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A Consistent Approach toward Atomic Radii

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Hybrid-density functional calculations on methyl group substituted elemental hydrides of the form H_3C-EH_n (E is any main block or d block transition element and n is 0, 1, 2, 3, or 4 depending on the position of E in the periodic table) give atomic radii (R_A) as the C−E bond distance minus half of the C−C bond distance of ethane. R_A values show good linear correlations with the experimental covalent radii, Slater's empirical set of atomic radii, and experimental carbon-based atomic radii particularly for the main block elements. Except a few cases, the sum of any two R_A values reproduces very well the corresponding mean single bond distances in molecules. Further, R_A values provide the calculation of an expected density (Ds′) of the element, which shows a good linear correlation with solid-state density of elements (Ds) when they are metals, suggesting similarity in their atomic packing. The percentage of free space (V_{free}) in the solid-state calculated using Ds′ and Ds suggests that all the metals have V_{free} below 66, all the metalloids have V_{free} between 66 and 71, and all the nonmetals have V_{free} above 71.

Introduction

The use of the term "atomic radius" is very common in the literature, especially in the fields of crystallography, material science, and chemistry. However, one can find several different sets of atomic radii in the literature, and the complete picture of the periodic table is not very easy to obtain from them because the selection of the atomic radius of an element often becomes arbitrary.[1−23] Bragg in 1920 used the idea that atoms in molecules and crystals can be treated as hard spheres to derive the first set of atomic radii.[1] Following this assumption, later Slater proposed an empirical set of atomic radii (R_{Slater}) for most of the elements[7] derived by the careful comparison of bond lengths in over 1200 bond types in ionic, metallic, and covalent crystals and molecules. He also found a strong correlation between the R_{Slater} and the quantum mechanically calculated radii of maximum charge density in the outermost shell of the atom.[8] Following this result, Clementi, Raimondi, and Reinhardt determined another set of atomic radii (R_{CRR}) from minimal-basis-set SCF wave functions for ground-state atoms.[11] Another quantity sometimes referred to as a good criterion of atomic size in molecules is the covalent radius ($R_{covalent}$), which is defined as half of the single bond length between two atoms of same kind.[4,10,14] Because the size of the neutral atom in the molecule largely depends on the substituents, coordination number, or ligands attached to it, the ideal systems for the covalent radii measurement are systems consisting of same atoms and having only single bonds. Although these criteria are difficult to achieve for many elements in the periodic table (a good example is nitrogen), one gratifying thing is that among the different set of atomic radii, the radii of main block elements show good agreement between each other, primarily because of the predictable nature of the bonding patterns of these elements in their compounds. On the other hand, assigning a single consistent set of atomic radii for transition elements (TEs) becomes problematic due to the various coordination patterns and spin states available for them. Further, the preferred coordination state as well as the spin state of TE systems often depends on the attached ligands. However, we note that the metallic radii simply taken as half of the M−M distance (M is a metal atom) in 12-coordinate metals is proposed as a good measure of the atomic size of a metal.[6]

It is therefore important to have a consistent approach to understand the periodic nature of atomic radii. Alcock[18] discussed such an approach based on carbon-based radii. In this approach, the radii are those derived by subtracting the radius of carbon atom from $C(sp^3)-X$ distances (abbreviated here as R_{Alcock}). An sp^3 carbon is ideally suited for this purpose because it has no lone pairs, no empty p- or d-orbitals, and is not of high electronegativity, therefore a consistent C−X distance could be obtained.[17,18] The radius of carbon is easily obtained from the C−C bond distances in saturated hydrocarbon chains[17] as 0.767 Å. Experimental carbon-based radii are available only for groups 13 to 17 and hydrogen and beryllium. The case of TEs is again a challenging problem because of the absence of a suitable $C(sp^3)$-X system where X is a TE moiety. However, a computational model of the $C(sp^3)-X$ system with almost all of the elements can be studied systematically using modern quantum mechanical methods. In this work, a method, which gives consistent carbon-based atomic radii suitable for all the main block elements and the d block transition elements, will be presented.

Methodology

It is already mentioned that the radius of a carbon atom in a saturated hydrocarbon is a good measure of its atomic radius.[17,18] For example, half of the C−C bond distance of ethane can be considered as the methyl group-based atomic radii of carbon atom (R_{carbon}). In a similar manner, the C−E (E is any element other than noble gases) bond distance, d_{C-E}, in molecules such as H_3C-H, H_3C-Li, H_3C-BeH, H_3C-BH_2, H_3C-NH_2, H_3C-OH, and H_3C-F can be used for obtaining the methyl group based atomic radius, R_A, of an element: i.e., $R_A = d_{C-E} - R_{carbon}$. Basically, the idea used here is to connect an element E with a methyl group and saturate its remaining normal valencies with hydrogen atoms. Because the C and E of C−E bond are saturated with hydrogen atoms, there is only little chance for

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TABLE 1: $CH_3{-}EH_n$-Based Atomic Radii (R_A) and Various Other Atomic Radii (All Value in Å)[a]

atom	R_A	$R_{covalent}$	R_{CRR}	R_{Slater}	R_{Alcock}	$R_{Pauling}$	Ds′	Ds	V_{free}
H	0.327	0.37	0.53	0.25	0.299	0.30	11504	89.8	99.2
Li	1.219	1.34	1.67	1.45			1518	535	64.8
Be	0.911	0.90	1.12	1.05	1.060		4726	1848	60.9
B	0.793	0.82	0.87	0.85	0.830		8607	2530	70.6
C	0.766	0.77	0.67	0.70	0.767	0.77	10585	2267	78.6
N	0.699	0.75	0.56	0.65	0.702	0.70	16290	1250	92.3
O	0.658	0.73	0.48	0.60	0.659	0.66	22234	1429	93.6
F	0.633	0.71	0.42	0.50	0.619	0.64	29697	1710	94.2
Na	1.545	1.54	1.90	1.80			2473	968	60.9
Mg	1.333	1.30	1.45	1.50			4072	1738	57.3
Al	1.199	1.18	1.18	1.25	1.180		6205	2700	56.5
Si	1.123	1.11	1.11	1.10	1.090	1.17	7871	2330	70.4
P	1.110	1.06	0.98	1.00	1.088	1.10	8975	1823	79.7
S	1.071	1.02	0.88	1.00	1.052	1.04	10355	1960	81.1
Cl	1.039	0.99	0.79	1.00	1.023	0.99	12533	3210	74.4
K	1.978	1.96	2.43	2.20			2003	856	57.3
Ca	1.745	1.74	1.94	1.80			2993	1550	48.2
Zn	1.187	1.31	1.42	1.35			15500	7140	53.9
Ga	1.199	1.26	1.36	1.30	1.250		16039	5904	63.2
Ge	1.179	1.22	1.25	1.25	1.220	1.22	17569	5323	69.7
As	1.209	1.19	1.14	1.15	1.196	1.21	16819	5727	66.0
Se	1.201	1.16	1.03	1.15	1.203	1.17	18092	4819	73.4
Br	1.201	1.14	0.94	1.15	1.199	1.14	18285	3140	82.8
Rb	2.217	2.11	2.65	2.35			3111	1532	50.8
Sr	1.928	1.92	2.19	2			4848	2630	45.7
Cd	1.429	1.48	1.61	1.55			15275	8650	43.4
In	1.385	1.44	1.56	1.55	1.41		17122	7310	57.3
Sn	1.380	1.41	1.45	1.45	1.39	1.40	17918	7310	59.2
Sb	1.421	1.38	1.33	1.45	1.37	1.41	16836	6697	60.2
Te	1.400	1.35	1.23	1.4	1.391	1.37	18430	6240	66.1
I	1.397	1.33	1.15	1.4	1.395	1.33	18460	4660	74.8
Cs	2.442	2.25	2.98	2.6			3620	1879	48.1
Ba	2.149	1.98	2.53	2.15			5488	3510	36.0
Hg	1.465	1.49	1.71	1.5			25281	13590	46.2
Tl	1.531	1.48	1.56	1.9			22570	11850	47.5
Pb	1.434	1.47	1.54	1.8			27881	11340	59.3
Bi	1.496	1.46	1.43	1.6			24748	9780	60.5

[a] At the B3LYP/6-31++G(d,p) level for H−Br and the B3LYP/Gen level for Rb−Bi. The density values Ds and Ds′ are in Kg/m^3. See text for details.

TABLE 2: $CH_3{-}TH_n$-Based Atomic Radii (R_A) and Various Other Atomic Radii (All Value in Å)[a]

atom	R_A	$R_{covalent}$	R_{CRR}	R_{Slater}	$R_{metallic}$	Ds′	Ds	V_{free}
Sc	1.337	1.44	1.84	1.60	1.641	7453	2985	60.0
Ti	1.274	1.36	1.76	1.40	1.462	7932	4507	43.2
V	1.236	1.25	1.71	1.35	1.346	10707	6110	42.9
Cr	1.128	1.27	1.66	1.40	1.282	14367	7140	50.3
Mn	1.180	1.39	1.61	1.40	1.264	13242	7470	43.6
Fe	1.091	1.25	1.56	1.40	1.274	17064	7874	53.9
Co	1.089	1.26	1.52	1.35	1.252	19521	8900	54.4
Ni	1.077	1.21	1.49	1.35	1.246	18604	8908	52.1
Cu	1.146	1.38	1.45	1.35	1.278	16755	8920	46.8
Y	1.482	1.62	2.12	1.80	1.801	10822	4472	58.7
Zr	1.377	1.48	2.06	1.55	1.602	13847	6511	53.0
Nb	1.353	1.37	1.98	1.45	1.468	14858	8570	42.3
Mo	1.240	1.45	1.90	1.45	1.400	19933	10280	48.4
Tc	1.287	1.56	1.83	1.35	1.360	18395	11500	37.5
Ru	1.212	1.26	1.78	1.30	1.339	22478	12370	45.0
Rh	1.229	1.35	1.73	1.35	1.345	24362	12450	48.9
Pd	1.240	1.31	1.69	1.40	1.376	22152	12023	45.7
Ag	1.362	1.53	1.65	1.60	1.445	16934	10450	38.3
La	1.653	1.95		1.65	1.877	12185	6146	49.6
Hf	1.364	1.50	2.08	1.55	1.580	27910	13310	52.3
Ta	1.346	1.38	2.00	1.45	1.467	29426	16650	43.4
W	1.256	1.46	1.93	1.35	1.408	36742	19250	47.6
Re	1.258	1.59	1.88	1.35	1.375	36742	21020	42.9
Os	1.222	1.28	1.85	1.30	1.353	41311	22610	45.3
Ir	1.227	1.37	1.80	1.35	1.357	45279	22650	50.0
Pt	1.227	1.28	1.77	1.35	1.387	41848	21090	49.6
Au	1.273	1.44	1.74	1.35	1.442	37894	19300	49.1

[a] Calculations at the B3LYP/6-31++G(d, p) level for Sc−Cu and at the B3LYP/Gen level for Y−Au. The density values Ds and Ds′ are in Kg/m^3. See text for details.

any other electrons to directly interact with it. Therefore, the R_A values are expected to show the inherent atomic size of E. However, this approach has some difficulty when applied to TEs because of the different possible coordination patterns and spin states. How can we circumvent these difficulties? Note that all of the $CH_3{-}EH_n$ systems mentioned above for the main block elements are closed-shell systems. To be compatible to these, we must use a closed-shell $CH_3{-}TH_n$ system too, where T is a transition element. For this purpose, let us assume that during the formation of $CH_3{-}TH_n$ two electrons go to a lone pair orbital and the remaining outer shell electrons participate in the bond formation with CH_3 and the hydrogens. To realize this, we must use 0, 1, 2, 3, and 4 T−H bonds for elements in groups 3, 4, 5, 6, and 7 and 3, 2, 1, and 0 T−H bonds for elements in groups 8, 9, 10, and 11, respectively. Note that these geometries may not be the most stable conformations. However, the computed C−T bond is expected to show the same behavior as the C−E bond of the main block elements, mainly due to the pairing of the outermost electrons of T. This will serve as a systematic and consistent way to understand the atomic radii in molecules.

To simplify the description, hereafter we collectively call all of the systems methyl−element−hydride (MEH) systems. Based on the above strategy, the geometry optimization of MEH systems containing elements up to bismuth (except Ce to Lu and noble gases) have been done at density functional theory level using the B3LYP functional[24] in Gaussian 98 set of programs.[25] For molecules containing elements up to bromine, the 6-31++G(d,p) basis set[26] is used in the calculations. For other molecules, a general basis set is used, which contains 6-31++G(d,p) for C and H, and LanL2DZ+pol for the other elements[27−29] (here, "pol" indicates an extra polarization function). This method is expected to give reliable geometries.

Results and Discussion

In this work, the atomic radii, R_A, is defined as C−E bond length minus half of the C−C bond length of ethane. In Tables 1 and 2, the R_A and atomic radii from other sources are depicted. Figure 1 gives the linear correlations between the R_A values of the main block elements and the corresponding $R_{covalent}$, R_{Slater}, R_{CRR}, and R_{Alcock}. As one can see, the R_A values are in very good agreement with the $R_{covalent}$ values (correlation coefficient, c.c., is 0.992). This correlation is particularly important because in the present study, except for the C−C bond, there is no pure covalent bond in $CH_3{-}EH_n$ systems. The empirical set of atomic radii proposed by Slater (R_{Slater}) based on experimental data also shows a good linear correlation with the R_A values. However, the linear correlation between R_A and R_{CRR} is not as good as that obtained with $R_{covalent}$ or the R_{Slater} radii values. A near perfect agreement can be seen between the R_A values and the R_{Alcock} (not available for TE) values based on the average $C(sp^3){-}X$ distances from X-ray diffraction data. In fact, the R_A fitting to the experimental data (R_{Alcock}) gives slope and *y*-intercept nearly one and zero, respectively. This result strongly supports the present approach to atomic radii. Table 1 also depicts Pauling's covalent atomic radii ($R_{Pauling}$),[5] which are nothing but half of the average X−X distances in molecules (the values for H and F are exceptions). It can be noted that $R_{Pauling}$ and R_A values are nearly the same for most of the atoms. However, deviations of 0.053, 0.049, 0.061, and 0.067 Å between these two quantities are observed for the atoms Si, Cl, Br, and I, respectively.

It is already mentioned that there is no good atomic radii data available for the transition metals. Unlike the main block

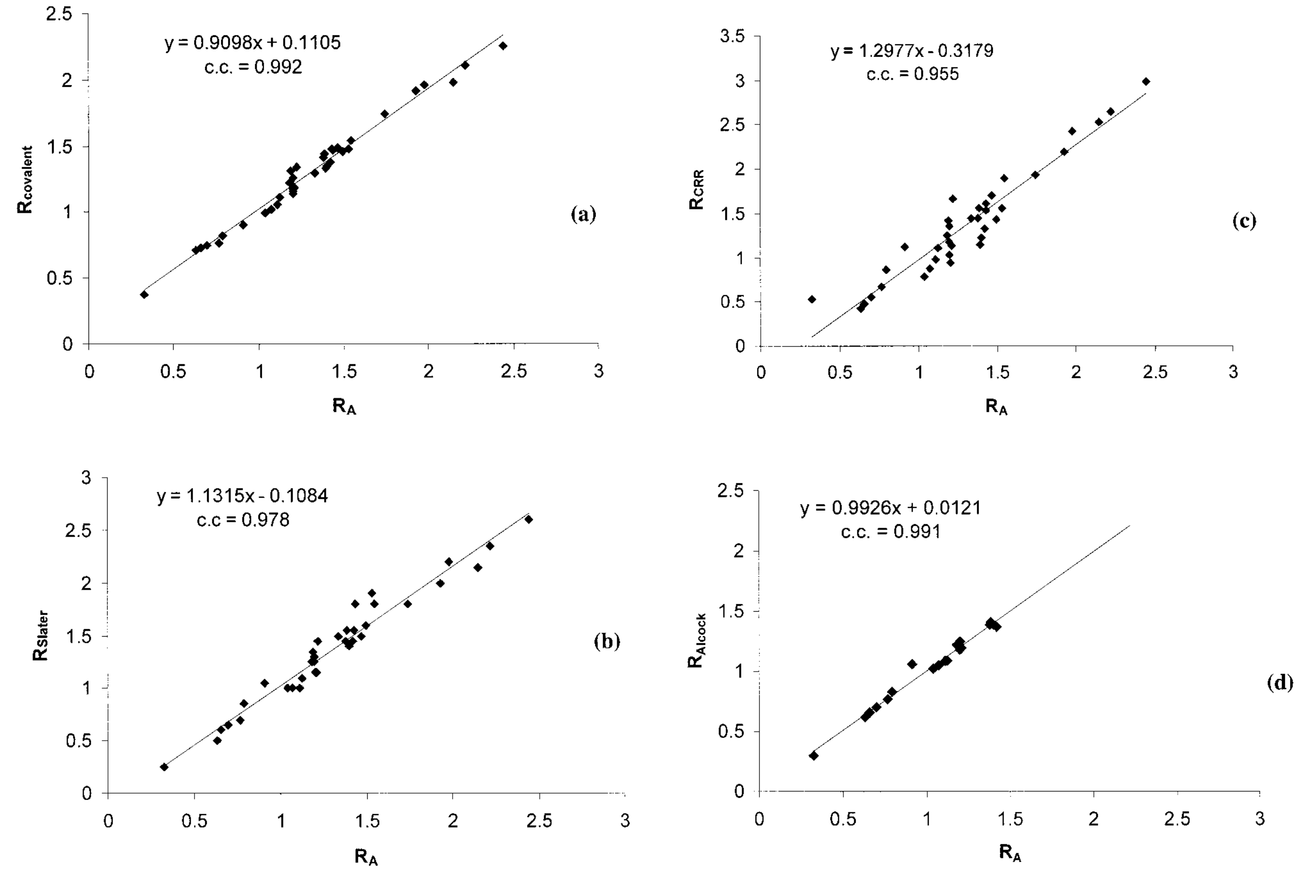

Figure 1. Correlations between the present scale of atomic radii (R_A) and other popular atomic radii scales. (a) Covalent; (b) Slater; (c) Clementi−Raimondi−Reinhardt; and (d) Alcock.

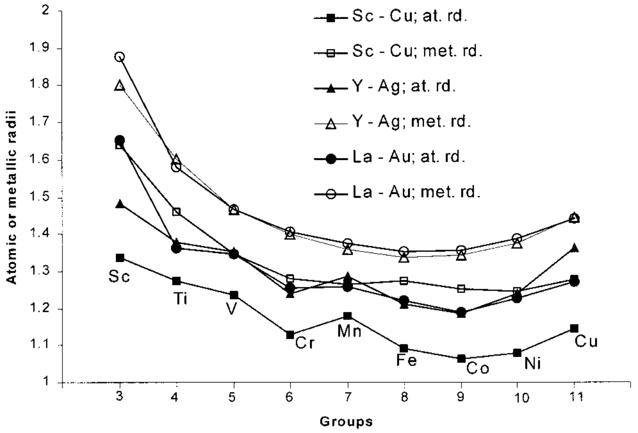

Figure 2. Comparison of atomic (R_A) and metallic ($R_{metallic}$) radii of transition elements.

elements, the R_A values obtained for TE show only poor linear correlations with the $R_{covalent}$, R_{Slater}, and R_{CRR}. These radii data used for comparison with R_A were derived without a systematic selection of the TE systems in terms of the coordination number, spin state, and the attached ligands and the theory used in the calculations was poor, they could be highly erroneous and therefore the poor correlation is somewhat expected. It is also easily seen from the fact that unlike the main block elements, the $R_{covalent}$, R_{Slater}, and R_{CRR} radii values of TE do not show any good agreement between each other. On the other hand, a consistent data that gives the atomic size of a TE could be the metallic radii, which are also given in Table 2. R_A and $R_{metallic}$ values exhibit almost a parallel trend (cf. Figure 2). Both of these quantities generally show a gradual decrease as one goes from the group 3 to the group 9 and after that there is a slight increase in their values. Exceptions to these observations are R_A values of Mn, Tc, and Re. Further, both R_A and $R_{metallic}$ values for the third row TE are almost the same as or even in some cases smaller than those for the second row elements in the same group. This behavior is expected due to the larger relativistic effects in the case of third row TE.[30]

Is there any other meaningful way to judge the goodness of the R_A values obtained in this study? A physical property of an element that can be directly correlated with its atomic size is the solid-state density (Ds), which is nothing but the mass of 1m^3 of the solid element at specified conditions. Generally Ds values correspond to the thermodynamically most favored allotrope of an element at ambient temperature. Because the volume enclosed by a sphere of radius R_A contains the atomic mass of an element, one can calculate the mass of 1 m^3 of the element as its expected density, Ds′ by assuming no free space in it. In Figure 3, the values of Ds and Ds′ given in Tables 1 and 2 are compared.[20,31,32] As one can see from this figure, all of the metals are nearly on a single line, which suggest that the atomic packing or the free space available in these systems is somewhat similar. On the other hand, the nonmetallic elements show quite large values for their expected density as compared to their actual density, indicating a lot of free space in these systems. The scenario becomes clearer by defining a percentage of free volume (V_{free}) in the solid state of an element as

$$V_{free} = 100\,(1 - \mathrm{Ds}/\mathrm{Ds}') \qquad (1)$$

V_{free} values are also given in Tables 1 and 2. A simple classification of the elements into metals, metalloids, and nonmetals based on V_{free} alone is immediately obtained. All of

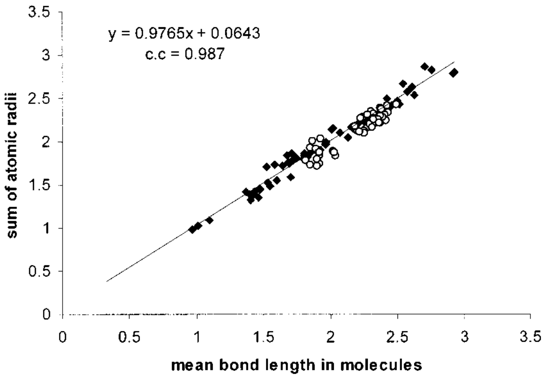

Figure 3. Correlations between the expected density (Ds′) and the solid-state density (Ds) of elements. The linear fit is for all of the metals.

TABLE 3: Mean Single Bond Length (*d*) in Compounds of Main Block Elements and the Corresponding Sum of Bonded Atom R_A Values (R_{Sum})[a]

bond	d	R_{sum}	bond	d	R_{sum}	bond	d	R_{sum}
As−N	1.858	1.908	C−I	2.162	2.163	N−S	1.710	1.770
As−Cl	2.268	2.248	C−N	1.469	1.465	N	1.425	1.398
As−F	1.678	1.842	C−O	1.432	1.424	N−Si	1.748	1.822
As−C	1.963	1.975	C−S	1.809	1.837	N−O	1.463	1.357
As−O	1.710	1.867	C−Si	1.863	1.889	N−P	1.730	1.809
As−S	2.275	2.280	C−Te	2.158	2.166	O−P	1.689	1.768
As−As	2.459	2.418	C−P	1.855	1.876	O−S	1.645	1.729
B−B	1.701	1.586	C−Se	1.970	1.967	O−Te	2.133	2.058
B−Br	1.967	1.994	Cl−P	2.008	2.149	P−P	2.214	2.220
B−C	1.597	1.559	Cl−S	2.072	2.110	P−Si	2.264	2.233
B−P	1.922	1.903	Cl−Si	2.020	2.162	Zn−I	2.574	2.584
B−S	1.806	1.864	Cl−Te	2.520	2.439	Zn−Br	2.390	2.388
B−Cl	1.833	1.832	F−S	1.527	1.704	Zn−Cl	2.255	2.226
B−F	1.365	1.426	F−N	1.406	1.332	Cd−Br	2.611	2.630
B−N	1.549	1.492	F−P	1.579	1.743	Cd−Cl	2.499	2.468
B−O	1.468	1.451	F−Si	1.694	1.756	Cd−I	2.754	2.826
C−C	1.530	1.532	H−N	1.009	1.026	Hg−Br	2.539	2.666
C−Cl	1.793	1.805	H−O	0.967	0.985	Hg−Cl	2.423	2.504
C−F	1.399	1.399	I−I	2.917	2.796	Hg−I	2.702	2.862
C−H	1.092	1.093	I−Te	2.926	2.799	Hg−S	2.624	2.536

[a] All values in Å.

the metals have V_{free} in the range of 36−66, and all of the nonmetals have V_{free} larger than 71. The V_{free} values of metalloids fall into the middle range of 66−71.

If the R_A values obtained here are a reliable measure of the atomic size in molecules, the sum of any two R_A values in Tables 1 and 2 must be very close to the corresponding interatomic single bond distances in molecules. A test on this criterion is done by comparing the sum of any two R_A values to the corresponding mean bond length, *d*.[32] A total of 113 different mean bond lengths can be obtained from ref 31, and the corresponding sums of the radii (R_A) of the bonded atoms (R_{sum}) are given in Tables 3 and 4. The number of *d* values showing absolute deviation from R_{sum} in the range of 0.00−0.05, 0.05−0.10, 0.10−0.15, and 0.15−0.19 Å are 50, 33, 20, and 10, respectively. In fact, comparatively larger deviations are obtained mainly for bonds involving transition elements, and generally the deviations of bonds involving other elements are less than 0.1 Å. Particularly noted in the main block elements are S−F, As−F, P−F, As−O, and Si−Cl bonds where the deviations are found to be 0.177, 0.164, 0.164, 0.157, and 0.142, respectively. The cause of such large deviations could be the large electronegativity values of F, O, and Cl, which are the first three most electronegative elements in the periodic table. The maximum deviation is only 0.028 Å for the bonds involving carbon, which is somewhat expected due to the MEH system-based derivation of R_A. R_A values therefore can be used confidently in the molecular modeling of organic molecules.

TABLE 4: Mean Single Bond Length (*d*) in Compounds of Transition Metals and the Corresponding Sum of Bonded Atom R_A Values (R_{Sum})[a]

bond	d	R_{sum}	bond	d	R_{sum}	bond	d	R_{sum}
O−Ti	1.847	1.932	S−V	2.378	2.307	Cl−Co	2.254	2.128
O−V	1.917	1.894	S−Mn	2.328	2.251	Cl−Ni	2.217	2.116
O−Cr	1.816	1.786	S−Fe	2.271	2.162	Cl−Cu	2.179	2.185
O−Mn	1.914	1.838	S−Co	2.254	2.160	Cl−Zr	2.426	2.416
O−Fe	1.913	1.749	S−Ni	2.187	2.148	Cl−Nb	2.374	2.392
O−Co	1.899	1.747	S−Cu	2.292	2.217	Cl−Mo	2.389	2.279
O−Ni	1.848	1.735	S−Mo	2.401	2.311	Cl−Tc	2.323	2.326
O−Cu	1.899	1.804	S−Tc	2.302	2.358	Cl−Ru	2.409	2.251
O−Zr	1.924	2.035	S−Ru	2.238	2.283	Cl−Rh	2.369	2.268
O−Nb	1.869	2.011	S−Pd	2.351	2.311	Cl−Pd	2.326	2.279
O−Mo	1.911	1.898	S−Ag	2.493	2.433	Cl−Ta	2.383	2.385
O−Rh	2.035	1.887	S−Ir	2.382	2.298	Cl−W	2.390	2.295
O−Pd	2.016	1.898	S−Pt	2.320	2.298	Cl−Re	2.368	2.297
O−W	1.900	1.914	Cl−Ti	2.313	2.313	Cl−Os	2.357	2.261
O−Re	1.890	1.916	Cl−V	2.224	2.275	Cl−Ir	2.361	2.266
O−Os	1.914	1.880	Cl−Cr	2.309	2.167	Cl−Pt	2.323	2.266
O−Pt	2.028	1.885	Cl−Mn	2.346	2.219	Cl−Au	2.276	2.312
S−Ti	2.432	2.345	Cl−Fe	2.195	2.13			

[a] All Values in Å.

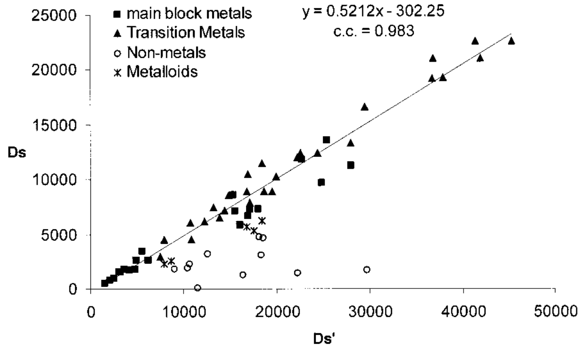

Figure 4. Correlations between the expected density (Ds′) and the solid-state density (Ds) of elements. The linear fit is for all the metals.

To get a pictorial representation of the whole scenario, *d* values are plotted against R_{sum} (the predicted bond length) in Figure 4. A correlation line with slope and intercept equal to 0.98 and 0.06, respectively, is also depicted in the figure for main block elements. It is gratifying to note that all of the points corresponding to the transition elements fall nearly on the same line, which further confirms the consistency of the present approach toward atomic radii.

Conclusions

A new reliable scale of atomic radii is obtained for all of the main group elements and transition elements based on theoretically calculated geometries of $H_3C{-}EH_n$ (depending on the position of E, in the periodic table, $n = 0, 1, 2, 3,$ and 4). The predicted radii are in very good agreement with the experimentally determined carbon-based radii. An additive model of atomic radii of bonded atoms generally describes the interatomic single bond distances in molecules. Further, the atomic sizes as realized from these radii are used for extracting a correlation of it with the solid-state density of the elements and thereby characterizing the elements into metals, metalloids, and nonmetals from a simple criterion involving the percentage of free space present in the solid state.

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