Linear Dependence on Covalent Radii of Atomic and Ionic Radii of Elements Calculated by Rahm, Hoffmann and Ashcroft

– Dedicated to Alfred B. Nobel (21 Oct.1833 – 10 Dec.1896) to commemorate the 120th Anniversary of his demise

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Abstract

The radii of free atoms calculated recently using DFT by Rahm, Hoffmann and Ashcroft have been correlated here with the covalent radii of elements of the Periodic Table. The linear dependences found are in accordance with the previous results obtained by the author between various types of radii of atoms. In particular, the comparison of the atomic radii and the Golden ratio based ionic radii of the alkali metal and halogen atoms with those presented by Rahm et al. shows that the latter also involve the Golden ratio.

1. Introduction

The present author has shown earlier [1] that various types of radii of atoms are linearly dependent on the Bohr radii obtained from their first ionization potentials. The recent new set of data on (free) atomic and ionic radii presented by Rahm et al [2] prompted the author to investigate their correlation with the covalent radii of atoms (A). The latter

is defined [3] as d(A) = d(AA)/2, where d(AA) is the bond length between the two atoms. Note: Here, d is used as the symbol for radius since it is an apportioned distance.

2. Data used and results

Elements of Groups I to VIII: The data on the atomic radii calculated using DFT (for details, see [2]) of elements, denoted here as R(A), are tabulated in [2]. The covalent radii, d(A) of the atoms are given in [4]. On plotting R(A) vs d(A), it was found that the graphs are linear as shown in the Figs. 1 (a-h) for the elements of Gps. I to VIII including lanthanides. The slopes and intercepts are given in the legends for the Figs.

Alkali metal and halogen atoms and ions: The author has shown earlier [5] that the interionic distances in alkali halide (MX) crystals are exact sums of the Golden ratio based ionic radii of the alkali metal cations (M^+) and halogen anions (X^-). Details about this can be found in [5-7]. For alkali metals (M), the cationic radii d(M^+) are given by,

$$d(M^+) = d(MM)/\phi^2 = 0.382\ d(MM) \qquad (1)$$

where d(MM) is the edge length in the bcc metal lattice and $\phi = (1 + 5^{1/2})/2 = 1.618..=$ ($\phi^2 - 1$) is the Golden ratio [8].

The anionic radii, d(X^-) of the halogen atoms (X) are given by,

$$d(X^-) = d(XX)/\phi = 0.618\ d(XX) \qquad (2)$$

where d(XX) is the covalent bond length in the halogen molecules. See [5-7, 9-11] for the correlation of calculated radii sum with the observed crystal ionic distances in alkali halides. The atomic radii d(A) and Golden ratio based cationic radii $d(A^+)$ for the alkali metal and halogen atoms [5-7, 9-11] are given here in Table 1. The corresponding atomic and ionic radii, R(A) and $R(A^+)$ from [2] are also given in Table1.

Fig. 2 shows the graphs of the atomic and cationic radii from Table 1 plotted vs the interatomic distances, d(AA) for the alkali metals. It is interesting to note that the linear dependence on d(AA) of the (free) cationic radii, $R(A^+)$, has the same slope, $1/\phi^2 = 0.382$ as the Golden ratio based radii [5], $d(A^+)$ vs d(AA) straight line (see Eq. 1).

In Fig. 3 are compared the corresponding radii for the halogen atoms and anions from Table 2. Here it is interesting that the straight lines corresponding to the Golden ratio based anionic radii [5,10], $d(A^-)$ and the (free) atomic radii [2], R(A) have the same slope, $1/\phi = 0.618$. These results show the role of Golden ratio in atomic dimensions.

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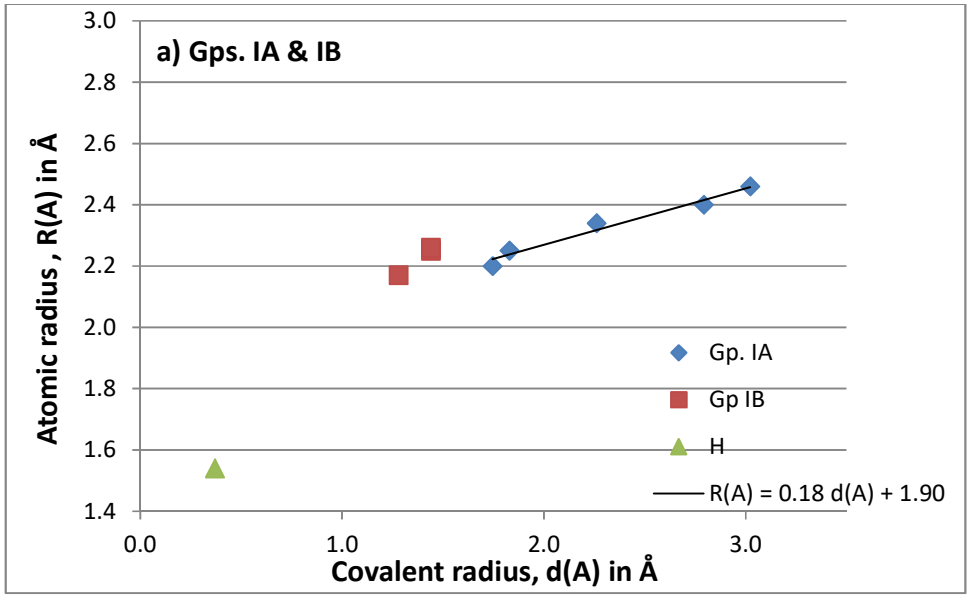
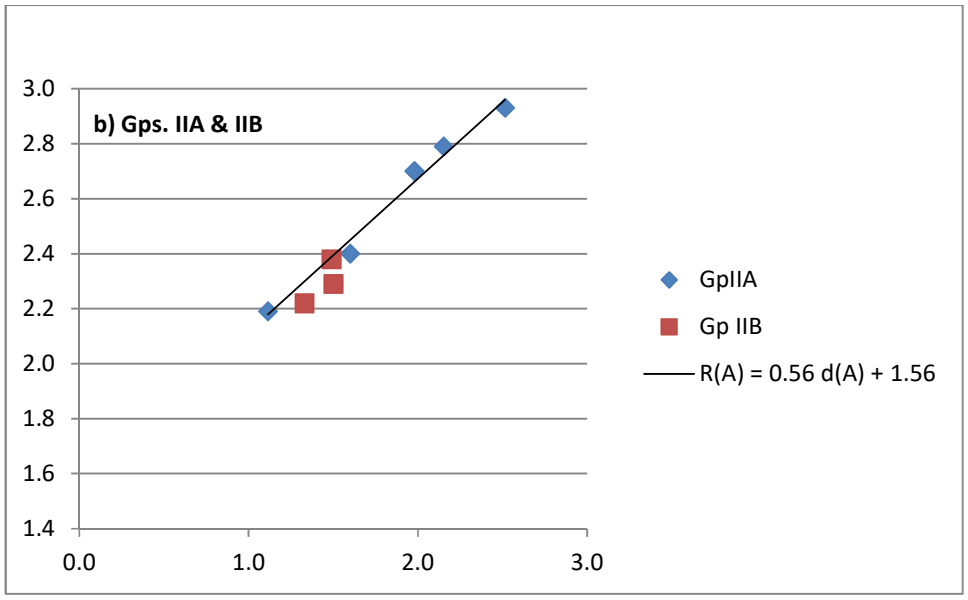
Table 1. Interatomic distances, d(AA), covalent radii, d(A), atomic radii, R(A) and ionic radii, d(A+) & R(A+) for alkali atoms. Values are in A

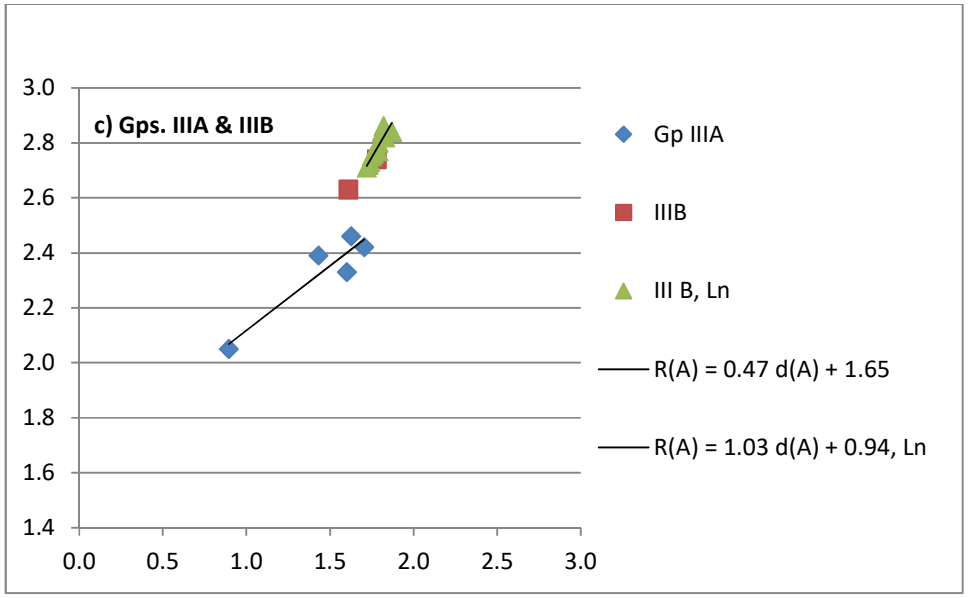
Atoms	d(AA)	d(A)	d(A+)	R(A+)	R(A)
Li	3.49	**1.75**	1.33	0.98	**2.20**
Na	3.66	**1.83**	1.40	1.33	**2.25**
K	4.52	**2.26**	1.73	1.75	**2.34**
Rb	5.59	**2.79**	2.13	1.91	**2.40**
Cs	6.05	**3.02**	2.31	2.12	**2.46**

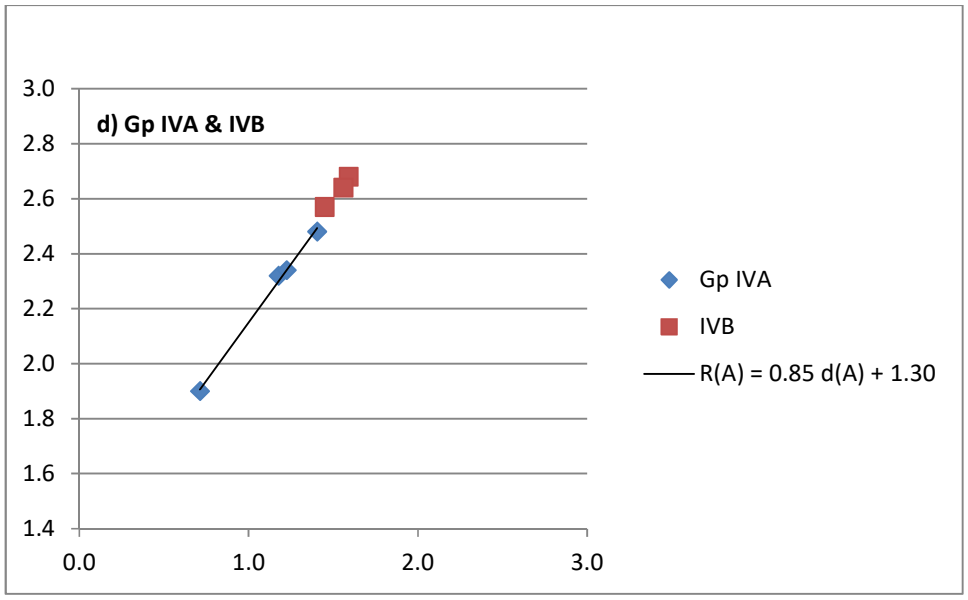
Table 2. Interatomic distances, d(AA), covalent radii, d(A), atomic radii, R(A) and ionic radii, d(A-) & R(A-) for halogens. Values are in A.

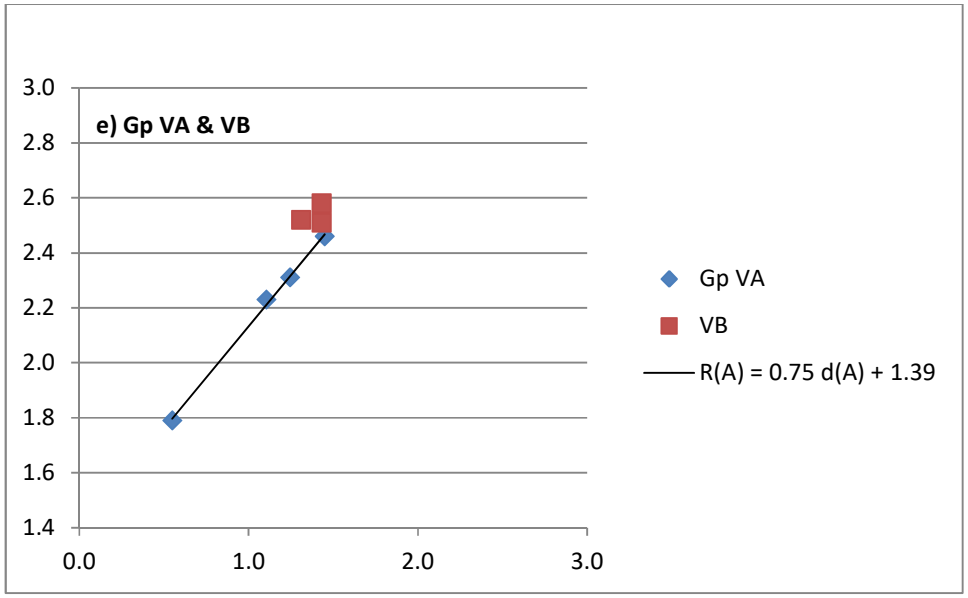
Atoms	d(AA)	d(A)	d(A-)	R(A-)	R(A)
F	1.42	**0.71**	0.88	1.92	**1.63**
Cl	1.98	**0.99**	1.22	2.29	**2.06**
Br	2.22	**1.11**	1.37	2.41	**2.19**
I	2.67	**1.33**	1.65	2.59	**2.38**

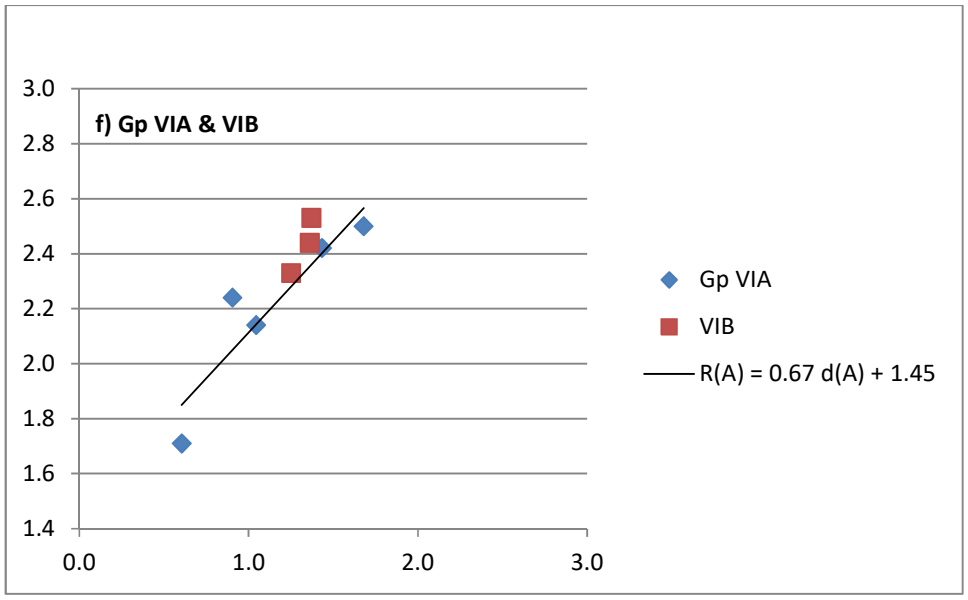

a) Gps. IA & IB
Atomic radius , R(A) in Å
Covalent radius, d(A) in Å
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
1.0
2.0
3.0
Gp. IA
Gp IB
H
R(A) = 0.18 d(A) + 1.90

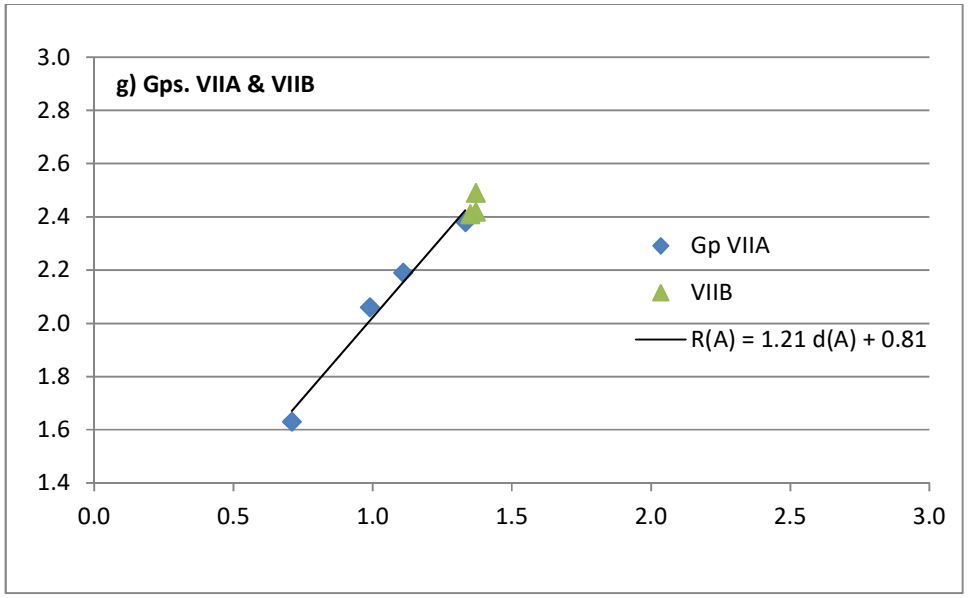

b) Gps. IIA & IIB
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
1.0
2.0
3.0
GpIIA
Gp IIB
R(A) = 0.56 d(A) + 1.56


c) Gps. IIIA & IIIB
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Gp IIIA
IIIB
III B, Ln
R(A) = 0.47 d(A) + 1.65
R(A) = 1.03 d(A) + 0.94, Ln


d) Gp IVA & IVB
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
1.0
2.0
3.0
Gp IVA
IVB
R(A) = 0.85 d(A) + 1.30


e) Gp VA & VB
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
1.0
2.0
3.0
Gp VA
VB
R(A) = 0.75 d(A) + 1.39


f) Gp VIA & VIB
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
0.0
1.0
2.0
3.0
Gp VIA
VIB
R(A) = 0.67 d(A) + 1.45



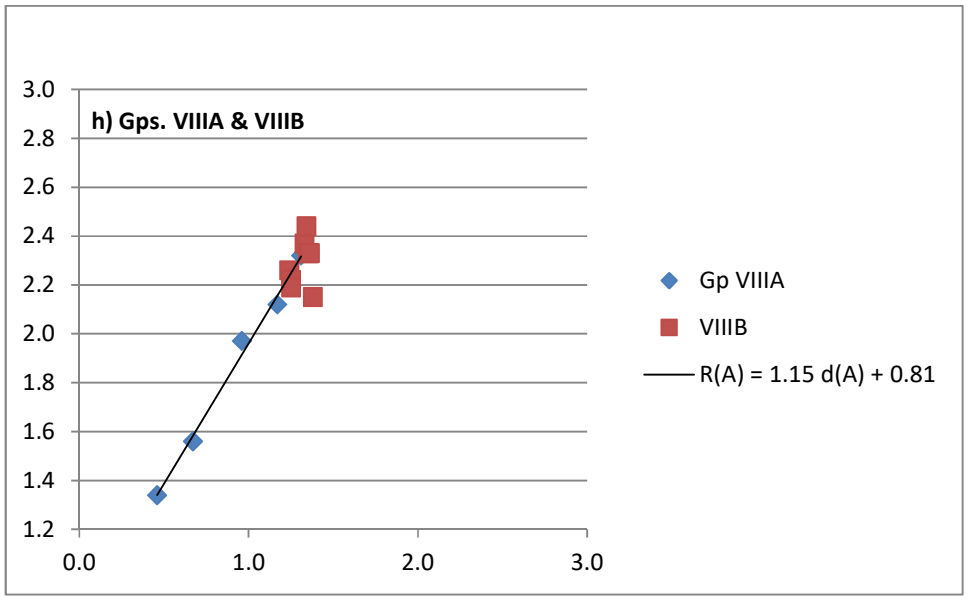


Fig. 1 a) - h). Linear dependence of calculated (free) atomic radii [2], R(A) on covalent radii [4], d(A) for elements of Gps. I A&B to VIII A & B

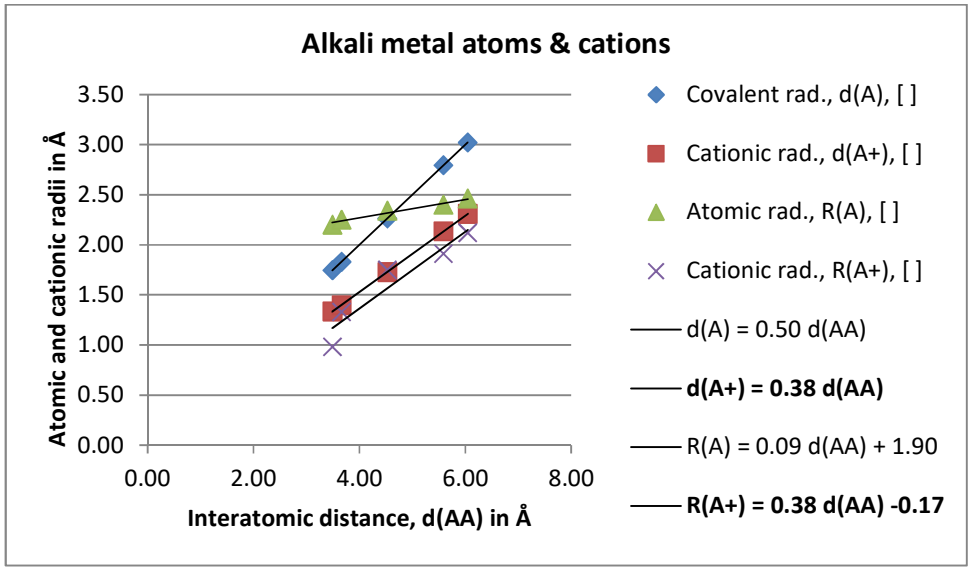


Fig. 2. Dependence of (free) atomic radii R(A) and cationic radii R(A+) from [2] and of covalent radii d(A) and cationic radii d(A+) from [5,10] on the interatomic distance, d(AA) (= edge length of the bcc metal lattice) [5]. The radii, d(A) = d(AA)/2 and d(A+) = d(AA)/ϕ2 = 0.38 d(AA), where ϕ is the Golden ratio. Note that the slope of R(A+) vs d(AA) is also 1/ϕ2 = 0.38, see Eq. 1.

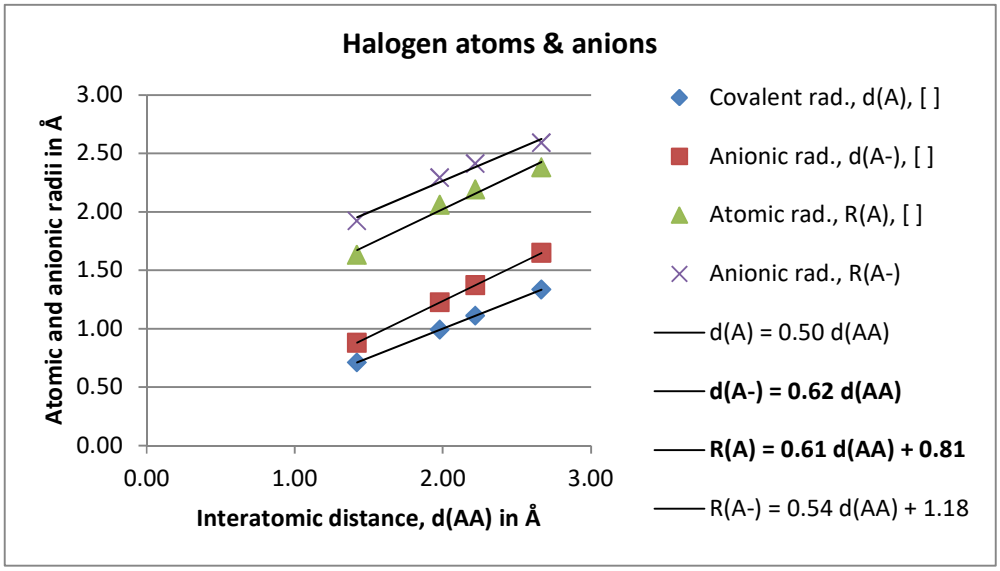


Fig. 3. Dependence of (free) atomic radii R(A) and anionic radii R(A-) from [2] and of covalent radii d(A) and anionic radii d(A-) from [5,10] on the interatomic distance, d(AA) (= covalent bond length). The radii, d(A) = d(AA)/2 and d(A-) = d(AA)/ϕ =0.62 d(AA), where ϕ is the Golden ratio. Note that the slope of R(A) vs d(AA) is equal to 0.61 ~ 1/f = 0.62, see Eq. 2.