting on the 2s orbital, because of imperfect screening of the nuclear charge by the 2p electrons. Similar trends of decreasing radii are seen across the d- and f-

blocks, albeit to a lesser extent. For the heavier main group elements additional p-levels instead increase the radii initially, as the relative contribution of more contracted d-levels diminishes. A somewhat special case is the filling of the first f-shell in Yb, which results in an increase in its radius. This is a consequence of an increased nuclear shielding of the outermost 6s shell by the completed 4f core.

An example of a distinct, yet expected, “anomaly” already mentioned from d-block, is Pd. The radius of Pd( $[Kr]5s^04d^{10}$ ), that is, 2.15 Å, is significantly smaller than either of its vertical neighbors Rh( $[Kr]5s^14d^9$ ), 2.33 Å and Ag( $[Kr]5s^14d^{10}$ ), 2.25 Å, and its horizontal neighbors Ni( $[Ar]4s^23d^8$ ), 2.19 Å and Pt( $[Xe]6s^15d^9$ ), 2.30 Å. By the rule of thumb mentioned, this contraction arises from the  $[Kr]5s^04d^{10}$  electronic configuration, which is different from all neighboring elements, which have either one or two 5s electrons (Figure 6). The Pd-anomaly is seen clearly experimentally,<sup>[12]</sup> which is interesting since one should not necessarily expect the ground state electronic configurations of isolated atoms to guide the behavior in a chemical environment.<sup>[43]</sup>

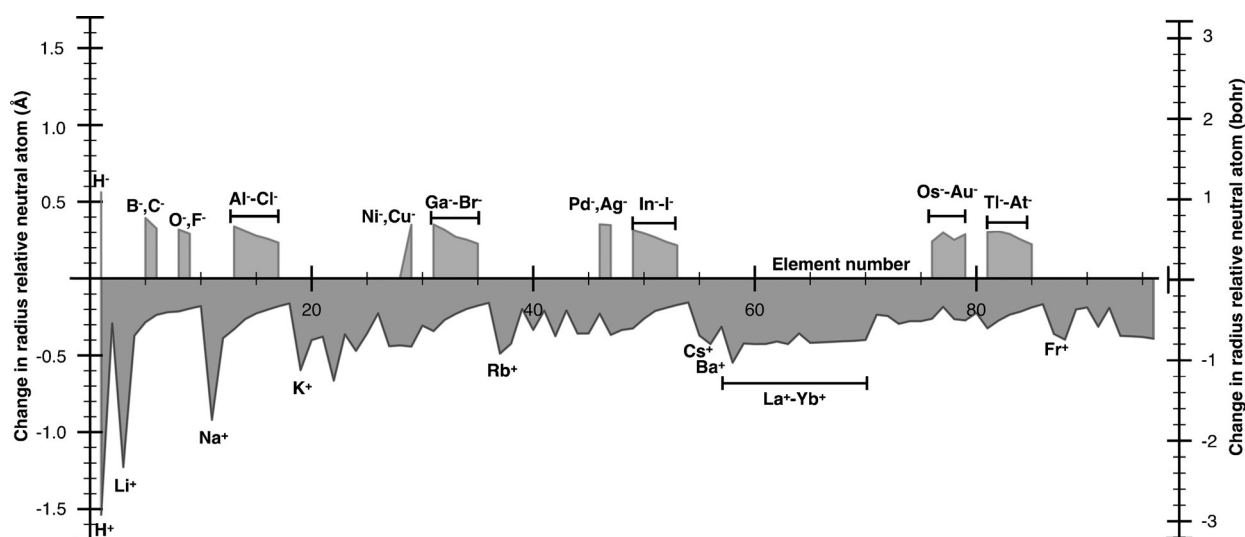


**Figure 6.** The small atomic radius of Pd, relative to all its neighbors in the Periodic Table, is a consequence of its outermost electron density deriving predominantly from d-levels, instead of s-levels.

Another similarly “anomalous” example from the d-block is Cr( $[Ar]4s^13d^5$ ), 2.33 Å, which calculates as smaller than its nearest neighbors V( $[Ar]4s^23d^3$ ), 2.52 Å and Mn( $[Ar]4s^23d^5$ ), 2.42 Å. This difference can be understood a consequence of the 4s frontier orbital of Cr, each d-sublevel being singly occupied.

## Cations and anions

Figure 3 also includes cationic radii for all investigated atoms. Another way to show the effect of charge is to display the change in radius on making a positive or negative ion of a given element. Figure 7 show the relative radial contractions in cations, along with a selection of relative expansions when atoms form anions (where these can be reliably calculated). Anionic radii are generally less common in the literature, but tabulations do exist.<sup>[17,22,30,43]</sup> The comparison may prove valuable when rationalizing the behavior of atoms in molecules with the atoms assigned different formal charges, with full awareness that in real molecules or extended structures any formal charges will be effectively “screened” by other electrons.



**Figure 7.** Radial expansion and contraction of an element upon electron uptake (top) and ionization (bottom). Anionic radii are provided for elements with sufficient electron affinity (EA) provided that our calculations are within 0.3 eV of the experimental EAs (NIST). Exceptions still tabulated are Pt, Au, and Pb where calculated EA's deviate approximately 1 eV from experiment (but remain positive).

The obvious expectation that radii of anions  $>$  neutrals  $>$  cations is confirmed throughout. Whereas the radial expansion upon electron attachment is fairly constant among the species investigated, namely 0.25 to 0.40 Å, the relative contraction upon ionization is greater for the lighter elements of Groups 1 and 2. The radii of the f-block elements are all similarly affected, and contract by around 0.4 Å.

Hydrogen, always different, merits special mention. Its cationic radius is zero, its anionic radius (2.10 Å) is also significantly larger than the neutral radius (1.54 Å), and intermediate between those of  $F^-$  (1.92 Å) and  $Cl^-$  (2.29 Å). This is in qualitative agreement with hydrides occupying large volumes in the condensed phase (often compared in size to fluorides). Partially positively charged hydrogen is predominant in molecular systems, some of these (HF is an example) forming polarized molecular crystals.

In an effective enhancement of a trend already mentioned for the neutral p-block elements, the cationic radii of  $Tl^+ < Pb^+ < Bi^+$  show a more clearly reversed trend compared to the corresponding (isovalent-electronic) lighter series; the radii of  $B^+ > C^+ > N^+$ .

## Conclusions

Atomic and cationic radii for free atoms and monovalent (and select mononegative) ions of the elements,  $Z=1-96$ , have been computed using the identical metric adopted for all atoms, that is the average distance from the nucleus where the electron density falls to 0.001 electrons per bohr<sup>3</sup>. Electron densities were obtained from all-electron relativistic density functional theory calculations close to the basis set limit.

There is a reasonable, actually a remarkably good, correlation between theoretical radii so defined with the van der Waals radii obtained from crystal structures. When we started out, we didn't expect such a good correlation as Figures 4, 5

and S1 (Supporting Information) show. And even after we saw the correlation for the noble gas atoms and crystal structures, it was not at all obvious that a  $\rho(r)=0.001$  ebohr<sup>-3</sup> marker would be good for estimating van der Waals separations across the periodic table. But it is. The reasons for discrepancies, such as those of alkali metal atoms, are discussed. As expected, the cation radii are smaller, and the anion radii calculated larger, than those of the neutral atoms.

## Computational methods

The radii we show have been derived using all-electron relativistic DFT calculations on the atomic ground states of elements 1–96. The “parameter free” PBE density functional of Perdew, Burke, Ernzerhof, made into a hybrid-exchange correlation functional by Adamo (PBE0)<sup>[45]</sup> was used, together with the very large and uncontracted atomic natural orbital-relativistic correlation consistent (ANO–RCC) basis set.<sup>[45]</sup> ANO–RCC was specifically designed for relativistic calculations, for which we used the Douglas–Kroll–Hess second-order scalar relativistic Hamiltonian.<sup>[46]</sup> Our calculations do not extend beyond element 96 because the ANO–RCC basis set is not available for the last elements. Average radii were calculated from atomic volumes obtained by analyzing electron densities on 125  $\mu\text{bohr}^3$  (18.5  $\mu\text{Å}^3$ ) grids, on which all grid points with a density below 0.001 ebohr<sup>3</sup> were discarded. The grids of all atoms except those in Groups 1, 2 and 18 are non-spherical, with some well-understood examples from other groups, for example, 7. The protocol we adopted allows for the estimation of average radii also for non-spherical charge densities with respect to axes originating fixed in atoms. An alternative to our DFT-based approach that would do away with the need of integrating the charge densities of non-spherical ground states is to do state-averaged multireference calculations (i.e. average the density of degenerate non-spherical states). The computa-

tional cost associated with such non-trivial calculations are great, and considering our planned future DFT-based XP-PCM implementations of our radii, we have not pursued such refinements.

Because electron correlation introduces only a second-order correction to the Hartree–Fock electron density,<sup>[47]</sup> radii calculated from such mean-field derived densities are, in fact, expected to be close to those derived from the exact electron density. DFT includes correlation effects in the orbitals, which improves the density, yet a majority of radii calculated with Hartree–Fock and with DFT are nearly indistinguishable.

Because the Be (<sup>1</sup>S<sub>0</sub>) ground state contains a large fraction of non-dynamic correlation we used this atom to test the sensitivity of our calculated radii with respect to the level of theory. Complete Active Space Self-Consistent Field CASSCF(2,4)/ANO-RCC calculations, including the 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals in the valence space, provided a radius of 2.178 Å, very close to the 2.186 Å obtained with PBE0. PBE0, in turn, offers a slight improvement from the 2.207 Å radius calculated at the Hartree–Fock level (see the Supporting Information).

The real advantage of DFT is that it allows for correct frontier orbital occupancy in difficult cases such as Mn, Cu, Gd, and Cm. We have confirmed the correct valence orbital occupation of all natural and cationic species by comparing to experimentally known ground states available on the NIST Atomic Spectra Database (NIST = National Institute of Standards and Technology). The electronic configurations of anions were assumed identical to next larger neutral atomic element.

All atomic calculations were carried out with Gaussian 09, revision C.01.<sup>[48]</sup> Grid-based volume integrations of the electron densities were performed using the algorithm of Tang, Sanville, and Henkelman.<sup>[49]</sup> Extended calculations on graphite were performed using the Vienna Ab initio Simulation Package, version 5.3.5,<sup>[50,51]</sup> using the PBE<sup>[52]</sup> functional. The standard projected augmented wave (PAW) potential<sup>[51,53]</sup> of carbon was used together with a plane-wave kinetic energy cutoff of 1200 eV, and a 15 × 15 × 3 *k*-point mesh. Energies and their gradients were converged to < 1 meV per atom. Dispersion interactions were included using the D3(BJ)<sup>[54]</sup> correction.

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