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Molecular Single-Bond Covalent Radii for Elements 1–118

Pekka Pyykkö* and Michiko Atsumi[a]

Abstract: A self-consistent system of additive covalent radii, $R(AB) = r(A) + r(B)$, is set up for the entire periodic table, Groups 1–18, $Z = 1$–118. The primary bond lengths, R, are taken from experimental or theoretical data corresponding to chosen group valencies. All $r(E)$ values are obtained from the same fit. Both E–E, E–H, and E–CH_3 data are incorporated for most elements, E. Many E–E′ data inside the same group are included. For the late main groups, the system is close to that of Pauling. For other elements it is close to the methyl-based one of Suresh and Koga [*J. Phys. Chem. A* **2001**, *105*, 5940] and its predecessors. For the diatomic alkalis MM′ and halides XX′, separate fits give a very high accuracy. These primary data are then absorbed with the rest. The most notable *ex*clusion are the transition-metal halides and chalcogenides which are regarded as partial multiple bonds. Other anomalies include H_2 and F_2. The standard deviation for the 410 included data points is 2.8 pm.

Keywords: ab initio calculations · alkali metals · covalent radii · heavy metals · single bonds · superheavy elements

Introduction

The aim of additive covalent radii is to express approximately, as given in Equation (1), a bond length as the sum of two atomic radii.

$$R_{AB} = r_A + r_B \quad (1)$$

A well-known source for such covalent radii for single bonds are books by Pauling.[1,2] For metallic bonding see reference [3]. A more recent list is the VCH periodic table.[4] In simple terms, the single bond corresponds to a σ^2 electron pair in a bonding molecular orbital, as in ethane, $H_3C–CH_3$, or to a corresponding net excess, as in Cl_2.

In pure-bred form the radii are obtained by halving a homonuclear bond, as shown in Equation (2).

$$r(E) = R(E - E)/2 \quad (2)$$

Another possibility is to choose, as a standard, a group of moderate electronegativity, such as a methyl group. Then the radius of element E is obtained by subtracting $r(C)$ from $R(E–C)$. This was used by Alcock[5] and later by Suresh and Koga,[6] who employed their own calculated $H_3C–EH_n$ distances as data set. For ionic radii in crystals, this has been the standard procedure since the times of Bragg[7] or Wasastjerna,[8] notably including the ionic radii by Shannon and Prewitt.[9,10] Batsanov[11] used both E–C and E–H distances. He, however, added an electronegativity correction. In his book[12] he added E–E data, but the details are not given. A later attempt to introduce different r for different oxidation states was also made by him.[13]

Based on massive data mining from the Cambridge Structural Data Base (CSD), and fixing the radii for carbon (separately for the three usual hybridizations), nitrogen, and oxygen, Cordero et al.[14] recently gave a new set of putative single-bond covalent radii for the elements 1–96.

Our approach to covalent radii is somewhat different. We treat all elements and all admitted data points as equal. All radii are then obtained self-consistently through a least-squares fit. Specific molecular coordination numbers and oxidation states are chosen for each element involved. We reported such a set of triple-bond covalent radii for elements from Be to E112 in reference [15]. Their later usage has given many further confirmations and no radical deviations for this set.

A problem which one of us has been studying since 1978[16] was that of effective covalent radii for bonds between transition metals (M = TM) and halides, X, on one hand, and the corresponding M–H and M–CH_3 bonds, on the other hand: If the Pauling halogen radii are accepted for

[a] Prof. Dr. P. Pyykkö, Dr. M. Atsumi
Department of Chemistry, University of Helsinki
P.O.B. 55 (A.I. Virtasen aukio 1), 00014 Helsinki (Finland)
Fax: (+35) 89-191-50169
E-mail: Pekka.Pyykko@helsinki.fi

these nominally single M−X bonds, rather small r(M) are obtained. To make the M–H and M–CH_3 distances fit, one then needs a large, "hydridic" r(H) of about 58 pm. The corresponding r(C) was 97 pm. Our proposal has, fortunately, been completely neglected by the scientific community. We here make a new proposition. Our recent work has led us to believe that the M−X bonds actually have a partial multiple-bond character, coming from π(X)→π(M) donation. Therefore our new proposition is to simply omit the transition-metal M−X bonds from any single-bond data set. TM–halogen bonds are not single. (Obviously, ionic attraction terms may also shorten the bond.) The included points will fit to a self-consistent system, from Group 1 to Group 18.

One earlier example of such, suggested, partial multiple bonding was UF_6. If all the occupied *g* MO:s would bond to U 6d and all the occupied *u* MO:s to U 5f, uranium hexafluoride would have a nominal bond order of 3/2, instead of one.[17]

Finally note that for crystals, instead of ionic radii, one can derive a self-consistent set of ion volumes.[18]

Abstract in Finnish: *Alkuaineille 1–118 on määrätty yksinkertaisille sidoksille luonteenomaiset kovalenttiset säteet, R(AB) = r(A) + r(B). Sekä kokeellisia että teoreettisia sidospituuksien R arvoja on käytetty aineistona. Kullekin alkuaineelle on käytetty sille tyypillisiä koordinaatiolukuja. Kaikki säteet r on määrätty tasa-arvoisin perustein samassa sovituksessa. Useimmille alkuaineille E on käytetty sidoksia E–E, E–H ja E–CH₃. Lisäksi pääryhmien sisäisiä E–E′ sidoksia on käytetty. Myöhäisten pääryhmien säteet r ovat lähellä Paulingin arvoja. Muiden alkuaineiden säteet ovat lähellä Sureshin ja Kogan [*J. Phys. Chem. A ***2001***, 105, 5940] metyylipohjaisia arvoja. Kaksiatomisille alkalimetallimolekyyleille MM′ ja halogeeneille XX′ suoritetut erilliset sovitukset antavat erittäin suuren tarkkuuden. Samat alkuaineet sisältyvät myös koko systeemiin. Tärkeä havainto on, että siirtymämetallien halidit ja kalkogenidit on jätettävä tarkastelun ulkopuolelle koska niiden sidokset on luokiteltava osittaisiksi moninkertaissidoksiksi. Aineisto käsittää 410 pistettä ja tulosten neliöllinen keskipoikkeama on 2,8 pm.*

Abstract in Japanese:
原子番号は 1 から 118 まで、族は 1 から 18 までの周期表の全ての元素に対する共有結合半径 r(A)の値を求めた。このシステムによって、多くの化合物の結合長は R(AB) = r(A) − r(B) という加成性で与えられる。先ず基準となる結合長 R のセットを、種々の原子価の結合に対応する実験および理論的データから選んだ。これらのデータのセットに合うように全ての r(E)値が得られた。ほとんどの元素 E については、E-E、E-H と E-CH3 のデータについても成立する。同族の元素の間では、多くの E-E′値も取り込んだ。主系列で族番号の大きい方の元素についてはポーリングの値に近い。ほかの元素についての値は、スレッシュと古賀 [J. Phys. Chem. A 2001, 105, 5940]や彼等以前の論文で、メチル基を基準にして決めたものに近い。2 原子アルカリ分子 MM′とハロゲン間分子 XX′については、それぞれ別個にフィットをさせると非常に高い精度の結果が得られる。次にこれらの基準となるデータ以外のものを取り込んだ。この際、遷移金属ハロゲン化物とカルコゲニド化合物は除外した。これらは、非整数の多重結合をつくると考えたからである。その他に除外したものには、H_2 と F_2 がある。410 のデータを含み、標準偏差は 2.8pm である。

The working equations are listed in the Appendix. The homonuclear systems (2) do introduce a certain emphasis for radii, included in them (see Equation (5)).

Results and Discussion

'Sharp' results for partial sets

Alkali metal dimers: A fit to the available experimental R_e values for the 13 alkali-metal dimers in Table 1 gives the very small standard deviation of $\delta = 0.84$ pm. These "sharp" alkali radii predict for the unknown CsK an R_e of 428.1 pm. The theoretical value of 425.3 pm by Korek et al.[19] is not accurate enough to be useful. For LiRb the sum of radii predicts an R_e of 344.7 pm. This correlation is shown in Figure 1.

Table 1. The experimental and calculated R_e values (in picometers) for alkali metal dimers.[a] The experimental reference is Huber and Herzberg,[55] unless otherwise stated.

Molecule	Exptl	Calcd	Ref.
Li_2	267.29	268.6	
LiNa	288.5	288.2	[56]
LiK	331.915	330.2	[57]
LiRb	–	344.7	
LiCs	366.81	366.5	[58]
Na_2	307.887	307.8	
NaK	349.9035	349.8	[59]
NaRb	364.35	364.3	[60]
NaCs	385.063	386.2	[61]
K_2	390.51	391.9	
KRb	406.85	406.4	[62]
KCs	–	428.1	
Rb_2	420.99	420.9	
RbCs	441.84	442.7	[63]
Cs_2	465.1	464.5	[64]

[a] The radii from this specialized fit are: Li 134.3, Na 153.9, K 195.9, Rb 210.4, Cs 232.2.

Here one should notice that the r(Cs) of 253 pm, used in the Wiley-VCH Table, appears to be a perpetuated misprint of an earlier value of "235" pm, used by Sanderson.[20] That older value is close to our current one.

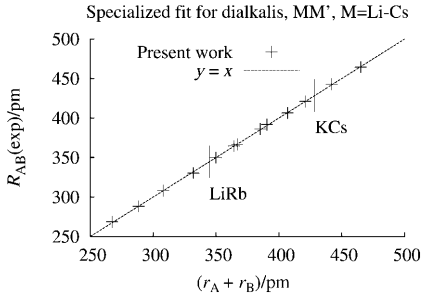

Figure 1. A comparison of the predicted bond lengths for alkali metal dimers with the experimental R_e values. For the data, see Table 1. No experimental R_e are available for LiRb and KCs.

In our comprehensive and final data set we add the available alkali hydride and methyl alkali distance data. Theoretical data for the heaviest alkalis are added, as well.

Dihalides: Similarly, a three-parameter fit to the six dihalides in Table 2 gives an excellent agreement for Cl–I. The mean-square deviation is only 0.29 pm. These halide radii

Table 2. The experimental and calculated R_e values (in picometers) for halogen dimers.[a] The experimental reference is Huber and Herzberg[55] in all cases.

Molecule	Exptl	Calcd
Cl_2	198.8	198.8
ClBr	213.6	213.5
ClI	232.1	232.6
Br_2	228.1	228.2
BrI	246.9	247.3
I_2	266.6	266.4

[a] The radii from this specialized fit are: Cl 99.4, Br 114.1, I 133.2.

are close to those of Pauling. If one subtracts these halogen radii from the experimental distances of the three fluorides XF, X = Cl–I, the resulting average r(F) becomes 61 pm.

The F_2 molecule is a special case. Its electronic structure has a strongly multiconfigurational character, see, for example, Blomberg and Siegbahn.[21] Pauling[22] first obtained his r(F) of 64 pm (identical with our final value) by erroneously using the bond length of, what later turned out to be an excited state of F_2.[23] We omit the F_2 data point as atypical from the present fit.

Alkali halides: At the opposite, ionic, extreme, the bond lengths of the alkali halides can be expressed as the sum of ionic radii (Table 3). In a broader sense, also the hydrides MH and the aurides MAu; M = Rb,Cs can be included, see Fit 2. Our fits should be regarded as a refinement of that of Collin and Smith.[24] In these fits the cations are small and the anions large.

Table 3. The fitted ionic radii (in picometers) for diatomic molecules MX. N is the number of data points and δ the mean-square deviation for the fit (1). Most R values are from Huber and Herzberg.[55] The "hard sphere" diatomic radii of Collin and Smith[24] are given for reference.

Atom	Fit 1[a]	Fit 2[b]	Ref. [24]
M = Li	37.8	39.0	44.61
Na	70.9	70.3	74.74
K	102.9	103.1	103.97
Rb	115.4	115.2	114.68
Cs	128.2	127.5	125.37
X = F	–	114.4	103.97
Cl	163.5	163.5	165.85
Br	178.9	178.8	179.71
I	201.6	201.5	199.08
Au	–	196.0	–
H	–	120.3	–

[a] $N = 15$, $\delta = 0.85$ pm. M = Li–Cs, X = Cl–I. [b] $N = 26$, $\delta = 1.56$ pm. M = Li–Cs, X = F–I, Au, H. NaF, CsF data points omitted.

In this fit the cation size differentials rather reflect the sizes of the outermost core orbitals. Hence Li^+, $1s^2$ is very small. The differentials of the halogen radii from Cl to I are similar for the covalent and ionic sets.

The total fit

General remarks: Both theoretical and experimental data were used in the present "total" fit. The primary data are given in Table 4. Some omitted cases are given in Table 5.

The computational methods and the fitting approach are discussed at the end. The converged radii are given in Figure 2 and the deviations from the predicted values are shown in Figure 3. Concerning the various groups of the periodic table we note the following:

Hydrogen: As discussed by Batsanov,[25] H_2 is anomalously long, having no core electrons. It is omitted from the present data set. If it were added, the r(H) would remain 32 pm but the standard deviation would increase by 0.04.

Group 1: For francium we use theoretical data for Fr_2, RbFr, and CsFr.[26] The additional hydride- and methyl-based data, and the heavy Fr change the alkali-only radii in Table 1 only slightly. As discussed earlier,[27] the CsH molecule has considerable 5d character in its bonding. It is hence anomalously short, and removed to Table 5.

Group 2: Here we include the neutral dihydrides MH_2 for M = Be–Ra, and the dimethyl compounds for M = Be–Ba. The recently studied single Mg–Mg bonds of about 285 pm[28,29] are coherent with the present r(Mg). The predicted Ca–Ca bonds[29] of about 380 pm are clearly longer than $2r$(Ca).

Group 3, lanthanides, and actinides: The lanthanides were treated by using computational data for the LnH_3, $(Cp)_2LnH$, and $Ln(CH_3)_3$ molecules. For actinides we mainly used our own calculations for model hydrides. Species with higher coordination numbers (than 3) were included for Th–Pu. Notice that Eu and Yb prefer to be divalent. An anomalously long r is then obtained, whether the LnL_2 or LnL_3 models are employed. The present YbH_2 R of 211.6 pm is near an HF value of 208 pm.[30] We therefore relegated the Ln^{II} data to Table 5 and used in the fit the data for Eu^{III} and Yb^{III}.

As discussed in the introduction for d-transition metals, also for the f-transition metal trihalides the M–X distances (M = Ln, An) are clearly shorter than predicted by the present radii.[31] Both multiple bonding and ionicity may contribute.

Group 4: Tetrahedral hydrides and methyl compounds were mainly used.

Group 5: Five-coordinate hydride and methyl compounds were used.

Table 4. The single-bonded species, used in the fit. In addition, all data in Table 1 are used. Unspecified references are from Huber and Herzberg.[55]

Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference
3	3	267.29	Li_2		1	10	99.1195	NeH^+	[85]	1	42	170.3	$CH{=}MoH_3$	[105]
6	6	153.1	C_2H_6	[65], p.914, [66]	1	11	188.66	NaH		1	42	170.2	$CH{=}MoH_2F$	[106]
6	6	153.7	$C(CH_3)_4$	[67]	1	12	173	MgH_2	[67]	1	43	159.8	TcH_5	PW
6	6	154	diamond	[65], p.913	1	13	157.5	Al_2H_6	[86], B3LYP	1	44	156.7	RuH_4	PW
7	7	145.3	N_2H_4	[65], p.803 (IR)	1	13	158.4	AlH_3	[86], B3LYP	1	45	161.7	RhH_3	PW
8	8	121.7	O_2F_2	[65], p.502	1	13	159	AlH_3	[67]	1	45	152	RhH_3	[107]
11	11	307.887	Na_2		1	13	159.7	AlH_3	[83], MP2	1	46	151.7	PdH_2	[108], open $^1A_1$ state
14	14	235	Si(s)	[65], p.986	1	14	148	SiH_4	[65], p.914	1	46	152.2	PdH_2	[79] p.550
14	14	236	$Si[Si(CH_3)_3]_4$		1	15	142.06	PH_3	[65], p.846	1	47	161.791	AgH	[96]
15	15	221.2	P_2Me_4	[68]	1	16	134	H_2S	[67]	1	48	166.4	CdH^+	
15	15	223	P(black)	[65], p.89	1	16	134.5	H_2S_2	[84]	1	48	167.917	CdH_2	[109]
16	16	202	S_2Me_2	[65], p.728	1	16	135	H_2S	[65], p.705	1	48	171.4	HCdCdH	PW, SDD
16	16	205.5	S_2H_2	[69]	1	16	135.2	H_2S_2	[69]	1	49	172.8	InH_3	[110]
17	17	198.79	Cl_2		1	17	127.49	HCl		1	49	175	InH_3	[83], MP2
19	19	390.51	K_2		1	18	128.056	ArH^+	[87]	1	49	175	InH_3	[111]
29	29	221.927	Cu_2	[70]	1	19	224	KH		1	50	170	SnH_4	[65], p.915
30	30	237.5	HZnZnH	[71]	1	20	200	CaH_2	[67]	1	50	171	SnH_4	[67]
30	30	236	Ar-ZnZn-Ar	[72]	1	20	203	CaH_2	[88], B3LYP	1	51	169.5	Sb_2H_4	[75]
30	30	230.5	(Cp*)ZnZn(Cp*)	[73]	1	21	181.3	ScH_3	[89]	1	51	170.4	SbH_3	[99]
32	32	241	Ge_2H_6	[65], p.914	1	21	183.5	ScH_3	[90], CCSD(T)	1	51	170.7	SbH_3	[65], p.879
32	32	245	Ge(s)	[74], p.24	1	22	168.8	TiH_4	[79], p.550	1	52	164	Te_2H_2	[69]
33	33	242.9	As_2Me_4	[68]	1	22	171.1	TiH_4	[91], BP86	1	52	164.4	Te_2H_2	[75]
34	34	229	Se_2Ph_2	[65], p.728	1	22	171.7	TiH_2Me_2	[92]	1	52	166	TeH_2	[67]
34	34	233	Se_2Me_2	[65], p.728	1	23	162.2	VH_5	PW	1	52	169	TeH_2	[100], B3LYP+SO
34	34	234.6	H_2Se_2	[75]	1	23	169.8	$HC{=}VH_2F^-$	[93]	1	53	160.99	HI	
35	35	228.105	Br_2		1	24	154.2	CrH_6(av)	[79], p.550	1	54	160.2813	XeH^+	[112]
37	37	420.99	Rb_2		1	24	153.5	CrH_6(av)	[94]	1	56	223	BaH_2	[67]
47	47	253.03	Ag_2	[76]	1	25	151.2	MnH_5	PW	1	56	228.1	BaH_2	[113]
48	48	269.6	HCdCdH	PW	1	26	148	FeH_4	PW	1	56	228.7	BaH_2	[88]
50	50	277.6	$Sn_2(CH_3)_6$	[77]	1	27	143.1	CoH_3	PW	1	57	211.1	LaH_3	[69], 4-comp. MP2
50	50	280	Sn(grey)	[78]	1	28	141.7	NiH_2	[79], p.550	1	57	212	LaH_3	[114]
51	51	281.8	Sb_2Me_4	[77]	1	28	142.6	NiH_2	[95]	1	57	214.2	$(Cp)_2LaH$	[115]
52	52	268.6	$Te_2(CH_3)_2$	[77]	1	29	146.2543776	CuH	[96]	1	58	194.2	CeH^+_3	[89]
52	52	276.2	H_2Te_2	[75], MP4	1	30	150.35	(Cp)ZnH	PW	1	58	195.9	$(Cp)_2CeH^+$	[115]
53	53	266.63	I_2		1	30	151.25	I-Zn-H	PW	1	59	208	PrH_3	[114]
55	55	465.1	Cs_2		1	30	151.4	ZnH^+		1	59	209.3	PrH_3	[89]
77	77	241.7	$H_2Ir{-}IrH_2$	[79], p.414	1	30	152.394	ZnH_2	[97]	1	59	211.2	$(Cp)_2PrH$	[115]
78	78	248.3	HPtPtH	[79], p.414	1	31	155.6	Ga_2H_6	[98]	1	60	207	NdH_3	PW
79	79	247.19	Au_2		1	31	156.7	GaH_3	[98]	1	60	209.9	$(Cp)_2NdH$	[115]
80	80	268.2	HHgHgH	PW	1	31	158.7	GaH_3	[83], MP2	1	61	206	PmH_3	PW
82	82	286.97	$(Bp)_3Pb{-}Pb(Bp)_3$		1	32	153	GeH_4	[67]	1	61	208.8	$(Cp)_2PmH$	[115]
82	82	288	$Pb_2(CH_3)_6$	[65], p.915	1	33	151.3	As_2H_4	[75]	1	62	204	SmH_3	PW
83	83	304	$Bi_2(SiMe_3)_4$	[75]	1	33	151.9	AsH_3	[65], p.879	1	62	207.8	$(Cp)_2SmH$	[115]
84	84	289.9	Po_2H_2	[75]	1	33	151.1	AsH_3	[99]	1	63	233	EuH^-_3	[114]
84	84	291	Po_2H_2	[69]	1	34	145	Se_2H_2	[69]	1	63	233.1	$(Cp)_2EuH^-$	[115]
85	85	297.9	At_2	[81]	1	34	145.9	Se_2H_2	[75]	1	64	202	GdH_3	PW
87	87	447	Fr_2	[26]	1	34	146	H_2Se	[65], p.705	1	64	205.9	$(Cp)_2GdH$	[115]
1	2	77.43	HeH^+	[82]	1	34	146.7	H_2Se	[100], B3LYP+SO	1	65	201	TbH_3	PW
1	3	159.4	LiH		1	35	141.456	HBr		1	65	204.5	$(Cp)_2TbH$	[115]
1	4	134	BeH_2	[67]	1	36	142.11904	KrH^+	[101]	1	66	200	DyH_3	PW
1	5	118	BH_3	[67]	1	37	236.6808	RbH	[102]	1	66	203.1	$(Cp)_2DyH$	[115]
1	5	119.1	BH_3	[83], MP2	1	38	215	SrH_2	[67]	1	67	199	HoH_3	PW
1	6	109	CH_4		1	38	216.4	SrH_2	[88], B3LYP	1	67	201.8	$(Cp)_2HoH$	[115]
1	6	111	C_2H_6	[65], p.914	1	39	197.1	YH_3	[89]	1	68	198	ErH_3	PW
1	7	100.8	N_2H_4	[84]	1	40	185	ZrH_4	[79], p.550	1	68	200.5	$(Cp)_2ErH$	[115]
1	7	101.1	$NH_2(CH_3)$	[65], p.914	1	40	186.8	ZrH_2Me_2	[103]	1	69	197	TmH_3	PW[80]
1	7	101.5	NH_3	[65], p.793	1	40	187	ZrH_4	[27]	1	69	199.4	$(Cp)_2TmH$	[115]
1	7	102.2	$NH(CH_3)_2$	[65], p.793	1	40	187.5	$CH_2{=}ZrHCl$	[104]	1	70	201.5	YbH_3	PW
1	8	96	H_2O	[65], p.653	1	41	175.5	NbH_5	PW	1	71	192.2	LuH_3	[69], 4-comp. MP2
1	8	97	H_2O_2	[69]	1	41	183.7	$HC{=}NbH_2F$	[93]					
1	9	91.76	HF		1	42	166.2	MoH_6(av)	[79], p.550					

Table 4. (Continued)

Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference
1	71	196	LuH_3	PW	1	94	208.1	PuH_3	PW,[131] B3LYP $^6A_2$	6	15	183.8	P_2Me_4	[68]
1	71	197.2	$(Cp)_2LuH$	[115]	1	95	202.6	AmH_3	PW	6	15	184.3	$P(CH_3)_3$	[65], p.846
1	72	183.2	HfH_4	[79], p.550	1	96	198.4	CmH_3	PW	6	15	184.7	$P(CH_3)_3$	[67] (ED)
1	72	185	HfH_4	[27]	1	97	199.6	BkH_3	PW	6	16	180.2	$S(CH_3)_2$	[67] (MW)
1	72	186.9	CH_2=HfHCl	[104]	1	99	197.2	EsH_3	PW	6	16	180.7		(ED)
1	73	176.9	TaH_5	PW	1	100	199.1	FmH_3	PW	6	16	181.9	MeSH	[84]
1	73	183.9	$HC{=}TaH_2F^-$	[93]	1	101	204.6	MdH_3	PW	6	17	178.5	$ClCH_3$	[67], (MW)
1	74	168.45	WH_6(av)	[79], p.550	1	102	207.8	NoH_3	PW	6	19	269.8	K-CH_3	[141]
1	74	169	WH_6(av)	[116,117]	1	102	212.2	NoH_2	PW, [132]	6	20	245.2	$CaMe_2$	[113]
1	74	171.9	$CH{=}WH_2F$	[106]	1	103	193.4	LrH_3	[69], 4-comp. MP2	6	20	248.7	$CaMe_2$	[142]
1	75	162.6	ReH_5	[79], p.391	1	103	197.2	LrH_3	PW	6	21	218.3	$ScMe_3$	[89]
1	75	163	ReH_5	PW	1	104	189.1	RfH_4	PW	6	22	205	TiH_2Me_2	[92]
1	75	166	$H_4Re{-}ReH_4$	[79], p.414	1	105	181.7	DbH_3	PW	6	22	208.5	$TiMe_4$	[143,144]
1	76	159.4	OsH_4	PW	1	105	180.9	DbH_5	PW	6	29	186.6	CuMe	[145]
1	76	160.1	OsH_4	[79], p.391	1	106	176.5	SgH_3	PW	6	29	192.2	$CuMe_2^-$	[145]
1	76	161.4	H_3Os-OsH_3	[79], p.414	1	106	178.688	SgH_6	PW	6	30	193	$Zn(CH_3)_2$	[67], (ED)
1	76	163.0	OsH_4	[118]	1	107	172.2	BhH_3	PW	6	31	196.7	$Ga(CH_3)_3$	[67], (ED)
1	76	165.3	ReH_4Me	[79], p.398	1	107	174.355	BhH_5	PW	6	32	194.5	$Ge(CH_3)_4$	[67], (ED)
1	77	154.5	IrH_2Me	[79], p.398	1	108	165.3	HsH_3	PW	6	32	195	$GeH_2(CH_3)_2$	[65], p.914
1	77	154.3	IrH_3	PW	1	108	165.6	HsH_4	PW	6	32	196	$(H_3Ge)_3CH$	[146], (ED)
1	77	154.8	IrH_3	[79], p.391	1	109	162.999	MtH_3	PW	6	32	197	$(H_3Ge)_4C$	[146], (ED)
1	77	155.3	H_2Ir-IrH_2	[79], p.414	1	110	156.855	DsH_2	PW	6	33	196.8	$As(CH_3)_3$	[67], (ED)
1	78	151.8	MePtH	[79], p.398	1	110	162.7	DsH_3	PW	6	34	194.3	$Se(CH_3)_2$	[67], (MW)
1	78	152	HPtPtH	[79], p.414	1	111	149.9	(E111)H	[133], SOPP/ CCSD(T)	6	35	193.2	$BrCH_3$	[67], (MW)
1	78	152	PtH_2	[79], p.550	1	111	151	(E111)H	[134]	6	37	285.9	Rb-CH_3	[141]
1	78	152.0	PtH_2	[95]	1	111	152.9	(E111)H	[135]	6	38	262.1	$SrMe_2$	[142]
1	78	152	$HPtCH_3$	[119,120]	1	111	154.3	(E111)H	PW ADF	6	39	234.8	YMe_3	[89]
1	79	152.3675	AuH	[96]	1	111	154.6	(E111)H	[136], BDF	6	40	227.3	$ZrMe_4$	[144]
1	80	159.44	HgH^+		1	112	151.7	$(E112)H^+$	[137]	6	41	220.4	$Nb(CH_3)_5$	[147]
1	80	163.315	HgH_2	[121]	1	112	158.3	$(E112)H^+$	[41]	6	47	211.1	AgMe	[145], MP2
1	80	168.7	HHgHgH	PW	1	113	168	$(E113)H_3$	[138], (av of 'T')	6	48	211.2	$Cd(CH_3)_2$	[67], (RR)
1	81	173	TlH_3	[122]	1	114	175	$(E114)H_4$	[124]	6	49	216.1	$In(CH_3)_3$	[67], (ED)
1	81	174.3	TlH_3	[83], MP2	1	115	193.8	$(E115)H_3$	PW	6	49	217.9	$In(CH_3)_3$	[148], B3PW91
1	81	179	TlH_3	[111]	1	116	204.7	$(E116)H_2$	[100], B3LYP+SO	6	50	213.4	$Sn(CH_3)_4$	[149]
1	82	174.3	PbH_4	[123]	1	116	204.7	$(E116)H_2$	[139]	6	50	214.4		[67], (ED)
1	82	175	PbH_4	[124]	1	116	205.9	$(E116)H_2$	[100], CCSD(T)+SO	6	51	216.3	$Sb(CH_3)_3$	[67], (ED)
1	82	175.4	Pb_2H_2	[123]	1	117	193.8	H(E117)	[126]	6	51	216.5	$Sb(CH_3)_5$	[150], (ED)
1	83	177.59	BiH_3	[125]	1	117	194.9	H(E117)	[127]	6	52	214.2	$Te(CH_3)_2$	[67], (ED)
1	84	174	Po_2H_2	[75]	1	117	198.3	H(E117)	[39], CCSD(T)	6	53	213.2	ICH_3	[67], (MW)
1	84	174	Po_2H_2	[69]	1	118	199.2	$(E118)H^+$	[41], CCSD(T)	6	56	275.7	$BaMe_2$	[142]
1	84	180.8	PoH_2	[100], B3LYP SO	3	6	203	$LiCH(SiMe_3)_2$	[140]	6	57	249.5	$LaMe_3$	[89]
1	85	173.7	HAt	[126], CCSD(T)	3	11	288.5	LiNa		6	57	257.6	$(Cp)_2La{-}CF_3$	[151]
1	85	174.2	HAt	[127]	3	19	331.915	LiK	[57]	6	59	246.1	$PrMe_3$	[89]
1	86	161.8	RnH^+	[41], CCSD(T)	3	55	366.81	LiCs	[58]	6	60	244	$NdMe_3$	[89]
1	87	250.9	FrH	PW	4	6	169.8	$Be(CH_3)_2$	[67]	6	61	243.1	$PmMe_3$	[89]
1	88	233.1	RaH_2	PW	5	6	157.8	$B(CH_3)_3$	[67]	6	62	241.7	$NdMe_3$	[89]
1	89	220.8	AcH_3	PW	6	7	146.6	$NH(CH_3)_2$	[65], p.793	6	63	270.1	$EuMe_3$	[89]
1	89	221.5	AcH_3	[69], 4-comp. MP2	6	7	147.4	$NH_2(CH_3)$	[65], p.793	6	64	239.3	$GdMe_3$	[89]
1	90	205.8	ThH_4	[128]	6	8	141.6	$O(CH_3)_2$	[65], p.500 (ED)	6	65	237.5	$TbMe_3$	[89]
1	90	207.1	ThH_4	[129]	6	8	142.5	MeOH	[84]	6	66	236.9	$DyMe_3$	[89]
1	90	207.1	ThH_4	[129]	6	9	138.9	FCH_3	[67]	6	67	235.8	$HoMe_3$	[89]
1	91	200.6	PaH_5	PW	6	11	231.5	Na-CH_3		6	68	234.7	$ErMe_3$	[89]
1	92	196.7	UH_6	[17]	6	12	212.6	$Mg(CH_3)_2$	[67]	6	69	234	$TmMe_3$	[89]
1	92	206.6	UH_3	[130], DFT $^4A_2$	6	13	195.7	$Al(CH_3)_3$	[67]	6	70	261.5	$YbMe_3$	[89]
1	93	202.9	NpH_4	PW	6	14	187	$(CH_3)_3SiH$	[65], p.914	6	71	232.4	$LuMe_3$	[89]
1	94	200.7	PuH_4	PW	6	14	187.5	$Si(CH_3)_4$	[67], (ED)	6	72	225.2	$HfMe_4$	[144]

Table 4. (Continued)

Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference	Z_1	Z_2	Distance	Species	Reference
6	73	216.6	$TaMe_5$ (av)	[150]	9	35	175.894	BrF		14	42	255.7	H_3 Si-MoH	[161]
6	73	219.8	$TaMe_5$	[147]	9	36	187.693	KrF_2	[153]	14	74	254.8	H_3 Si-WH	[161]
6	74	206.1	WH_5Me	[79], p.398	9	53	190.9759	IF		17	35	213.665	BrCl	
6	74	214.6	WMe_6	exp. see [152]	9	54	193.48	XeF_4	[154]	17	53	232.0878	ICI	
6	75	201.2	ReH_4Me	[79], p.398	9	54	195	XeF_4	[155], RCI	17	54	230.6	$XeCl^+$ in $[XeCl][Sb_7F_{11}]$	[162]
6	76	200.1	OsH_3Me	[79], p.398	9	54	197.436	XeF_2	[153]	17	116	273.6	$(E116)Cl_2$	[139]
6	77	200.4	IrH_2Me	[79], p.398	9	86	205	RnF_4	[155], RCI	19	37	406.85	KRb	[62]
6	78	200	$HPtCH_3$	[119]	9	86	210.3	RnF_2	[156]	29	47	237.35	AgCu	[163]
6	78	200.4	HPtMe	[79], p.398	9	86	213.5	RnF_2	[157], CCSD(T)	29	79	233.03	AuCu	[164]
6	79	201.7	AuMe	[145], MP2	9	118	221.7	$(E118)F_2$	[157], CCSD(T)	34	50	257.9	av Sn–Se in CSD	[165]
6	79	204.8	AuMe	[79], p.398	9	118	215	$(E118)F_4$	[155], RCI(D_{4h})	35	53	246.8989	IBr	
6	80	208.3	$Hg(CH_3)_2$	[67], (ED)	9	118	214	$(E118)F_4$	[155], RCI (T_d)	35	116	288.4	$(E116)Br_2$	[139]
6	80	209.4		(RR)	11	19	349.935	NaK	[158]	37	55	441.8	RbCs	[166, 167]
6	81	220.6	$Tl(CH_3)_3$	[67], (ED)	11	37	364.35	NaRb	[159]	37	87	434	RbFr	[26]
6	82	223.8	$Pb(CH_3)_4$	[67], (ED)	11	55	385.063	NaCs	[61]	53	116	310.0	$(E116)I_2$	[139]
6	83	226.7	$Bi(CH_3)_3$	[67], (ED)	14	15	224.8	$P(SiH_3)_3$	[65], p.846	55	87	452.4	CsFr	[26]
8	30	177.01	$Zn(OH)_2$	PW	14	16	212.9	$S(SiH_3)_2$	[160]	85	116	321.3	$(E116)At_2$	[139]
9	17	162.8313	ClF		14	34	227	$Se(SiH_3)_2$	[65], p.705	116	117	342.0	$(E116)(E117)_2$	[139]

[a] PW = present work. [b] Mean value of two different X-ray experiments. [c] Mean value for X = Cl and Br.

Group 6: Six-coordinated hydride and methyl compounds were used. Because both adopt low-symmetry, C_{3v} structures, an average of the two distances was taken.

Group 7: ML_5 systems were used.

Table 5. List of some outlier data points, which are not included in the fit. "PW" = present work.

Z_1	Z_2	Distance	Species	Reference	Reason[a]
83	83	305.34	Bi_2R_4, R = $(Me_3Si)_2CH$	[168]	aa
1	54	191.6	HXeH	[34]	a
1	55	249.38	CsH	[27]	b
1	63	233.	EuH_3^-	[114]	c
1	63	233.1	$(Cp)2EuH^-$	[115]	c
1	70	224.2	YbH_3^-	[114]	c
1	70	222.5	$(Cp)2YbH^-$	[115]	c
1	70	211.6	YbH_2	PW	c
1	72	178.2	HfH_3^+	[98]	d
1	95	200.2	AmH_2	PW	dd
3	6	195.9	$LiCH_3$	[140]	d
5	8	136	$B(OH)_3$(s)	[65] p. 1067	d
6	22	199.1	$TiMe_3^+$	[89]	d
6	22	213	$TiBz_4$	[169]	e
6	40	214.7	$ZrMe_3^+$	[89]	d
6	40	221.2	ZrH_2Me_2	[103]	d
6	63	270.1	$EuMe_3$	[89]	c
6	58	233.2	$CeMe_3^+$	[89]	ee
6	70	261.5	$YbMe_3^-$	[89]	c
6	72	214.7	$HfMe_3^+$	[89]	d
8	14	163.4	$O(SiH_3)_2$	[65] p. 500	d
8	32	176.6	$O(GeH_3)_2$	[65] p. 500	d
9	18	197	HArF	[35]	a
79	111	256.7	(E111)Au	[136]	f
111	111	264.6	$(E111)_2$	[136]	g

[a] Abbreviations: aa: diminish statistical weight of homonuclear Bi–Bi bonds; a: far too long, compared to present radii; b: too short, uses 5d orbitals; c: too long, being a divalent lanthanide; d: short; dd: divalent; e: long; "Bz" = benzyl, $C_6H_5CH_2$-; ee: tetravalent and short; f: long; g: open-shell.

Group 8: ML_4 systems were used.

Group 9: ML_3 systems were used.

Group 10: ML_2 systems of C_{2v} symmetry were used.

Group 11: ML, M = H, Me. In the coinage-metal group (M = Cu, Ag, Au, Rg) (Rg = roentgenium, E111), the monovalent systems ML, L = H, Me were used. The intermetallics AgCu and AuCu were added. The resulting r(Au) is 4 pm smaller than r(Ag).

Group 12: ML_2 systems were used. The Zn–Zn distances of the new dizinc compounds fit in well.

Group 13: ML_3 systems were used. As discussed by Himmel and Gaertner,[32] variations of Ga–Ga distances occur in the range 239–254 pm for putative single bonds. The present $2r$(Ga) is 248 pm.

Group 14: Elements of Group 14 were treated as tetracoordinate. Concerning the homonuclear E–E distances we include, in addition to molecular data, solid diamond, Si, Ge, and grey tin. As noted by Pauling on p. 247 of reference [2], the E–E′ distance in SiC is anomalously short. He attributed it to an ionic contribution. Another reason could be the involvement of Si d orbitals. We omit SiC. More generally this anomalous shortness affects the bonds in the neighborhood (Si, P, S)–(O, F). Pitzer[33] evoked differences in core repulsion between 2nd-row (2s2p) and 3rd-row (3s3p) elements, to explain it.

Concerning the Group 14 halides, EX_4, for E = Ge–Pb and X = I, the present radii give distances, close to the experimental ones.[31] For the more ionic systems X = F–Br, the experimental R are below the sum of radii.

Single-bond covalent radii

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 32																	He 46
2	Li 133	Be 102											B 85	C 75	N 71	O 63	F 64	Ne 67
3	Na 155	Mg 139											Al 126	Si 116	P 111	S 103	Cl 99	Ar 96
4	K 196	Ca 171	Sc 148	Ti 136	V 134	Cr 122	Mn 119	Fe 116	Co 111	Ni 110	Cu 112	Zn 118	Ga 124	Ge 121	As 121	Se 116	Br 114	Kr 117
5	Rb 210	Sr 185	Y 163	Zr 154	Nb 147	Mo 138	Tc 128	Ru 125	Rh 125	Pd 120	Ag 128	Cd 136	In 142	Sn 140	Sb 140	Te 136	I 133	Xe 131
6	Cs 232	Ba 196		Hf 152	Ta 146	W 137	Re 131	Os 129	Ir 122	Pt 123	Au 124	Hg 133	Tl 144	Pb 144	Bi 151	Po 145	At 147	Rn 142
7	Fr 223	Ra 201		Rf 157	Db 149	Sg 143	Bh 141	Hs 134	Mt 129	Ds 128	Rg 121	E112 122	E113 136	E114 143	E115 162	E116 175	E117 165	E118 157
CN	1	2	3	4	5	6	5	4	3	2	1	2	3	4	3	2	1	1,2

6	La 180	Ce 163	Pr 176	Nd 174	Pm 173	Sm 172	Eu 168	Gd 169	Tb 168	Dy 167	Ho 166	Er 165	Tm 164	Yb 170	Lu 162
7	Ac 186	Th 175	Pa 169	U 170	Np 171	Pu 172	Am 166	Cm 166	Bk 168	Cf 168	Es 165	Fm 167	Md 173	No 176	Lr 161
CN	3	4	5	3,6	3	3	3	3	3	3	3	3	3	3	3

Figure 2. The proposed single-bond covalent radii in pm. The CN are typical coordination numbers assumed for the elements.

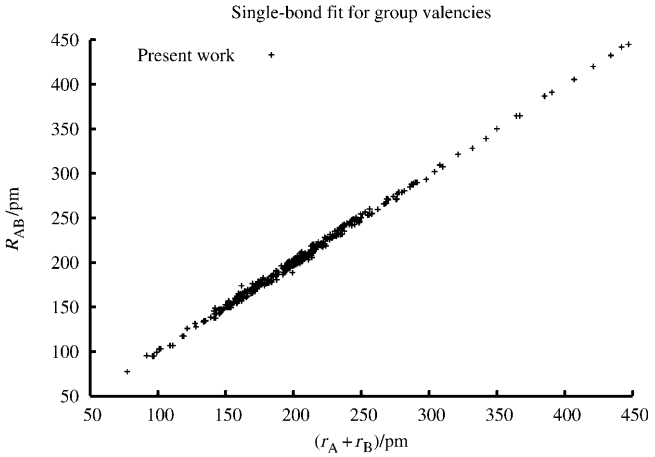

Figure 3. The correlation between predicted and observed bond lengths for the full data set in Table 4.

Group 15: Here we mainly used ML_3 systems of C_{3v} symmetry. Concerning the Group 15 halides, EX_3, for E = Sb, Bi, and X = I, the present radii give distances, close to the experimental ones.[31] For the more ionic systems X = F–Br, the experimental R are below the sum of radii.

Group 16: ML_2 systems were used, for elements up to E116.

Group 17: The halide coordination number was 1.

Group 18: For the noble gases He–(E118), the hydride ions $(Ng)H^+$ were included in the data set. For He, Ne, and Ar these were the only data points. For Kr–(E118), also the difluorides and for Xe–(E118) the tetrafluorides were added. Although the "tension" between the hydride ions and the fluorides yields the largest errors of the fit, it was felt valuable to include both of them for the noble gases. It also should be noted that the calculated Ng–E distances of many of the noble-gas compounds, newly observed in matrices, are much longer than the sum of the present radii. An example is XeH_2, Xe–H 193.4,[34] compared to a Σr of only 163 pm. In a simple picture, this system is bound by a single σ_u^2 two-electron-three-center (2e3c) bond. Another example is the first argon compound, HArF, having H–Ar 133,[35] Σr 128 but Ar–F 197, Σr 160 pm. In other words, their covalent bonds can be clearly weaker than those included here. The present Group 18 bonds are comparable with those of their Group 17 neighbors.

The present noble-gas radii for Ne–Xe are comparable with those of Sanderson[20] of 71, 98, 112, and 131 pm, respectively.

The Xe–Au distance of XeAuF[36] in Table 6 agrees well with the present radii. Note however, that the valence isoelectronic $IAuI^-$ would be too short. The weakness of the noble-gas bonding and the strength of a TM–X bond may give two cancelling errors.

Table 6. Further comparisons with data points, not included in the fit.

Z_1	Z_2	$r_A + r_B$	R_{exptl} or R_{calcd}	Species	Reference
1	7	103	103	NH_4^+	[65] p. 792
5	6	160	161	$[Cp(CO)_2Mn_2(\mu)\text{-}BtBu)]$	[170]
5	25	204	202	$[Cp(CO)_2Mn_2(\mu)\text{-}BtBu)]$	[170]
9	18	160	162.0	ArF^+	[171]
54	79	255	254.5675	Xe–AuF	[36]

Periodic trends

Among the alkali metals in Group 1, francium is smaller than caesium, due to relativistic effects. Along a long row, a broad minimum would seem to occur near Groups 8–10, with a reservation for the changes of oxidation state. Among the p-block elements, a monotonous decrease of r would seem to take place, from Group 13 to or almost to Group 18. An interesting anomaly is that gallium is slightly smaller than aluminum.

As regards the row, the main-group elements show the trend $2p << 3p < 4p < 5p \leq 6p$. Note here the anomalously small size of the nodeless 2p shell[37,38] On the 6p row, the homonuclear Bi–Bi bonds are longer than the neighbor-

ing Pb–Pb and Po–Po bonds, whereas the Bi–H and Bi–C bond lengths are comparable with the Pb and Po ones. Examples of all three bonds were included in the final data set.

Along the actinide row, the obtained single-bond radii are larger than the lanthanide ones for Ac and Th. After a descent between Pa and Np, they approach the lanthanide ones towards the end of the series. Among the lanthanides, europium and ytterbium prefer to be divalent, f^7 and f^{14}, respectively. The corresponding covalent radii are larger than the trivalent ones. Here we used the latter, like Cordero et al.,[14] whereas the Wiley-VCH table[4] uses the divalent Eu and Yb radii.

The single-bond radii of the 6d elements in Groups 4–10 are a few pm larger than for their 5d analogues. On the contrary, E111 (Rg) and E112 are clearly smaller than the corresponding elements Au and Hg, respectively. A similar trend was observed earlier for the triple bonds.[15]

The superheavy 7p elements E113–E118 suffer from large spin-orbit (SO) effects. Compared to their 6p analogues, E113 and E114 are smaller. In their electronic structure the lower, $7p_{1/2}$ component is predominant. The elements E115–E118 are clearly larger than their 6p analogues. Now the $7p_{3/2}$ is the highest valence orbital. This contrast between the monohydrides of E113 and E117 was noticed earlier by Han et al.[39]

One also must notice the possibility of p–s-hybridization where the 7p mixes with the higher-lying, empty, 8s atomic orbital.[40,41]

Hoffmann's isolobal systems comprise systems, like $(OC)_5Mn–L$, for a singlet σ bond.[42] We find that for hydrides, L = H, the sum of the present M and H radii is comparable to, or a little below the calculated or experimental M–H distances.[43,44] The calculated M–CH_3 and M–M distances for such systems are clearly larger than predicted by the present radii.

From single to double to triple: It is aesthetically pleasing if the covalent radii, r_n, for bond order n obey for each element, E, the relation given in Equation (3).

$$r_1 > r_2 > r_3 > \quad (3)$$

Comparing the present r_1 values in Figure 2 with the analogous r_3 of reference [15] and our preliminary r_2, we see that this condition mostly holds. When it does not, as for r(Ag), the r_3 is suspicious. The full comparison is left for future work.

Beyond triple bonds: Nagarajan and Morse[45] used their results for transition-metal diatomics to deduce the "multiple-bond radii" V 89, Cr 84, Nb 104, and Mo 97 pm. They correspond to a bond-order n of 5–6 and are, indeed, shorter still than our triple-bond radii.

Further Validation

Metal–metal bonds: A general observation by Pauling[46] is that the metal–metal single-bond lengths are quite variable. For instance, Fe–Fe distances of 240–280 pm are quoted by him. It therefore is preferable to use such M–M distances as a test of radii, determined otherwise.

The observed Pt–Hg bonds of about 252 pm[47] are close to the sum of radii. A random selection of other recent data is given in Table 6.

Comparison with previous sets: As seen from Figure 4, the present radii are perhaps closest to the spirit, and often the values, of Suresh and Koga[6] and Batsanov.[12] A comparison with the CSD fit of Cordero et al.[14] is shown in Figure 5. Their statistically large but unsorted data base yields (C, N, O)-based radii that tend to be larger than ours, probably because larger coordination numbers than ours were included. For such applications, their radii are presumably better. A comparison with the VCH set is seen in Figure 6. It agrees

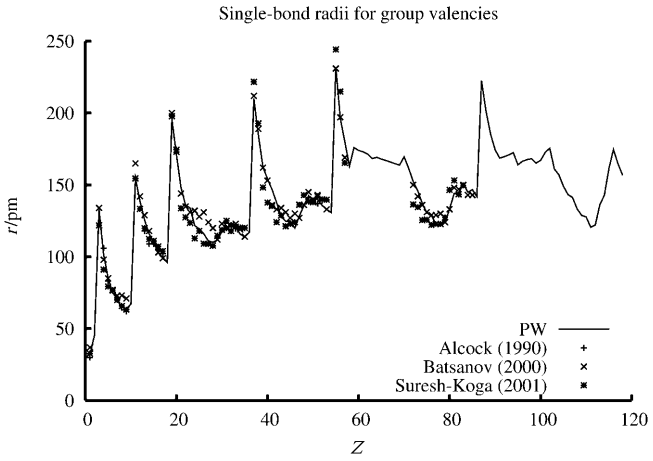

Figure 4. A comparison of the present radii, given by the line, with those of Alcock,[5] Suresh and Koga[6] and Batsanov.[12]

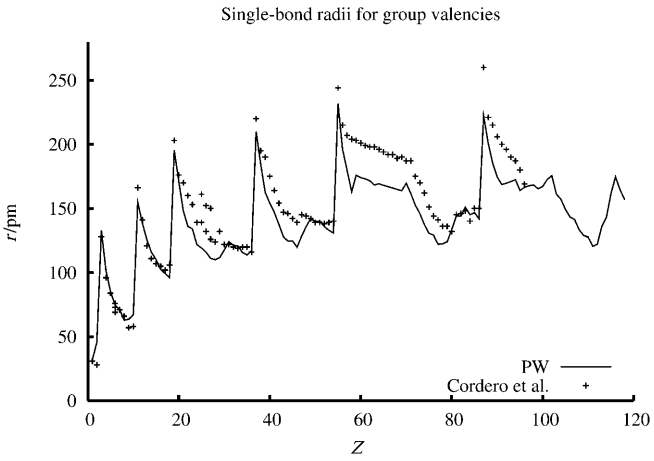

Figure 5. A comparison of the present radii, given by the line, with those of Cordero et al.[14]

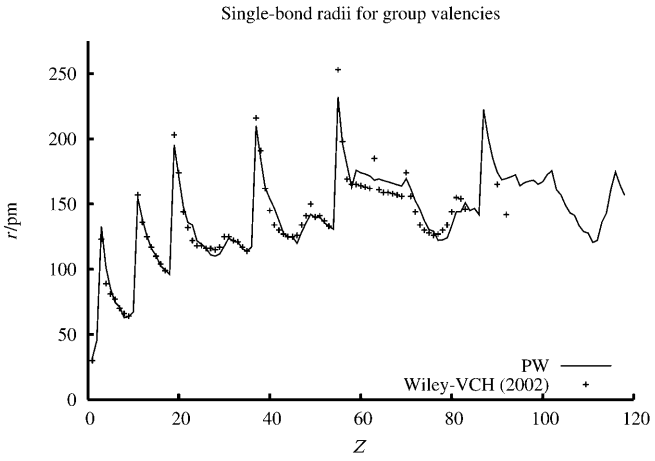

Figure 6. A comparison of the present radii, given by the line, with the VCH ones.[4]

fairly well with the present one, except for the trivalent lanthanides where the VCH radii are smaller. A shift of the minima for the 3d, 4d, and 5d metals is also seen. The alkali-metal radii, especially r(Cs), should be changed against the present ones. The small Th and U radii may refer to an attempt to include their bonds to halides among covalent single bonds.

Conclusions

While there is no theoretical obligation for additive covalent radii [Eq. (1)] to work at all, we here find that for narrow classes of compounds, such as diatomic dialkalis or dihalides, their mean-square error δ lies below 1 pm when the present radii are used. For general elemental combinations, of the elements 1–118, in the subset allowed here, we present a self-consistent set of additive single-bond covalent radii with δ below 3 pm, for the data set used. These radii have a potential predictive value when assessing the corresponding experimental data. We repeat that the set is not designed for M−X bonds between transition metals M and halides X because these are considered by us to be partial multiple bonds. Further data can be used to either improve, or partially invalidate the present system of radii.

Computational Details

Data and fitting methods: Both experimental and computed bond lengths were used. The experimental data comprise both gas-phase molecular data and some crystal-structure data. No attempt was made to even out the "noise", corresponding to the standard deviation.

The same iterative program was used as in the triple-bond work.[15] It is based on the penalty function over homonuclear and heteronuclear pairs [Eq. (4)].

$$\sum_k (\Delta_k)^2 = \sum_i^{K_{homo}} (R_{ii}-2r_i)^2 + \sum_{ij}^{K_{hetero}} (R_{ij}-r_i-r_j)^2 \quad (4)$$

Putting its derivatives with respect to r_i equal to zero, one obtains the iterative algorithm [Eq. (5)].

$$r_i^{(N+1)} = \frac{1}{4K_{\mathrm{homo}} + K_{\mathrm{hetero}}}\left[\sum_i^{K_{\mathrm{homo}}} 2R_{ii} + \sum_j^{K_{\mathrm{hetero}}} (R_{ij}-r_j^{(N)})\right] \quad (5)$$

Here K is the number of data points in each set and N the iteration. No convergence difficulties or signs for multiple minima were noticed. The final data set (Table 4) had 410 points, used for fitting the 118 radii. The standard deviation, given by Equation (6) was 2.8 pm.

$$\varepsilon = \left[(\sum_{\mathrm{tot}}^{K} \Delta^2)/K_{\mathrm{tot}}\right]^{1/2} \quad K_{\mathrm{tot}} = K_{\mathrm{homo}} + K_{\mathrm{hetero}} \quad (6)$$

Quantum-chemical methods: Quantum-chemical calculations were carried out using density functional methods, as implemented in the packages Gaussian 03[48] for transition-metal hydrides and ADF[49] for actinides and transactinides. The density functional BP86[50] with the following basis set combination was used in the former case. The scalar relativistic effects for the transition metals were included via quasirelativistic small-core pseudopotentials, so called ECP, of the Stuttgart group.[51] The corresponding basis sets of the transition metals were augmented by two polarization f-functions and one g-function, see reference [52]. For the main-group elements we used an aug-cc-pVTZ basis. The structures were optimized with standard gradient methods available in Gaussian 03. To deal with all actinides and transactinides with the same accuracy, ADF was chosen for those calculations, the reason being that similar frozen cores and basis-sets are available in this program for all actinides and transactinides. Relativistic effects were then treated with the "zeroth-order regular approximation" (ZORA).[53] The innermost electrons of the heavy metals were treated as frozen, using small frozen cores. For all elements, the TZ2P basis sets and the density functional PBE[54] were used.

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