

Direct Dependence of Covalent, Van Der Waals, and Valence Shell Radii of Atoms on their Bohr Radii for the Main Group Elements

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Recent work by the author has shown that ionic, atomic, and the ground state Bohr radii (a_B) of elements are inter-related. An earlier work by others has shown that the ratio, van der Waals radii/de Broglie wavelengths is nearly constant for each group of some non-metallic elements. Since a_B and the de Broglie wavelength are directly related, the author shows here that, in fact, for all the main group elements from 1A – 8A, the van der Waals radii are directly proportional to a_B . It was found that the valence shell and covalent radii also vary linearly with a_B . Thus, all the above radii (R) can be unified by a single linear equation, $R = ma_B + c$. Therefore, a_B can be considered as a unit of length for the above radii as much as for the smaller Compton wavelength and classical radii (sum) of electron and proton.

Key Words: Unified linear equation, Bohr radius as unit of length, hydrogen in Group 1A, Sommerfeld ellipse, table of data, comparative diagram of radii

INTRODUCTION

It was pointed out (Bondi 1964; Morrison 1955) over 40 years ago, with the available data then, that the ratio of the van der Waals radii (R_{vdW}) of atoms to their de Broglie wavelengths (λ_{dB}) is nearly a constant for each group of non-metallic elements. The de Broglie wavelength ($\lambda_{dB} = 2\pi a_B$) is related to the ground state Bohr radius (a_B) and, a_B , in turn, to ground state energy (or the ionization potential). Using existing data (Bondi 1964; Batsanov 2001; www.webelements.com), it was found that R_{vdW} varies linearly with a_B not only for the non-metallic elements, but also for all the elements from Group 1A to 8A. The straight lines have different slopes and non-zero intercepts (unlike in Bondi 1964; Morrison 1955). In Batsanov (2001), which has data for elements of groups 1A – 7A, two sets of data are given for the van der Waals radii, one from crystallographic data [which are comparable with the values given by Bondi (1964) and

in www.webelements.com for elements of Groups 5A – 7A], and the other, denoted as equilibrium values, are for the isolated atoms. The latter are larger since the atoms have more free space than in the crystalline lattices. For elements of other groups, the graphs are not linear and are not considered here.

The data given in www.webelements.com for the valence shell radii (R_{v-s}) and covalent radii $d(A)_{cov}$, show that they are also linearly dependent on a_B . Since the covalent radius $d(A)_{cov}$ is defined (Pauling 1960) as half the inter-atomic bond distance $d(AA)_{cov}$ between atoms of the same kind, the letter d is used here for the radius. The slopes and intercepts reproduce all the radii to about (+/-) 0.07 Å, which is within the scatter in the reported values.

Thus, presented below in sections are new findings that there are linear correlations between R_{vdW} , R_{v-s} , $d(A)_{cov}$ and a_B . This shows that each of the radii is actually a sum of 2 lengths: one, a multiple of a_B , and the other, a constant

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for each group of elements from 1A–8A. For preliminary report, see Heyrovská (2008).

Dependence of van der Waals radii (R_{vdW}) on the Bohr radii, a_B

The values of R_{vdW} for various elements from (www.webelements.com) and Batsanov (2001) are given here in columns 3, 5, and 7 in Table 1. The data in columns 5 and 7 are for crystals and equilibrium values for isolated atoms, respectively, from Batsanov (2001).

The first ionization potentials (I_1) from www.webelements.com were used for calculating a_B from the relation (Heyrovská 2005),

$$a_B = e/2\kappa I_1 \quad (1)$$

where e is the charge and κ is the electrical permittivity of vacuum; see data in column 2, Table 1.

It is interesting to point out, as a side note, that for many main group elements in the Periodic Table, there

Table 1. Bohr radii, a_B , van der Waals radii, R_{vdW} , (1: www.webelements.com; 2: Batsanov 2001), valence shell radii, R_{v-s} , (1) and covalent radii, $d(A)_{cov}$, (1; Pauling 1960: gp.3A) of atoms. (In parenthesis, m,c: slope, intercept). All radii are in Å

Atom(Gp.)	a_B	$R_{vdW}(1)$	$R_{vdW}^*(1)$	$R_{vdW}(2)$	$R_{vdW}^*(2)$	$R_{vdW}(2)$	$R_{vdW}^*(2)$	R_{v-s}	R_{v-s}^*	$d(A)_{cov}$	$d(A)_{cov}^*$
8A: (m,c)		(2.56, 0.68)		cryst.	cryst.	equil.	equil.	(1.93, -0.26)		(2.37, 0.79)	
He	0.29	1.4	0.75					0.30	0.56	1.50	0.69
Ne	0.33	1.54	0.85					0.36	0.64	1.57	0.79
Ar	0.46	1.88	1.17					0.63	0.88	1.86	1.08
Kr	0.51	2.02	1.32					0.73	0.99	2.02	1.22
Xe	0.59	2.16	1.52					0.91	1.14	2.20	1.40
Rn	0.67							1.00	1.29		
7A: (m,c)		(1.86, 0.71)		(2.15, 0.61)		(2.08, 0.82)		(1.96, -0.41)		(2.16, -0.18)	
F	0.41	1.47	0.77	1.50	0.89	1.65		0.41	0.81	0.74	0.89
Cl	0.56	1.75	1.03	1.80	1.19	2.05		0.68	1.09	0.99	1.20
Br	0.61	1.85	1.14	1.90	1.31	2.10		0.77	1.19	1.15	1.32
I	0.69	1.98	1.28	2.10	1.48	2.22		0.95	1.35	1.33	1.49
6A: (m,c)		(1.95, 0.48)		(1.93, 0.50)		(2.36, 0.45)		(1.95, -0.58)		(2.95, -0.98)	
O	0.53	1.52	1.03	1.55	1.02	1.71	1.25	0.46	1.03	0.60	1.56
S	0.69	1.80	1.35	1.80	1.34	2.06	1.64	0.75	1.35	1.03	2.05
Se	0.74	1.90	1.44	1.90	1.42	2.18	1.74	0.82	1.44	1.16	2.18
Te	0.80	2.06	1.55	2.10	1.54	2.36	1.89	1.00	1.56	1.43	2.36
Po	0.86							1.09	1.67	1.67	
5A: (m,c)		(1.27, 0.92)		(1.80, 0.71)		(1.85, 0.87)		(1.54, -0.23)		(2.72, -0.78)	
N	0.50	1.55	0.63	1.60	0.89	1.79	0.92	0.54	0.76	0.55	1.35
P	0.69	1.80	0.87	1.95	1.24	2.14	1.27	0.84	1.06	1.11	1.86
As	0.73	1.85	0.93	2.05	1.32	2.25	1.36	0.89	1.13	1.25	1.99
Sb	0.83			2.20	1.50	2.41	1.54	1.07	1.28	1.45	2.26
4A: (m,c)				(1.58, 0.69)		(1.41, 1.05)		(1.48, -0.35)		(1.98, -0.56)	
C	0.64	1.70		1.70	1.01	1.96	0.90	0.61	0.95	0.71	1.27
Si	0.88	2.10		2.10	1.40	2.26	1.25	0.95	1.31	1.18	1.75
Ge	0.91			2.10	1.44	2.32	1.29	0.96	1.35	1.23	1.81
Sn	0.98			2.25	1.55	2.46	1.38	1.14	1.45	1.41	1.94
3A: (m,c)				(1.02, 0.92)		(1.22, 1.00)		(1.06, -0.10)		(1.93, -0.76)	
B	0.87			1.80	0.89	2.05	1.06	0.81	0.92	0.90	1.67
Al	1.20			2.10	1.23	2.40	1.47	1.11	1.28	1.43	2.32
Ga	1.20			2.10	1.22	2.41	1.46	1.06	1.27	1.40	2.32
In	1.24			2.20	1.27	2.53	1.52	1.23	1.32	1.69	2.40
Tl	1.18			2.20	1.20	2.53	1.44	1.30	1.25	1.73	2.27
2A: (m,c)				(1.25, 0.96)		(1.40, 1.13)		(2.06, -0.55)		(2.11, -0.46)	
Be	0.77			1.90	0.97	2.23	1.08	1.09	1.59	1.14	1.63
Mg	0.94			2.20	1.18	2.42	1.32	1.37	1.94	1.60	1.99
Ca	1.18			2.40	1.47	2.78	1.65	1.84	2.43	1.98	2.49
Sr	1.26			2.55	1.58	2.94	1.77	2.05	2.61	2.15	2.67
Ba	1.38			2.70	1.73	3.05	1.93	2.35	2.85	2.51	2.92
1A: (m,c)				(1.43, 0.39)		(1.25, 0.99)		(2.24, -1.36)		(2.04, -0.71)	
H	0.53	1.20		1.17	0.76			0.53		0.37	1.08
Li	1.34	1.82		2.20	1.91	2.63	1.67	1.64	2.99	2.00	2.72
Na	1.40	2.27		2.40	2.00	2.77	1.75	1.79	3.14	2.15	2.86
K	1.66	2.75		2.80	2.37	3.02	2.07	2.3	3.72	2.66	3.38
Rb	1.72			2.90	2.46	3.15	2.15	2.49	3.86	2.79	3.51
Cs	1.85			3.00	2.64	3.30	2.31	2.82	4.15	3.07	3.77

are some linear relations connecting the aqueous redox potentials and the ionization potentials (Heyrovská 2000 2001). Also, some interesting regularities have been observed among the various ionization potentials of the main group elements (Liebman 1973).

The linear dependence of R_{vdW} on a_B for elements of various groups are shown in Figure 1 for the data from [3] and in Figure 2 for data from Batsanov (2001) (to avoid too much overlapping and crowding, the lines corresponding to equilibrium values are not shown). Fig. 2 includes elements from groups 1A – 7A. For elements of group 3A, the points are a bit scattered. The straight lines are expressed here by the equations, where m and c are the slope and intercept respectively. Thus,

$$R_{vdW} = R_{vdW}^* + c_{vdW} \quad (2a)$$

$$R_{vdW}^* = m_{vdW} a_B < R_{vdW} \quad (2b)$$

The values of m_{vdW} (> 1) and c_{vdW} (< 1) are given in Table 1. The values of R_{vdW}^* are tabulated in columns 4, 6, and 8 in Table 1. For the crystallographic and equilibrium values of R_{vdW} from Batsanov (2001), the values of R_{vdW}^* are mostly close to each other, but the intercepts c differ. Thus, R_{vdW} actually consists of R_{vdW}^* , which depends on a_B , and c_{vdW} , a constant for each group of elements.

Dependence of valence shell radii, R_{v-s} on the Bohr radii, a_B

The valence shell radii R_{v-s} of atoms defined (www.webelements.com; Mann 1968) as ‘the radius at which the magnitude of wave function is greatest for the valence orbitals’, tabulated in www.webelements.com are presented here in column 9, Table 1. These radii are also linearly dependent on a_B , as can be seen from Figure 3. They can be represented by equations similar to Eqs. (2),

$$R_{v-s} = R_{v-s}^* + c_{v-s} \quad (3a)$$

$$R_{v-s}^* = m_{v-s} a_B > R_{v-s} \quad (3b)$$

where the slopes, $m_{v-s} > 1$ and the intercepts, c_{v-s} have negative values. This shows that the Bohr radius dependent part of the valence-shell radius, $R_{v-s}^* > R_{v-s}$ and is nearly $2a_B$ ($= \lambda dB/\pi$) (the major axis of the Sommerfeld ellipse) for atoms of many groups. Note that the point for H belongs to the straight line for the alkali metals of group 1A.

The linear relations given by Eqs. 2 and 3 can be used for estimating the unknown R_{vdW} and R_{v-s} of elements, using the values of a_B . For example for Bi, $R_{vdW,cryst}$ and R_{v-s} are 2.49 and 1.29; and for Pb, they are 2.22 and 1.09 Å.

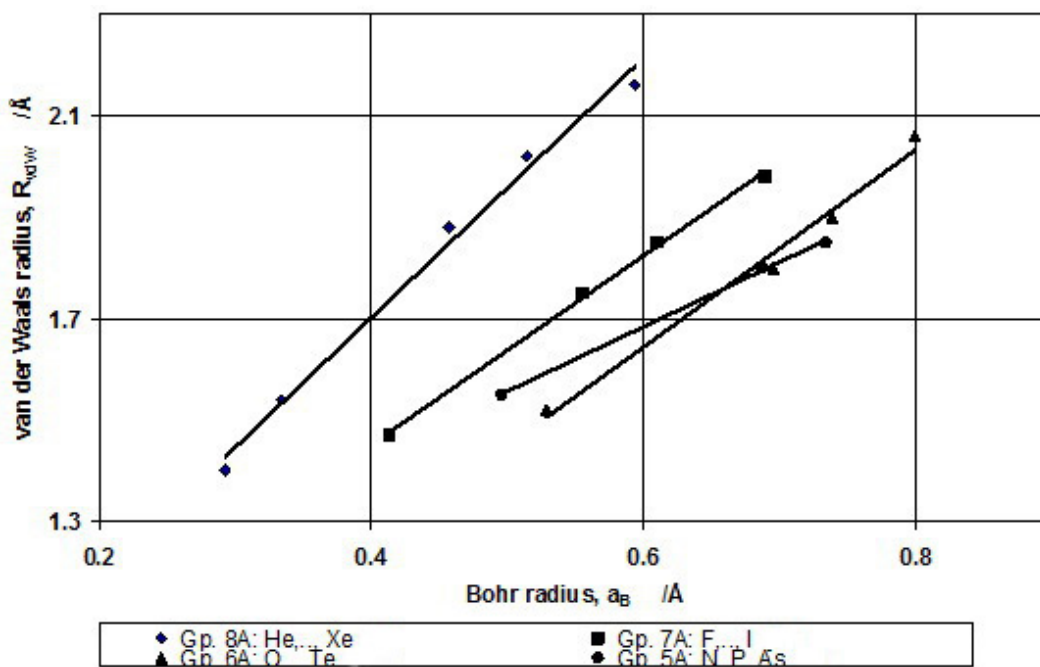


Figure 1. Linear dependence of van der Waals radii, R_{vdW} from (www.webelements.com) on the ground state Bohr radii, a_B , for elements of main groups 5A – 8A; see Eq. (2a).

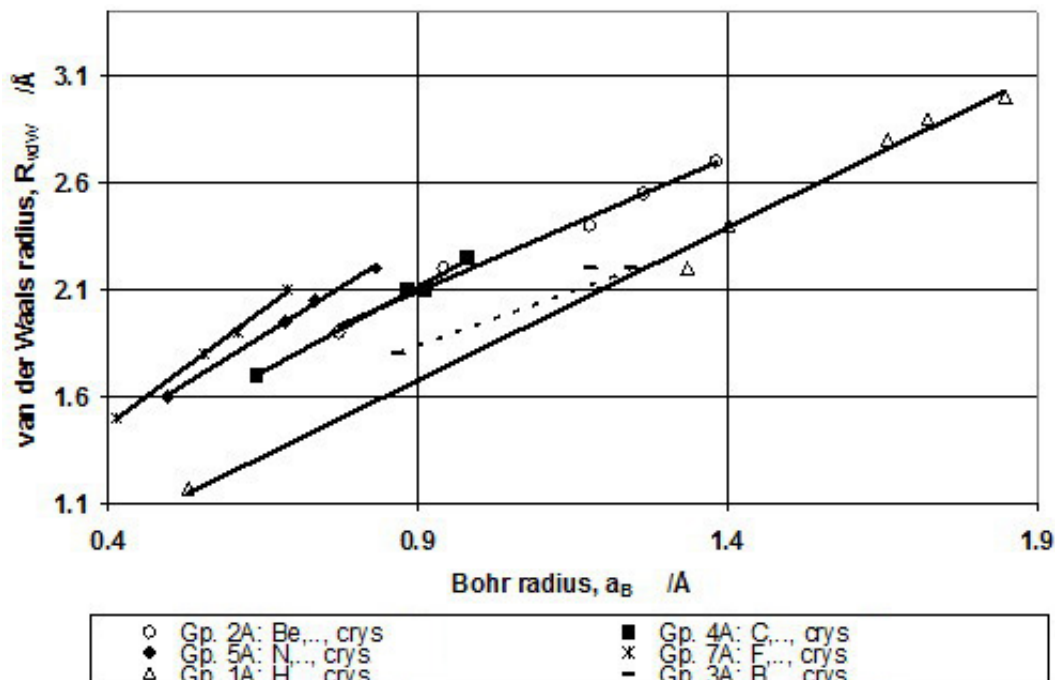


Figure 2. Linear dependence of van der Waals radii, R_{vdW} from Batsanov (2001) on the ground state Bohr radii, a_B , for main group elements, 1A - 7A; see Eq. (2a). Note that the point for H is on the same line as for Group 1A elements

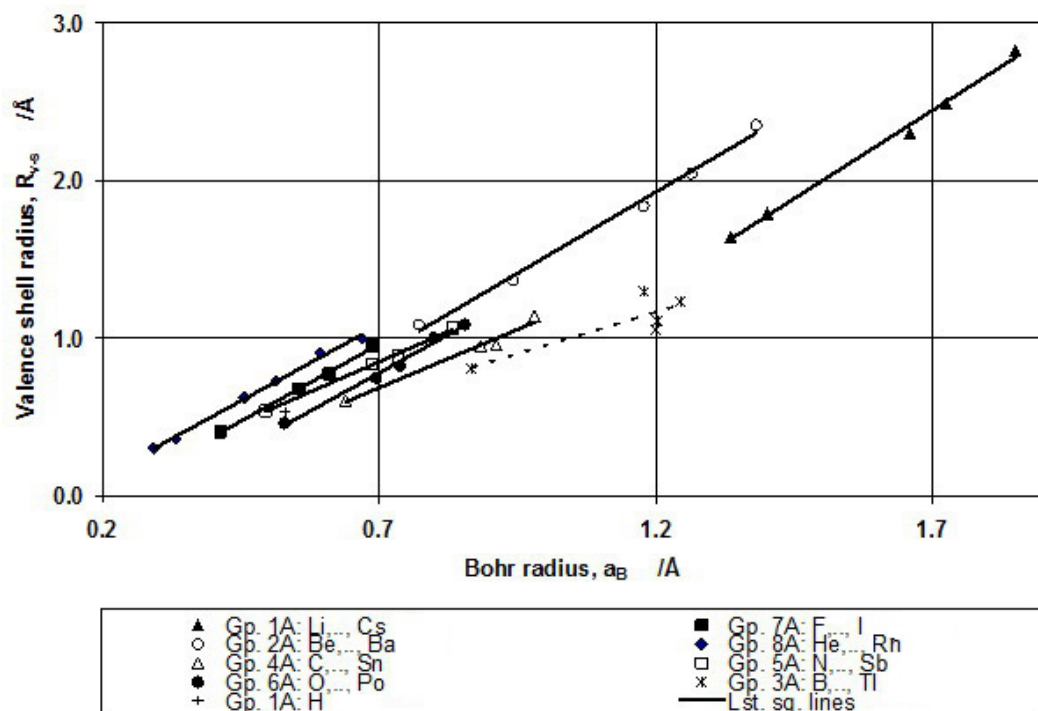


Figure 3. Linear dependence of valence shell radii, R_{vs} (www.webelements.com) on the ground state Bohr radii a_B , for main group elements, 1A – 8A; see Eq. (3a)

Dependence of the covalent radii, $d(A)_{\text{cov}}$ on the Bohr radii, a_B

The data for the covalent radii $d(A)_{\text{cov}}$ from www.webelements.com are given in column 11, Table 1. Figure 4 shows that $d(A)_{\text{cov}}$ is also linear with a_B as in Figs. 1 - 3. The straight lines can be represented by,

$$d(A)_{\text{cov}} = d(A)_{\text{cov}}^* + c_{\text{cov}} \quad (4a)$$

$$d(A)_{\text{cov}}^* = m_{\text{cov}} a_B > d(A)_{\text{cov}} \text{ (except for group 8A)} \quad (4b)$$

The values of the slopes m_{cov} and intercepts c_{cov} and of $d(A)_{\text{cov}}^*$ are in Table 1. For elements of most of the groups (1A, 2A, 4A and 7A), m_{cov} is close to 2 and $d(A)_{\text{cov}}^* \sim 2a_B$ ($\sim R_{v-s}^*$), whereas for those of the inert gases, $m_{\text{cov}} \sim 2.4$ and for elements of groups 5A and 6A, $m_{\text{cov}} \sim 3$. Except for group 8A atoms, the intercepts c_{cov} are negative and the Bohr radius dependent part, $d(A)_{\text{cov}}^* > d(A)_{\text{cov}}$. Note again that, as in Figure 3, the point for H falls on the same straight line as for the group 1A alkali metals.

Figure 5 (drawn to scale) shows the relative comparisons of the Bohr radii (a_B) and the pairs of radii,

R_{vdW}^* & R_{vdW} , R_{v-s}^* & R_{v-s} and $d(A)_{\text{cov}}^*$ & $d(A)_{\text{cov}}$ for elements of groups 1A – 8A.

Dependences of R_{vdW} and R_{v-s} on $d(A)_{\text{cov}}$

Since R_{vdW} , R_{v-s} , and $d(A)_{\text{cov}}$ are all linearly dependent on a_B , both R_{vdW} and R_{v-s} are directly proportional to $d(A)_{\text{cov}}$. It was suggested by Pauling (1960) that R_{vdW} differs from $d(A)_{\text{cov}}$ by a constant $\sim 0.8 \text{ \AA}$. Here, it was found that this difference depends on a_B as shown by,

$$R_{\text{vdW}} - d(A) = (m_{\text{vdW}} - m_{\text{cov}})a_B + (c_{\text{vdW}} - c_{\text{cov}}) \quad (5)$$

The values (see Table 1) show that the suggestion in Pauling (1960) is a near approximation.

In conclusion, it can be seen that all the above radii (R) can be expressed in terms of the Bohr radii by a single linear equation,

$$R = ma_B + c \quad (6)$$

Thus, the Bohr radii of the main group elements can be considered as a unit of length for their above other radii as much as a_B for hydrogen for the smaller Compton wavelength (αa_B), and the sum of the classical radii of the proton and electron ($\alpha^2 a_B$), where α is the fine structure constant.

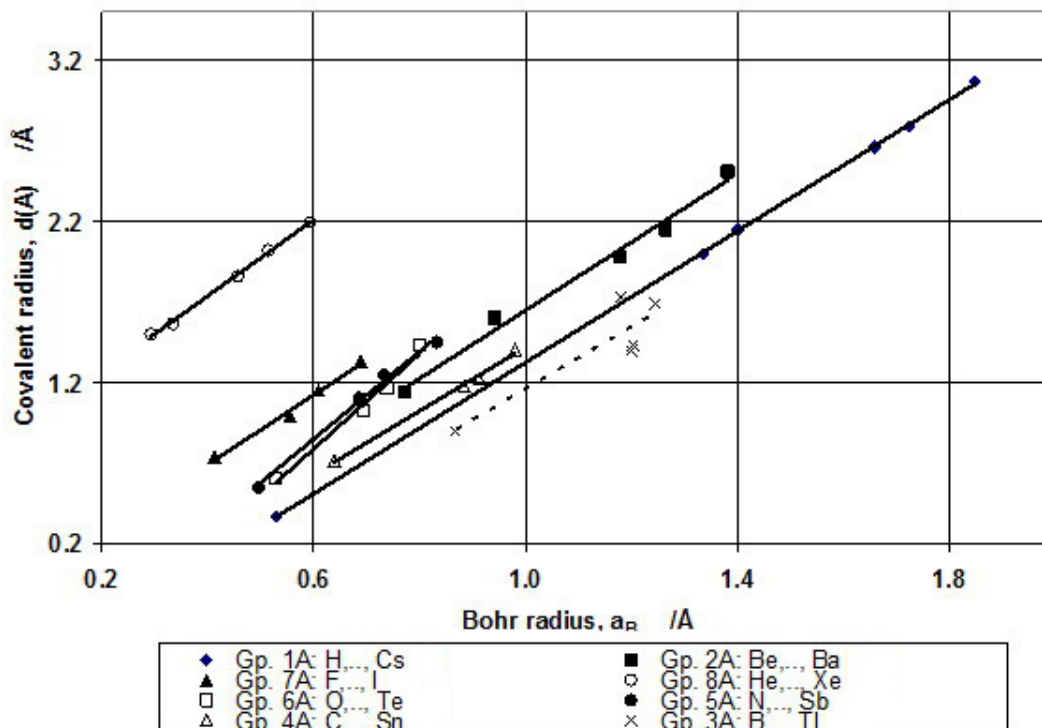


Figure 4. Linear dependence of covalent radii $d(A)_{\text{cov}}$ (www.webelements.com) on the ground state Bohr radii for main group elements, 1A – 8A; see Eq. (4a). For Li (www.webelements.com), $d(A)_{\text{cov}}$ is half the diagonal of a square with the side equal to the length from the body center to the corner of the cube. Note that the point for H is on the same line as for Group 1A elements

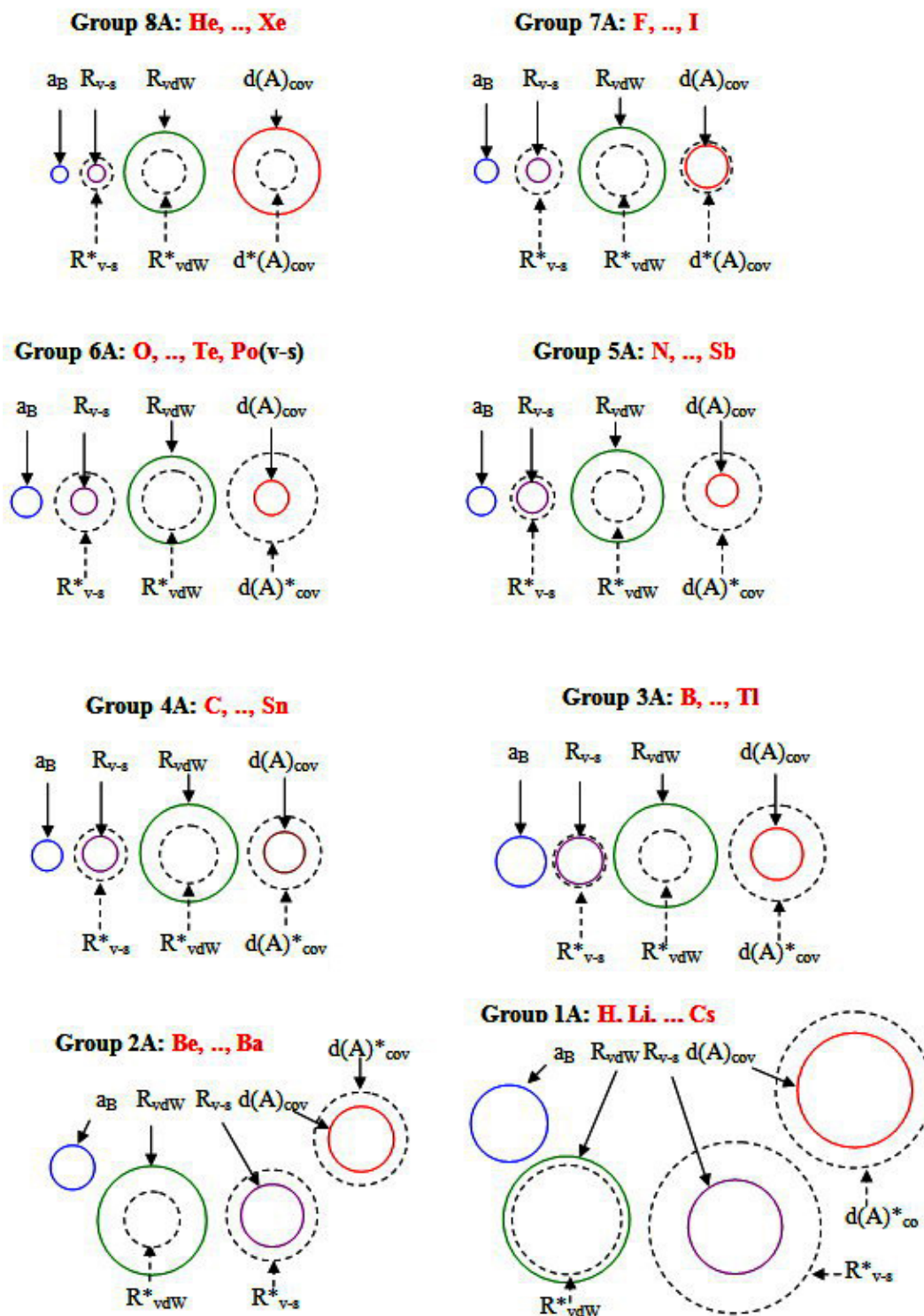


Figure 5. Comparison of the radii a_B , R_{vdW}^* & R_{vdW} , R_{v-s}^* & R_{v-s} , $d(A)_{cov}^*$ and $d(A)_{cov}$ (as radii of circles) for main group elements 1A–8A. Data for R_{vdW} from Batsanov (2001) (from crystallographic data) have been used for groups 1A–6A and all other data are from www.webelements.com; see Table 1. Note the gradations in the radii: $a_B < R_{v-s} < R_{vdW} < d(A)_{cov}$ (group 8A); $a_B < R_{v-s} < R_{vdW} > d(A)_{cov}$ (groups 2A and 4A–7A); $a_B \sim R_{v-s} < R_{vdW} > d(A)_{cov}$ (group 3A); $a_B < R_{v-s} < R_{vdW} \sim d(A)_{cov}$ (group 1A)

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