Consistent van der Waals Radii for the Whole Main Group

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Atomic radii are not precisely defined but are nevertheless widely used parameters in modeling and understanding molecular structure and interactions. The van der Waals radii determined by Bondi from molecular crystals and data for gases are the most widely used values, but Bondi recommended radius values for only 28 of the 44 main-group elements in the periodic table. In the present Article, we present atomic radii for the other 16; these new radii were determined in a way designed to be compatible with Bondi's scale. The method chosen is a set of two-parameter correlations of Bondi's radii with repulsive-wall distances calculated by relativistic coupled-cluster electronic structure calculations. The newly determined radii (in Å) are Be, 1.53; B, 1.92; Al, 1.84; Ca, 2.31; Ge, 2.11; Rb, 3.03; Sr, 2.49; Sb, 2.06; Cs, 3.43; Ba, 2.68; Bi, 2.07; Po, 1.97; At, 2.02; Rn, 2.20; Fr, 3.48; and Ra, 2.83.

1. Introduction

van der Waals radii, as tabulated by Bondi,[1] have been used for a wide range of applications.[2–10] Bondi radii result from a refinement of the work of Pauling,[11] who determined standard values of atomic radii from contact distances between nonbonded atoms in molecular crystals. Although one may question the choices of data used by Bondi[12] and although he did not have the same kind of data available for all elements that he considered, the accuracy of Bondi's radii was later confirmed by Gavezotti[13] and Rowland and Taylor,[14] who compared Bondi radii to contact distances for small organic molecules from the Cambridge Structural Database.[15]

The concept of a van der Waals radius is intrinsically approximate because atoms in molecules are not spherical, whereas assigning them a single radius implies a spherical model. Bondi radii are based on molecular crystals, and Allinger[16] pointed out that Bondi radii are "distances of closest approach" that are shorter than gas-phase equilibrium distances. Bondi's van der Waals radii represent average or typical values, and they cannot be equated precisely to a distance that can be uniquely defined in terms of potential energy surfaces for any specific system. Numerous authors[17–19] have since observed that the contact distance between atoms Z and Y varies as a function of the angles between the Z···Y axis and the bonds at Z and Y. Those authors[17–19] also observed that Z···Y contacts that are off of the bond axes are typically longer than those along the bond axes, and Nyburg[19] further observed that some of Bondi's radii are much closer to the off-bond-axis contact distances.

Despite the various caveats that may be made, Bondi's values for the van der Waals radii are certainly very reasonable, the best argument for which is that they have been found useful for an inordinately large number of applications by later workers. The value for hydrogen atom has, however, been found to be problematic. Rowland and Taylor,[14] taking advantage of the large amount of additional crystal data that have been accumulated since Bondi's study, made a systematic analysis of intermolecular contact distances in organic crystals and redetermined the values of the van der Waals radii. They found that Bondi's values were consistent with the new data with the single exception of hydrogen, for which they suggested lowering the van der Waals radius from 1.2 to 1.1 Å. Bondi's value of 1.2 Å describes well the size of H in H···H contacts, but for interactions with other elements, the smaller value is more appropriate. Bondi had drawn similar conclusions, but he favored using the higher value as a standard. We accept the Rowland−Taylor recommendation for H.

Given the importance of van der Waals radii, their prediction has been the subject of many different approaches. These approaches include radii based on the minimum in potential energy curves,[20,21] Slater-type orbitals,[22–24] isodensity surfaces of the atomic wave function,[25–27] de Broglie wavelengths,[1] other computed properties,[28] and periodic trends.[29] In this Article, another approach is presented. The new method is based on gas-phase complexes of the elements with a probe, and it is designed such that, for main-group elements for which Bondi proposed a radius, the new method yields a value in good agreement with that radius.

Some considerations, including the level of theory and basis set, involved in choosing the method to reproduce Bondi's radii are given in section 2. Section 3 then presents the calculations that lead to the final correlations along with the 16 newly determined radii. Combining these with Rowland and Taylor's recommendation for H and Bondi's recommendations for the other 27 main-group elements leads to a consistent set of van der Waals radii for all main-group elements. Because the present Article is solely concerned with main-group elements, neither the transition metals (Ni, Cu, Zn, Pd, Ag, Cd, Pt, Au, Hg) nor the actinide (U) discussed by Bondi are addressed; however, if we combine his radii for these elements with the 44 main-group radii, we have a consistent set of radii for 54 elements.

2. Methodology

Our calculations of van der Waals radii begin with the calculation of ground-state potential energy curves for the interaction of an atom with a probe. Because the van der Waals

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TABLE 1: van der Waals Radii (in Å) Determined with Ne Probes by Using CCSD(T) with Three Basis Sets, As Compared to One Another and to Experiment[a]

	1	2	13	14	15	16	17	18
	H							He
SDD (MWB)[b]	1.75							1.43
MG3[c]	1.81							1.32
ANO-RCC[d]	1.66							1.33
experiment[e]	1.68							1.31
	Li	Be	B	C	N	O	F	Ne
SDD (MWB)[b]	3.68	2.66	1.52	1.31	1.55		1.10	1.40
MG3[c]	2.97	2.19	1.64	1.31	1.61	1.10	1.20	1.34
ANO-RCC[d]	3.20	2.41	1.70	1.30	1.62	1.37	1.18	1.40
experiment							1.19[f]	1.39[g]
	Na	Mg	Al	Si	P	S	Cl	Ar
SDD (MWB)[b]	3.95	3.18	2.31	1.61	2.63	2.21	1.81	1.79
MG3[c]	2.56	2.37	1.86	1.54	2.05	2.18	1.57	
ANO-RCC[d]	3.27	2.71	2.03	1.61	2.14	1.83	1.59	1.74
experiment						1.83[h]	1.60[i]	

[a] The calculations in this table do not include relativistic effects or counterpoise corrections. For this table, the choice of which orbitals to correlate follows the top scheme in Table 3 except for Si, for which the 2p orbitals were correlated for this table. [b] The large-core variant of the MWB basis set.[37–40] [c] The MG3 basis set[41–45] is equivalent to a 6-311++G(3d2f,2df,2p) basis for H−Si, and it corresponds to an improved 6-311+G(3d2f) basis for P−Ar. [d] Atomic natural orbital−relativistic correlation consistent (ANO-RCC) basis set.[46–48] [e] For H, the accurate value is taken as a distance of 3.07 Å for Ne−H (ref. 50a) minus 1.39 Å for Ne. For He, the accurate values is based on refs. 50b, 50c. [f] Ne−F data from Becker et al.,[52] with the neon radius from Farrar et al.[51] [g] Ne−Ne data from Farrar et al.[51] [h] Ne−S data from Aquilanti et al.,[53] with the neon radius from Farrar et al.[51] [i] Ne−Cl data from Aquilanti et al.,[54] with the neon radius from Farrar et al.[51]

radius is a characteristic of nonbonding interactions, the probe is required to be a closed-shell singlet, such as Ne or a closed-shell molecule. We found that molecules give van der Waals radii that correlate better with Bondi's values, so our final method is based on molecules, in particular HF approaching the atom collinearly with H toward the atom, HF approaching the atom collinearly with F toward the atom, and CH_4 approaching the atom along the bisector of an H−C−H bond (thus the vector from C to the atom is normal to a line connecting two of the hydrogens). However, our calculations of probe radii and our decisions about the treatment of core electrons and basis sets are based on Ne probes, and so we will consider Ne probes as well.

As mentioned in the Introduction, Bondi's van der Waals radii are more closely associated with the distance of closest approach than with the equilibrium distance in the gas phase, and so we will define them in the present Article on the basis of the classical distance of closest approach. The distance to which two systems will approach depends on their kinetic energy and impact parameter, and we assume zero kinetic energy and zero impact parameter, as explained next. In the ground state, as the probe approaches the atom, the potential energy, relative to the probe infinitely separated from the atom, becomes negative, and then it becomes positive as the subsystems approach more closely. The distance at which the potential energy passes through zero is the distance of closest approach in a head-on collision in the limit where the kinetic energy tends to zero. It is called the repulsive wall distance and is, by the definition used here, equal to the sum of the van der Waals radius of the probe and the van der Waals radius of the atom. The van der Waals radius of an atom of element Z is called σ_Z.

The van der Waals radius of neon was determined first, by considering the neon dimer, for which σ_{Ne} is one-half of the repulsive wall distance. Next, we considered the interaction of the other probes with Ne. Because the Ne radius has been determined, it can be subtracted from the sum of the van der Waals radii, and that yields the Ne-probe van der Waals radius of the probe.

In the case of atoms in the boron group, carbon group, chalcogens, and halogens, the outer p subshell is partially occupied. There are two possible directions of approach of a probe to the same atomic configuration of the atom, the state where the probe approaches the least filled p-orbital and the state where it approaches the most filled p-orbital. We found that the former is the ground state for approach by Ne or by the F atom of HF, whereas the latter is the ground state for approach by the H atom of HF or by methane.

The interatomic potential for each complex was initially mapped using single-point energies spaced at ~0.2 Å intervals, and then the region around the repulsive wall distance was refined until the location of the repulsive wall (i.e., the zero of the potential) was determined to a sufficient precision.

The prediction of accurate nonbonding potentials in the gas phase is sensitive to the choice of theory; the effect of this level upon predicted dimer properties has been the subject of extensive research. (See Ruette et al.[30] for a bibliography of theoretical papers on computing gas-phase dimer properties.) It has been consistently found that use of a large enough basis set and coupled cluster theory with single and double excitations and a quasi-perturbative treatment of connected triple excitations, called CCSD(T), reproduces experimental dimer properties quite well.[31–35] The calculations presented in this Article were all carried out at the CCSD(T) level using the MOLPRO[36] computer program.

The choice of basis set[37–48] can have a significant effect upon the accuracy of calculated nonbonding interactions. Table 1 shows results obtained with three different basis sets. Our final choice was the atomic natural orbital-relativistic correlation consistent (ANO-RCC)[46–48] all-electron basis set. The ANO-RCC basis set was obtained from the MOLCAS basis-set library[49] and converted into a format that can be used by MOLPRO.[36] Table 1 shows that the ANO-RCC basis set gives results that are within 0.02 Å of the experimental repulsive wall distances[50–54] when they are available.

Generally, it is not necessary to correlate all electrons. If one arranges the electrons into shells with a given principal quantum

TABLE 2: Effect of Correlating 3d Core Orbitals upon Computed van der Waals Radii (in Å) Where the 3d Orbitals Are Correlated or Frozen, the [Ar] Core Is Frozen in Either Case, and the 4s and 4p Subshells Are Correlated[a,b]

basis set	Ga	Ge	As	Br	Kr
frozen 3d	1.98	1.62	2.26	1.78	1.91
correlated 3d	1.88	1.56	2.20	1.72	1.89

[a] CCSD(T)/ANO-RCC with Ne probe without relativistic effects and counterpoise correction. For this table, the choice of which orbitals to correlate follows the top scheme in Table 3 unless specified (e.g., correlated 3d). [b] The Ne probe radius used for this table is 1.399 Å, from CCSD(T)/ANO-RCC without relativistic effects and also without counterpoise correction.

TABLE 3: Correlated and Uncorrelated Orbitals for Main-Group Elements

	uncorrelated orbitals	correlated orbitals
In the Scheme Used To Develop ANO-RCC		
H−He		1s
Li−Be		1s2s
B		1s2s2p
C−Ne	[He]	2s2p
Na	[He]	2s2p3s
Mg	[He]2s	2p3s
Al	[He]2s	2p3s3p
Si−Ar	[Ne]	3s3p
K	[Ne]	3s3p4s
Ca	[Ne]3s	3p4s
Ga−Ge	[Ar]	3d4s4p
As−Kr	[Ar]3d	4s4p
Rb−Sr	[Ar]3d4s	4p5s
In−Xe	[Kr]	4d5s5p
Cs−Ba	[Kr]4d5s	5p6s
Tl−Rn	[Xe]	5d6s6p
Fr−Ra	[Xe]5d6s	6p7s
In the Scheme Used in Tables *4−11*		
H−He		1s
Li−Be		1s2s
B−Ne	[He]	2s2p
Na−Mg	[He]	2s2p3s
Al−Ar	[Ne]	3s3p
K−Ca	[Ne]	3s3p4s
Ga−Kr	[Ar]	3d4s4p
Rb−Sr	[Ar]3d	4s4p5s
In−Xe	[Kr]	4d5s5p
Cs−Ba	[Kr]4d	5s5p6s
Tl−Rn	[Xe]	5d6s6p
Fr−Ra	[Xe]5d	6s6p7s

TABLE 4: Effect of Including Scalar Relativistic Effects by the Douglas−Kroll (DK) Hamiltonian upon Computed van der Waals Radii (in Å)[a,b]

	Ga	Ge	As	Br	Kr
nonrelativistic	1.88	1.56	2.20	1.72	1.89
relativistic (DK)	1.84	1.52	2.19	1.70	1.87

[a] CCSD(T)/ANO-RCC with Ne probe without counterpoise corrections; 3d orbitals are correlated and [Ar] core is frozen following the bottom scheme in Table 3. [b] The Ne probe radius used for this table is 1.399 Å for nonrelativistic calculations and 1.401 Å for relativistic calculations, from CCSD(T)/ANO-RCC calculations without counterpoise corrections.

TABLE 5: Effect of Counterpoise Correction on van der Waals Radii (in Å)[a,b]

	K	Ca	Ga	Ge	As	Se	Br	Kr
without CpC	4.32	3.30	1.84	1.52	2.19	1.90	1.70	1.87
including 1/2CpC	4.34	3.33	1.85	1.53	2.21	1.93	1.72	1.89

[a] CCSD(T)/ANO-RCC+DK with Ne probe. [b] The Ne probe radius used for this table is 1.401 Å without CpC and 1.408 Å with (1/2)CpC, from CCSD(T)/ANO-RCC calculations with relativistic effects.

TABLE 6: van der Waals Radii (in Å) Computed Using Ne as the Probe

	1	14	15	16	17	18
	H					He
σ_Z	1.67					1.33
standard radius[a]	1.10					1.40
		C	N	O	F	Ne
σ_Z		1.30	1.63	1.37	1.18	1.41
Bondi radius		1.70	1.55	1.52	1.47	1.54
		Si	P	S	Cl	Ar
σ_Z		1.62	2.16	1.85	1.61	1.76
Bondi radius		2.10	1.80	1.80	1.75	1.88
			As	Se	Br	Kr
σ_Z			2.21	1.93	1.72	1.89
Bondi radius			1.85	1.90	1.83	2.02

[a] Rowland−Taylor for H; Bondi for He.

number n, and if the outermost occupied orbitals have $n = v$, then it is usually sufficient to correlate only electrons with $n = v$ (valence electrons) and $v - 1$ (the outermost shell of the core), and sometimes it is not necessary to correlate all electrons with $n = v - 1$. (Correlating a large number of electrons increases the computer time and storage needed for the calculations, and eventually, if too many electrons are correlated, one needs more basis functions for core orbitals, and the calculations become too expensive.) Electrons that are not correlated are called frozen. The effect of correlating the outer core electrons can be quite large; this is shown in Table 2. Hence, the use of a basis set such as ANO-RCC that is designed to correlate some of the core electrons is essential. ANO-RCC was designed[46−48] to include the correlation of a certain subset of electrons, as indicated in the upper part of Table 3. In our work, though, that scheme was modified to correlate more electrons, as indicated in the lower half of the table. The scheme in the lower half of Table 3 is used for all calculations after Table 2.

In Tables 1 and 2, the calculations are nonrelativistic, although the ANO-RCC basis set was explicitly designed to be used with the Douglas−Kroll[55,56] (DK) relativistic Hamiltonian; therefore this basis set was used uncontracted for nonrelativistic calculations on atoms heavier than Ar. Table 4 shows that relativistic effects on the van der Waals radii are small even for atoms as heavy as Kr. However, relativistic effects become significant as early as the 3d transition metals[57,58] and they become more significant in the post-3d elements. In all subsequent calculations (after Table 4), the calculations were performed entirely using the relativistic DK Hamiltonian.

An additional consideration is the effect of basis set superposition error (BSSE) on the predicted energies. This is significant for an all-electron basis set such as ANO-RCC. To account for the effect of BSSE, a counterpoise correction[59] (CpC) can be included. It has been observed that the value at the infinite-basis-set limit sometimes tends to converge to a value roughly halfway between the fully counterpoise corrected and the uncorrected energies.[60,61] Table 5 shows atomic radii computed using 1/2 of the CpC correction. The counterpoise corrections computed this way generally vary between 0.01 and 0.04 Å and consistently make the radii larger, which is a consequence of the fact that BSSE overstabilizes the complex.

TABLE 7: van der Waals Radii (in Å) Computed with Three Probes As Compared to Bondi−Rowland−Taylor Radii[a]

group	1	2	13	14	15	16	17	18
	H							He
σ_Z from H of HF	1.25							1.35
σ_Z from F of HF	1.45							1.32
σ_Z from CH_4	1.39							1.43
standard radius[a]	1.10							1.40
	Li			C	N	O	F	Ne
σ_Z from H of HF	2.03			1.19	1.42	0.96	1.14	1.41
σ_Z from F of HF	0.30			0.94	1.53	1.20	1.01	1.41
σ_Z from CH_4	2.30			1.72	1.46	1.75	1.51	1.41
Bondi radius	1.81			1.70	1.55	1.52	1.47	1.54
	K	Mg		Si	P	S	Cl	Ar
σ_Z from H of HF	2.27	2.03		1.59	1.77	1.30	1.40	1.60
σ_Z from F of HF	0.79	1.89		*b*	1.88	1.51	1.29	1.69
σ_Z from CH_4	2.37	2.18		2.25	1.81	2.04	1.83	1.64
Bondi radius	2.27	1.73		2.10	1.80	1.80	1.75	1.88
	K		Ga		As	Se	Br	Kr
σ_Z from H of HF	2.70		1.47		1.84	1.39	1.50	1.69
σ_Z from F of HF	1.04		1.20		1.92	1.56	1.36	1.78
σ_Z from CH_4	2.68		1.29		1.85	2.08	1.90	1.72
Bondi radius	2.75		1.87		1.85	1.90	1.83	2.02
			In	Sn		Te	I	Xe
σ_Z from H of HF			1.61	1.76		1.58	1.68	1.85
σ_Z from F of HF			1.27	1.08		1.70	2.33	1.93
σ_Z from CH_4			2.75	2.27		2.25	2.05	1.88
Bondi radius			1.93	2.17		2.06	1.98	2.16
			Tl	Pb				
σ_Z from H of HF			1.61	1.78				
σ_Z from F of HF			1.24	1.10				
σ_Z from CH_4			2.75	2.36				
Bondi radius			1.96	2.02				

[a] Rowland−Taylor for H; Bondi for He. [b] Not available.

TABLE 8: Coefficients of the Final Model

	noble gases	open-shell p-block nonmetals	p-block metals	s-block elements
b	0.000	0.318	1.206	2.121
c	1.743	0.000	0.000	0.000
d	−0.639	0.708	0.000	−1.108

In the rest of this article, we use the CCSD(T)/ANO-RCC method with the DK method for relativistic effects, one-half the counterpoise correction, and the correlation scheme in the lower half of Table 3. This illustrates an important advantage of having chosen the ANO-RCC basis set, that this basis set is available over a very large portion of the periodic table, which allows one to compute atomic radii using a consistent approach rather than a patchwork of radii calculated with different basis sets.

Table 6 shows that the radii computed using Ne as a probe are very roughly the same size as Bondi radii, but they do not exhibit the same periodic trends as Bondi radii. For instance, Bondi radii for the pnictogens are consistently smaller than those of the carbon group or chalcogen atoms in the same row, whereas the gas-phase dimer radii based on Ne complexes have the reverse trend. The Bondi radii were computed from a collection of Z•••Y contact distances where Z and Y were any number of different atoms. This means that the attractive interactions are not purely dispersion-like, but include electrostatic and inductive effects (the latter, such as dipole−induced dipole interactions, are sometimes called polarization effects) that are probably better simulated using molecular probes (for example, HF probes interact with the atom by dipole−induced dipole interactions in addition to dispersion-like interactions, and open-shell atoms often have nonzero permanent quadrupole moments that can also interact with permanent and induced moments on the probe).

We next considered hydrogen fluoride as a probe. HF is isoelectronic with Ne. Because the two atoms of the probe have distinct properties, we used both ends of the probe. In all cases, the atom approached HF along the molecular axis of HF. The geometry of the probe was held frozen throughout these calculations at an internuclear H−F distance of 0.917720 Å, which was optimized at the CCSD(T)/ANO-RCC level of theory.

We also considered CH_4 as a probe. CH_4 is also isoelectronic with Ne, but it is more polarizable. Unlike HF, it is nonpolar.

The approach we adopted is to seek to write a multilinear regression with no intercept:

$$\sigma_Z = b\sigma_Z(\text{H of HF}) + c\sigma_Z(\text{F of HF}) + d\sigma_Z(\text{CH}_4) \quad (1)$$

and to try to find values of the constants *b*, *c*, and *d* such that the left-hand side of eq 1 agrees with the standard values for the main-group elements for which Bondi determined the van der Waals radii, except substituting the Rowland−Taylor value for H. This formula then can be used to predict the van der

TABLE 9: van der Waals Radii (in Å) from Final Correlations As Compared to Bondi−Rowland−Taylor Radii

model group	1	2	13	14	15	16	17	18
	H							He
final model	1.10							1.39
standard radius[a]	1.10							1.40
	Li			C	N	O	F	Ne
final model	1.75			1.60	1.49	1.54	1.40	1.55
Bondi radius	1.81			1.70	1.55	1.52	1.47	1.54
	Na	Mg		Si	P	S	Cl	Ar
final model	2.19	1.88		2.09	1.84	1.85	1.74	1.89
Bondi radius	2.27	1.73		2.10	1.80	1.80	1.75	1.88
	K		Ga		As	Se	Br	Kr
final model	2.74		1.77		1.90	1.91	1.82	2.00
Bondi radius	2.75		1.87		1.85	1.90	1.83	2.02
			In	Sn		Te	I	Xe
final model			1.95	2.12		2.09	1.99	2.16
Bondi radius			1.93	2.17		2.06	1.98	2.16
			Tl	Pb				
final model			1.94	2.15				
Bondi radius			1.96	2.02				

[a] Rowland−Taylor for H; Bondi for He.

TABLE 10: Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Root Mean Squared Error (RMSE) of the Final Correlations for Reproducing Standard Radii for Different Classes of Atoms

class	MSE (Å)	MUE (Å)	RMSE (Å)
noble gases (He, Ne, Ar, Kr, Xe)	0.00	0.01	0.01
p-block open-shell nonmetals (C, N, O, F, Si, P, S, Cl, As, Se, Br, Te, I)	0.00	0.04	0.05
p-block open-shell metals (Ga, In, Sn, Tl, Pb)	0.00	0.06	0.08
s-block elements (H, Li, Na, K, Mg)	0.00	0.06	0.08

Waals radii for the other elements. The coefficients in eq 1 are obtained by minimizing the root-mean-square error using the generalized reduced gradient code of Lasdon et al.[62] as implemented in Microsoft Excel.

3. Results

The radii for the elements with the three molecular probes are given in Table 7 for all of the main-group atoms for which Bondi presented radii. In a few cases (e.g., Li, Na, and K) when the probe is the F atom of HF, the radii are much smaller than those obtained with other probes; this indicates that this kind of probe can lead to a significant covalent interaction. Therefore, the values based on the F atom of the HF probe will be used only for fitting noble gases.

We attempted to fit the Bondi radii using these data and eq 1. We found that we could not fit all of the standard values well with a single *b*, *c*, and *d*, even if we treated noble gases separately and even if we set *c* equal to zero to eliminate radii with significant covalent interaction. Including Ne-probe radii in the fit also did not lead to a good global fit. Therefore, we

TABLE 11: van der Waals Radii (in Å) Computed With Probes in Final Model for the Four Classes of Elements

	1	2	13	14	15	16	17	18
		Be	B					
σ_Z from H of HF		1.741	1.124					
σ_Z from CH_4		1.953	2.205					
			Al					
σ_Z from H of HF			1.528					
		Ca		Ge				
σ_Z from H of HF		2.423		1.599				
σ_Z from CH_4		2.549		2.263				
	Rb	Sr			Sb			
σ_Z from H of HF	2.834	2.586			2.012			
σ_Z from CH_4	2.694	2.696			2.014			
	Cs	Ba			Bi	Po	At	Rn
σ_Z from H of HF	3.026	2.768			2.050	1.634	1.738	
σ_Z from F of HF								1.967
σ_Z from CH_4	2.696	2.877			2.009		2.080	1.914
	Fr	Ra						
σ_Z from H of HF	3.026	2.813						
σ_Z from CH_4	2.652	2.833						

TABLE 12: Consistent van der Waals Radii for All Main-Group Elements[a]

1	2	13	14	15	16	17	18
H							He
1.10							1.40
Li	Be	B	C	N	O	F	Ne
1.81	**1.53**	**1.92**	1.70	1.55	1.52	1.47	1.54
Na	Mg	Al	Si	P	S	Cl	Ar
2.27	1.73	**1.84**	2.10	1.80	1.80	1.75	1.88
K	Ca	Ga	Ge	As	Se	Br	Kr
2.75	**2.31**	1.87	**2.11**	1.85	1.90	1.83	2.02
Rb	Sr	In	Sn	Sb	Te	I	Xe
3.03	**2.49**	1.93	2.17	**2.06**	2.06	1.98	2.16
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
3.43	**2.68**	1.96	2.02	**2.07**	**1.97**	**2.02**	**2.20**
Fr	Ra						
3.48	**2.83**						

[a] Bold values are from the present work, value for H is from Rowland and Taylor, and other values are from Bondi.

investigated using different sets of parameters for different chemical classes of elements. We eventually adopted the goal of having a mean unsigned error no larger than 0.06 Å for any of the classes while using the minimum number of classes and using no more than two of the three possible parameters for a given class (i.e., we restrict the correlations to linear or bilinear with no intercept). We examined various ways to group the elements into classes and found that a very reasonable fit could be made to the standard radii by recognizing four classes of elements: noble gases, open-shell p-block nonmetals, p-block metals, and s-block elements. The coefficients of the resulting correlations are given in Table 8, a comparison of the fitted radii to the standard ones is in Table 9, and the mean errors as compared to the Bondi−Rowland−Taylor standard values are in Table 10. This approach produced reasonable results, which can then be used to obtain radii for all main-group elements for which Bondi did not report radii. The additional data needed for these elements were calculated and are given in Table 11. In these calculations, we treated the open-shell p-block elements Al and Po as metals and B, Ge, Sb, Bi, and At as nonmetals.

Table 12 gives the prescribed van der Waals radii for all main-group elements, including the new values obtained as described in the previous paragraph. Unlike atomic radii determined from internuclear distances in bonds (covalent radii, metallic radii),[63–65,66a] van der Waals radii do not follow a generally monotonic trend as one moves across or down in the periodic table. One possible way to explain some of the trends is by classifying the elements as metal, nonmetal, and semimetal. We note though that classifications of some nonmetals as semimetals or metalloids are not unique because they depend on the properties that are chosen for the classification.[66b,67–69] Nevertheless, even without using a strict classification, Table 12 shows that the van der Waals radii of incompletely filled p-block elements increase with decreasing metallic nature as we move to the right along a period and then decrease with increasing nonmetallic nature. The trends in the table are seen to result from (i) the shape (s or p) of the highest occupied atomic orbital, (ii) the classification of the element as a metal or nonmetal, and (iii) the subclassification of p-block elements into noninert nonmetals (incomplete p subshell) and inert gases (complete p subshell). These factors are evident in Table 12 in the higher van der Waals radii of s-block elements relative to those for p-block elements, in the relatively large sizes of some elements near the metallic−nonmetallic border as compared to other partially filled p-block elements in their respective periods (B, Si, Ge, Sn, and Bi are larger than either their left-side neighbor or their right-side neighbor in the periodic table), and the larger size of the noble-gas elements with completely filled p orbitals.

4. Summary

We determined van der Waals radii for the main-group elements by calculating the locations of the repulsive wall in the potential energy curve for the interactions of the elements with various probes, and then determining linear and bilinear correlations with the standard radii of Bondi and Rowland and Taylor. The correlations, based on a maximum of two parameters per class of elements, reproduce the standard van der Waals radii with mean unsigned deviations of 0.01, 0.04, 0.06, and 0.06 Å for the four classes of main-group elements. These correlations are useful because they provide us with a straightforward approach to determine consistent van der Waals radii for the rest of the main-group elements, and we have produced such radii.

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