Orbital Radii and Environment-Independent Transferable Atomic Length Scales

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Abstract: The importance of the orbital radii, r_l, obtained from the classical turning point of the valence electron wave function of angular momentum, l, in obtaining interatomic distances for all bonding situations is demonstrated. Single bond interatomic distances may be expressed in terms of a universal multiplicative constant of a core s orbital radius and another universal additive term which is close to the interatomic distance in the hydrogen molecule. These relationships are obtained from the dependence of the radii of positive or negative singly charged ionic species, CR^+ and CR^-, on r_l. The shortening of the distances in multiple bond systems or in systems involving transition metal d electron elements is described by a simple universal function, F_S, associated with the number of unpaired valence electrons. A principle of maximum mechanical hardness based on minimization of bond distances is proposed to obtain correct distances in heteropolar MX bonds. The application of these rules to a large number of compounds with ionic, covalent, metallic, and nonbonded interactions yield interatomic distances which are within 2% of the observed distances. A brief discussion is made on the physical significance of the transferable length scales CR^+ and CR^- in the context of discrimination of structure based on radius ratio and the requirement of a universal equilibrium chemical potential for transferability.

I. Introduction

Much of the chemical insights involved in the understanding of properties of molecules and solids is based on the pioneering interpretation by Pauling[1] of distances in equilibrium structures in terms of some standard distances of model compounds, real or assumed. Such bond distances are usually obtained from atomic length scales such as ionic radii, covalent radii, metallic radii, and van der Waals' following the chemically appealing intuition that interatomic distances would depend on the bonding situation.[1] A simple understanding of such single-atom length scales remains[2] as "perhaps the single most critical elemental variable", especially since other properties could follow[3–6] from it.

A qualitative improvement on Pauling's understanding of atomic length scales would be to demonstrate the validity of transferable environment-independent atomic length scales that are valid for *all* bonding situations. Considerable success in this direction has been obtained[7–9] from the angular-momentum-dependent orbital radii (referred to hereafter as r_l for the angular momentum quantum number, l) from the classical turning point compared to the empirical radii based on interatomic spacing in crystals.[10–12] More recently, efforts have been made to define radii such as a mean valence radius[13] obtained from atomic valence electron charge density and to relate these radii to the electronegativity and also for obtaining interatomic distances. Such methods require a prior knowledge of the electronegativity and system-dependent functions of the number of valence electrons. We propose a universal method based on r_l for obtaining interatomic distances for *all* bonding situations without requiring a prior knowledge of the electronegativity scale.

It has been recently shown[14] that the set of system independent Cohen–Zunger orbital radii,[7,8] r_l, derived from density functional theory has a simple relationship to the empirical environment-dependent cationic or anionic radii.[12] A set of radii CR^+ and CR^- were associated with each element, with

$$CR^+ = C_l^+ r_l + D_l^+ \tag{1a}$$

and

$$CR^- = C_l^- r_l + D_l^- \tag{1b}$$

with l being the average of s and p orbitals ($l = \langle sp \rangle$). The radii CR^+ and CR^- are seemingly independent of valence or coordination number. The valence determines the number of bonds, and relation 2 gives the distance in each bond. Moreover, it was shown[14] that the sum of such "ionic" radii associated with *positively* and *negatively* charged species may be used to obtain interatomic distance, $d_{\mathrm{M-M}}$, in *homopolar* bonds or in nontransition metal elements, as if the length scales are independent of the nature of the bonding interactions. Thus:

$$d_{\mathrm{M-M}} = CR^+ + CR^- \tag{2a}$$

$$= C_l r_l + D_l \tag{2b}$$

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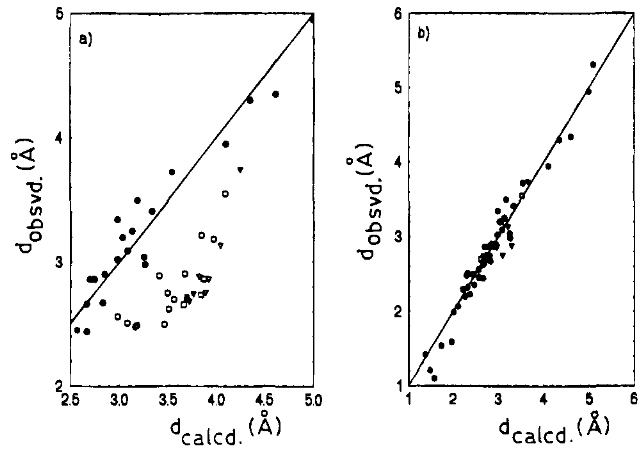

Figure 1. (a) The plot of d_{obsd} (from ref 17) *vs* $d_{M-M,calcd}$ for the transition elements using eq 2 and the nonrelativistic value of r_s from ref 8; open circles, 3*d* elements; squares, 4*d* elements; triangles, 5*d* elements; filled circles, nontransition metal elements. (b) Plot of d_{obsd} (from ref 17) *vs* $d^S_{M-M,calcd}$ for all the elements using eqs 3 and Table 2 for the values of *S* used. The lines correspond to $d_{obsd} = d_{calcd}$.

so that all interatomic distance of the elements could be expressed in terms of an universal multiplicative constant, C_l of a core orbital radii, r_l, and a constant additive length scale, D_l which was found to be close to the interatomic separation of the hydrogen molecule when $r_l = r_{\langle sp \rangle}$, the average of r_s and r_l.

In this paper we have extended the relationship of the core orbital radii to the interatomic distances for all bonding situations including that between transition metal elements, multiple bonds, heteropolar bonds, as well as nonbonded interactions. For this purpose we have modified our earlier relation by an universal parameter,[15] F_S, that accounts for the changes in bond distance with the number *n* of unpaired valence electron. A method is given for obtaining the direction of charge transfer in heteropolar *M*−*X* bonds which is independent of any prior knowledge of the electronegativity or even the number of valence electrons once *n* is defined. This method is thus quite different from that reported recently by Zhang *et al.*[16]

II. Transferable Length Scales

Given the form of eqs 1 and 2 there is no *a priori* reason for the particular choice of r_l in eq 2. A plot of the bond distance,[17] d_{M-M}, against the corresponding r_l for non-transition metal elements[18] yields various values for C_l and D_l from eq 2b for various *l* (Table 1). D_s is close to the interatomic separation of the hydrogen molecule. This suggests that only r_s may be sufficient for the prediction of interatomic distances to a first approximation. Zhang *et al.*[13] have already noted that just r_s may be sufficient for describing bonding properties and electronegativity in elements.

1. Relation between Homopolar Distances in Transition Metal Elements and Multiple Bond Distances. Equation 2b ($l = s$) shows large deviations when applied to the interatomic distance of transition metal elements (Figure 1a). Expressing[16] the number of unpaired electrons in terms of a spin ($S = n/2$), with *n* being obtained[19] from the position of the atom in the periodic table, it is found[20] by curve fitting that

$$d^S_{M-M} = d_{M-M}/F_S \tag{3a}$$

with d_{M-M} being obtained from eq 2b and with

$$F_S = C(S)[S(S+1)]^{n(S)} \tag{3b}$$

Table 1. Values of Coefficients $C_pC_l^+$, and C_l^- and $D_pD_p^+$, and D_l^- for Various Values of *l*

r_l	C_l	D_l (Å)	C_l^+	D_l^+ (Å)	C_l^-	D_l (Å)
$r_{\langle sp \rangle}$[a]	4.50	0.74	1.96	−0.29	2.54	1.03
r_s	4.74	0.73				
r_p	3.10	1.25				
r^0_G[b]	4.73	0.74	2.24	−0.37	2.49	1.11

[a] $r_{\langle sp \rangle}$ is the arithmetic average of r_s and r_p for various elements. The values of the various coefficients have been taken from ref 14. [b] See section II.2 for details.

The best fit is obtained for $C(S) = 1.19$ and $n(S) = 0.08$. We show in Figure 1b the plot of the calculated "spin-corrected" interatomic distance, d^S_{M-M}, using eqs 3 for the transition metal (3d, 4d, and 5d) elements and the nonrelativistic Zunger−Cohen value[8] for r_s. Equation 3 are *applicable to any element* that has unpaired valence electrons but are not applicable to elements having core unpaired electrons such as the rare-earth elements with core 4f electrons. In calculating the interatomic distances of La, the value of *S* is taken as $^1/_2$ just as in Y or Sc.

Expression 3b gives values of F_S = 1.16, 1.26, 1.32, 1.37, 1.41 for S = $^1/_2$, 1, $^3/_2$, 2, and $^5/_2$, respectively. The observed ratio of single bond/double bond and single bond/triple bond ratio in carbon compounds[17] are 1.16 and 1.28, respectively. The corresponding average ratios for the first row elements as tabulated by Pauling[21] are 1.18 and 1.31, respectively. *The relation between intermetallic distance in transition and non-transition metal elements maybe similar to that between single bond and multiple bond distances of integral bond order.*

2. Experimental Orbital Radii. We have first evaluated an experimental value of a radius, r_G, from the room-temperature interatomic distances of nontransition elements using the general form of eq 2b and the coefficients C_s and D_s of Table 1. The fit of r_G thus obtained (Table 2) with r_s yields $r_G = 1.04r_s - 0.01$, where r_s is the nonrelativistic Zunger−Cohen radii.[8] The coefficients CR^+_G and CR^-_G are then obtained by the following procedure. The van der Waals' radii,[22] r_{VDW}, are found to be closely related to the calculated characteristic value[23] of singly charged negative ions, r_m, using only the electrostatic potentials, or the radii r_D, calculated by Deb *et al.*[24] at the point where the chemical potential is given only by the electrostatic potential. The experimentally determined values of r_{VDW} may be used to obtain a starting relationship between r_G and CR^-. Thus, the values of CR^-_G and D^-_G (Table 1) have been obtained from

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(17) The bond distances for the elements (p F219) and compounds (p 220) have been obtained from: *CRC Handbook of Physics and Chemistry*, 61st ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981.

(18) We do not use the relativistic values of r_l as tabulated in ref 2 because of our considerations of an experimental value of the orbital radius derived from interatomic distances.

(19) The nominal number of unpaired valence electrons, *n*, has been obtained from the position of the element in the periodic table (see Table 1). Thus the elements, Sc, Y, La, in column IIIb have $n = 1$, and so on, reaching a maximum of $n = 5$ for the VIIb elements Mn, Tc, Re, and decreasing to $n = 1$ for the Ib elements, Cu, Ag, Au. We stress here that the number of these unpaired electrons may have nothing to do with the number of localized electrons seen in experiments. We shall later use values of *S* for nontransition metal elements to indicate the number of unpaired valence electrons required to account for the shortening of the bond.

(20) We have tried to relate F_S to several other functions of the *S* spins such as *S* itself, or $(2S + 1)$. The relation given in eq 3b fits best for n = 1−5.

(21) Pauling, L. Reference 1, Table 7−5, p 228.

(22) Pauling, L. Reference 1, Table 7−20, p 260. See also: *Lange*'s *Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill, New York, 1985; p 3−121.

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Table 2. Values of the Orbital Radii Obtained by Different Methods

element[d]	orbital radii (au) r_s[a]	$r_{\langle sp\rangle}$[a]	r_G[b]	r^0_G[b]	$\{r^s_{nd}\}$[c]
H	0		0	0	
Li	0.99	0.80	0.92	$\underline{1.04}$	0.85
Be	0.64	0.44	0.59	0.59	0.60
B	0.48	0.40	0.34	$\underline{0.41}$	0.47
C	0.39	0.32	0.32	0.32	0.38
N	0.33	0.27	0.26	0.26	0.32
O	0.29	0.23	0.26	$\underline{0.22}$	0.28
F	0.25	0.20	0.27	$\underline{0.18}$	0.25
Na	1.10	1.32	1.19	$\underline{1.18}$	1.04
Mg	0.90	1.01	0.98	0.98	0.91
Al	0.77	0.84	0.85	0.85	0.81
Si	0.68	0.71	0.64	0.64	0.73
P	0.60	0.62	0.59	0.59	0.66
S	0.54	0.55	0.53	0.53	0.61
Cl	0.50	0.51	0.50	$\underline{0.52}$	0.56
K	1.54	1.84		$\underline{1.46}$	1.60
Ca	1.32	1.50	1.28	$\underline{1.20}$	1.44
Sc (0.5)	1.22	1.38	1.19	1.19	1.34
Ti (1.0)	1.15	1.29	1.16	1.16	1.26
V (1.5)	1.09	1.21	1.07	1.07	1.18
Cr (2.0)	1.07	1.22	1.07	1.07	1.13
Mn (2.5)	0.99	1.11		$\underline{1.07}$	1.07
Fe (2.0)	0.95	1.06	1.06	1.06	1.02
Co (1.5)	0.92	1.01	1.01	1.01	0.97
Ni (1.0)	0.96	1.09	0.96	0.96	0.93
Cu (0.5)	0.88	1.16	0.89	0.89	0.90
Zn (0.5)	0.82	0.94	0.94	$\underline{0.87}$	0.86
Ga	0.76	0.80	0.68	0.68	0.82
Ge	0.72	0.78	0.70	0.70	0.78
As	0.67	0.71	0.68	0.68	0.75
Se	0.62	0.64	0.63	0.63	0.72
Br	0.58	0.60	0.62	0.62	0.69
Rb	1.67	2.05	1.68	$\underline{1.65}$	1.83
Sr	1.42	1.61	1.42	1.42	1.42
Y (0.5)	1.32	1.47	1.35	1.35	1.58
Zr (1.0)	1.27	1.41	1.30	1.30	1.50
Nb (1.5)	1.23	1.38	1.12	1.12	1.44
Mo (2.0)	1.22	1.36	1.19	1.19	1.38
Ru (2.0)	1.15	1.30	1.15	1.15	1.27
Rh (1.5)	1.11	1.26	1.11	1.11	1.23
Pd (1.0)	1.08	1.22	1.09	1.09	1.20
Ag (0.5)	1.05	1.19	1.04	1.04	1.15
Cd (0.5)	0.99	1.11	1.08	1.08	1.11
In	0.94	1.03	1.00	$\underline{0.89}$	1.06
Sn	0.88	0.94	0.91	0.91	1.02
Sb	0.83	0.88	0.86	0.86	0.99
Te	0.79	0.84	0.85	0.85	0.95
I	0.76	0.79	0.77	$\underline{0.78}$	0.92
Cs	1.71	2.16	1.82	$\underline{1.71}$	2.20
Ba	1.52	1.70	1.45	1.45	1.45
La (0.5)	1.38	1.55	1.44	1.44	1.95
Hf (1.0)	1.30	1.46	1.28	1.28	1.50
Ta (1.5)	1.25	1.39	1.20	1.20	1.45
W (2.0)	1.22	1.37	1.20	1.20	1.41
Re (2.5)	1.19	1.34	1.14	1.14	1.37
Os (2.0)	1.17	1.32	1.17	1.17	1.33
Ir (1.5)	1.16	1.32	1.12	1.12	1.29
Pt (1.0)	1.24	1.30	1.09	1.09	1.27
Au (0.5)	1.21	1.33	1.04	1.04	1.24
Hg	1.07	1.20		1.11	1.20
Tl	1.02	1.12	1.07	1.07	1.17
Pb	0.96	1.05	1.10	$\underline{1.22}$	1.13
Bi	0.92	0.95	1.14	1.14	1.10

[a] r_s and $r_{\langle sp\rangle}$ obtained from classical turning point (ref 8). [b] r_G and r^0_G obtained from interatomic distances of elements and compounds (see text); the r^0_G values which differ from r_G are underlined. [c] Outermost s function nodal point (from ref 2). [d] The values in parentheses are the S values used to calculate r_G from the interatomic distances.

the plot of r_G against the van der Waals' radii, r_{VDW}, as tabulated in the literature.[22] It is then straightforward to obtain the corresponding values of CR^+_G and D^+_G using eqs 1 and 2. The r_G, C^-_G, C^+_G, D^-_G, and D^+_G values thus obtained were then further refined to obtain new values of r^0_G by fitting the interatomic distance in heteropolar compounds of nontransition elements, keeping rule I in mind. The new value (Table 1) of the orbital radii, r^0_G, is related to CR^- and CR^+ by

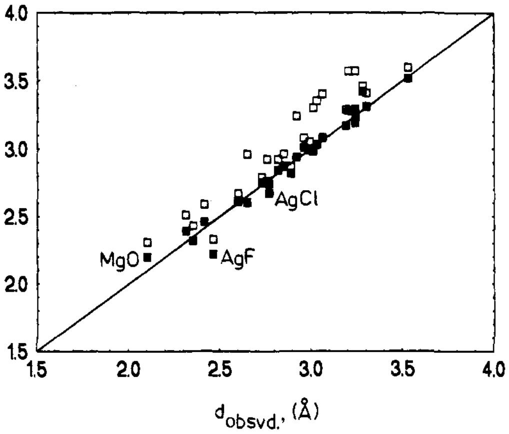

Figure 2. Plot of the calculated values, d_{calcd} *vs* observed $M-X$ distance, $d_{MX,obsd}$ of octet compounds with rock-salt structure (as listed in ref 8): $d_{M-X,calcd}$ ($=CR^+_M + CR^-_X$, filled symbols) and d_{X-M}, calcd ($=CR^+_X + CR^-_M$, open symbols). Interatomic distances have been taken from ref 25. The line is a guide to the eye for the correct distances.

$$CR^- = 2.49r^0_G + 1.11 \text{ (in Å)} \tag{4a}$$

and

$$CR^+ = 2.24r^0_G - 0.37 \text{ (in Å)} \tag{4b}$$

3. Heteropolar Bonds. a. A Principle of Mechanical Hardness. The nature of eq 2 suggests immediately that this relation may be applied to heteropolar compounds MX ($M \neq X$). However, *in the absence of any prior knowledge of the electronegativity of the elements* it is not straightforward to decide which of the two elements, M and X, are to be positively (or negatively) charged. We use a principle of—what may be termed as—maximum mechanical hardness (PMMH) defined as

Principle of Maximum Mechanical Hardness. *PMMH requires that for heteropolar compounds the interatomic separation, given by the sum of two components associated with positive and negative charge, is that distance which is the smallest*

from which we obtain

Rule I: *The interatomic distance is to be computed with the constraint that the element with the smaller value of r_s for $S = 0$ or with the smaller value* CR^-_S *(see Section II.3.c) for the chosen value of S ($S \neq 0$) would be the element that is associated with the negative charge.*

Rule I follows naturally from PMMH and the observation that $C_l^+ < C_l^-$ in Table 1 or eq 4.

b. Applicability of Rule I. We show in Figure 2 the plot of interatomic distances[25] of MX (both M and X not being transition metal ions) with rock-salt structure vs that computed using the convention that $d_{M-X} = CR^+_M + CR^-_X$ and $d_{X-M} = CR^+_X + CR^-_M$ and relations 2a and 4. d_{M-X} fits well to the experimental distance while d_{X-M} is always considerably larger. This shows the consistency of the values of r^0_G with rule I. A consequence of the applicability of rule I is that the interatomic

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(25) The interatomic distances for all MX compounds have been obtained from (a) Wyckoff and (b) Landolt-Bornstein *Structure Data of Elements and Intermetallic Phases* (New Series); Hellwege, K. H. Ed.; Springer: Heidelberg, 1971; Vol. 6.

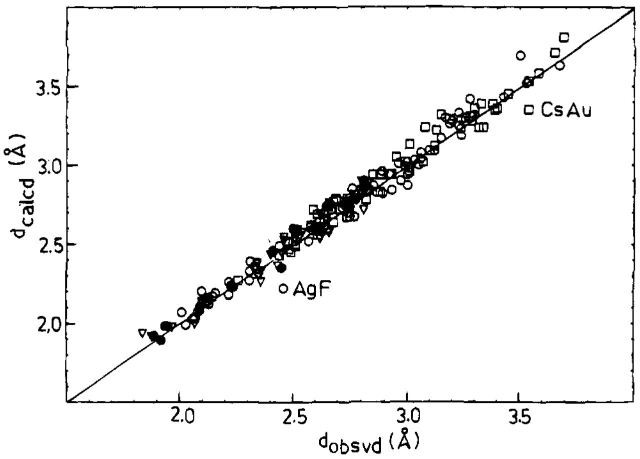

Figure 3. Plot of $d_{\mathrm{M-X,calcd}}$ vs $d_{\mathrm{M-X,obsd}}$ for compounds with rock-salt structure (open circles), CsCl structure (squares), ZnO structure (filled circles), and ZnS structure (triangles). Interatomic distances have been taken from ref 25. See section II.3.c for details of the calculation of interatomic distances.

distance in heteropolar bonds is less than the sum of the covalent radii, r_{cov}, of the contributing atoms since r_{cov} is usually taken as $d_{\mathrm{M-M}}/2$ (eq 1) when $d_{\mathrm{M-M}}$ is the single-bond distance. The relation between rule I and the Schomaker–Stevenson coefficients[26] will be presented in another communication.

c. Interatomic Distances in Solids. In the case of compounds of transition metal atoms with the rock-salt structure, new radii CR^+_S ($=CR^+/F_S$) and CR^-_S ($=CR^-/F_S$) have to defined for the finite number of unpaired valence electrons. The interatomic distances are then calculated using rule I and the value of r^0_G of Table 2. The value of S or F_S is varied until the right distance is obtained, even in the case of nontransition elements in some cases. The plots of d_{obsd} vs d_{calcd} for compounds with rock-salt, ZnO, ZnS, and CsCl structures are given in Figure 3. The MX compounds with rock-salt and CsCl structures are given below with the numerals in the brackets corresponding to the number of unpaired valence electron. The convention is that the first element or the first numeral corresponds to the M element associated with positive charge.

Rock-Salt Structure. CoO(10), CrN(11), FeO(10), HfC(11), *LaAs*(01), *LaBi*(11), *LaN*(01), *LaP*(01), *LaS*(01), *LaSb*(01), *LaSe*(01), *LaTe*(01), MnO(10), MnS(10), MnTe(10), NbO(11), NbC(11), NiO(10), *SrO*(10), *SrS*(10), *SrSe*(10), *SrTe*(01), TaC(11), TaO(01), TiC(11), TiN(11), TiO(11), VC(11), VN(11), VO(11), *YN*(01), *YTe*(11), ZrB(11), ZrC(11), ZrN(11), ZrO(20), ZrP(11), ZrS(11), *YO*(10).

Cesium Chloride Structures. AgMg(11; 1.037), AgZn(11), AlCo(04), AlFe(03), AlIr(−3*), AlNi(02), AlPd(02), AlRu(03), AuMg(11), AuZn(11), BaCd(10), BaHg(01), BaZn(10), CaCd(01), CaHg(01), CaIn(00), CaTl(01), CdAg(11), CoBe(31), CoGa(11), CsAu(01), CuBe(11), FeCo(43), FeGa(11), HfCo(23), HfOs(24), HfRu(24), HgMn(12), InSb(00), IrGa(11), LaAg(11), LaCd(11), LaHg(11), LaIn(10), LaZn(10), LiAg(11), LiHg(01), LiPb(01), LiPd(02), LiTl(02), MgHg(01), MgRh(03), MgSc(01), MnNi(22), NiGa(01), NiIn(11), NiZn(1), OsV(23), PdBe(21), PdIn(11), RbAu(02), RhFe(24), RhGa(11), RhIn(11), RhMn(33), RuGa(11), ScAg(11), ScAu(11), ScCd(11), ScCo(13), ScCu(11), ScHg(11), ScIr(13), ScNi(12), SrHg(11), SrMg(01), TiCo(23), TiIr(23), TiNi(22), TiOs(22), TlMg(00), VMn(35), YAg(11), YAu(11), YCd(11), YCu(11), YHg(11), YIn(10), YMg(10), ZrCo(23), ZrMn(12), ZrOs(22).

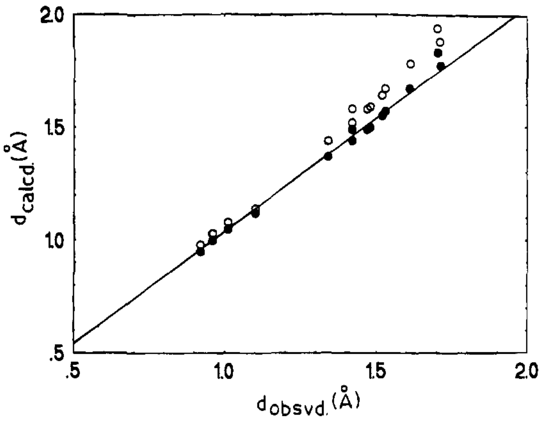

Figure 4. Plot of the calculated metal–hydrogen distance d_{calcd} *vs* $d_{\mathrm{MH,obsd}}$ in binary compounds of hydrogen (from ref 1, Table 7–4, p 226). Filled symbols are those calculated for $d_{\mathrm{M-H}}$ ($=CR^+_{\mathrm{M}} + CR^-_{\mathrm{H}}$) and open symbols are those calculated for $d_{\mathrm{H-M}}$ ($=CR^+_{\mathrm{X}} + CR^-_{\mathrm{M}}$).

A proper understanding of the assigned values of n (obtained essentially by curve fitting) will have to await an examination of the physico-chemical properties. However, the changes in n for any element in the various compounds listed above are consistent with chemical intuition. For example, in the intermetallic compounds with the CsCl structure, n is close to the value used for the elements. All the 3d transition metal monoxides MnO, FeO, CoO, NiO, as well as MnS, MnSe, and MnTe have the configuration $MX(10)$. The other unpaired d electrons are now to be identified as the inner-shell or core electrons. The decrease in cationic size with increasing valence in the transition metal ions listed by Shannon, for example, may now be related to a decrease in the number of core electrons. A further justification for the n values may lie in the radius-ratio criterion for delineation of crystal structures discussed in section III.1.

d. Bonding with Hydrogen. From rule I and the value of r^0_G for hydrogen in Table 1, it is apparent that for *all* bonds involving hydrogen, the hydrogen atoms must be considered to be the element associated with the negative charge. Thus for all $M-H$ bonds the correct distance will be given by $d_{\mathrm{M-H}} = CR^+_{\mathrm{M^+}} + CR^-_{\mathrm{H}}$ even in compounds such as HCl. This is, of course, currently counterintuitive. Nevertheless, we find that rule I is applicable to $M-H$ bonds as well for compounds[27] varying from HCl to NH_3. We show in Figure 4 the calculated values of $d_{\mathrm{M-H}}$ and $d_{\mathrm{H-M}}$ using the same procedure as above. It is seen that $d_{\mathrm{M-H}}$ gives accurate results. Rule I, which is applicable only for obtaining interatomic distances at equilibrium, makes no commitment to the actual nature of the charge associated with the constituent atoms in a bond after a distance has been settled upon.

e. Molecular Compounds and Nonbonded Interactions. We have calculated the value of $d_{\mathrm{M-X}}$ for some of the inorganic compounds[17] on the basis of rule I by varying the value of S and using the spin-corrected radii CR^-_S and CR^+_S in equation 4 as before. The results are given in Table 3. Both r_G and r^0_G (Table 2) have been used. As can be seen from Table 3, r_G gives slightly better fit. Both sets of radii give a slightly higher value of the interatomic distances with (Figure 5)

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(26) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37. See also: Pauling, L. *Reference* 1, p 229.

(27) There has been a compressive tabulation of bond distances by: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans. Suppl.* **1989**, *S1*–S83. The M–H bond distance involving transition metal atoms may be obtained from this tabulation. For the present, we have taken the classical data of L. Pauling, (ref 1, Table 7–4, p 226) for consideration since the applicability of rule I is better judged when the element of S is not introduced as another adjustable parameter.

Table 3. Observed (Ref 17) and Calculated Distances (see Section II.3.e) in Inorganic Compounds

	d_{M-X} (Å)			d_{X-X} (Å)		
compound	obsd[@]	calcd[a]	calcd[b]	obsd	calcd[a,c]	calcd[a,c]
PF_3	1.54	1.55^{11}	1.49^{01}	2.35	2.33^{22}	
PCl_3	2.04	2.10	2.13	3.13	3.05^{11}	3.10^{11}
PBr_3	2.18	2.26	2.28	3.73	3.86	3.90
AsF_3	1.71	1.71^{01}	1.79^{01}	2.40	2.33^{22}	2.54^{22}
$AsCl_3$	2.16	2.21	2.24	3.27	3.29^{10}	3.35^{10}
$AsBr_3$	2.33	2.36	2.39	3.58	3.59^{10}	3.63^{10}
AsI_3	2.55	2.57	2.59	3.94	3.97^{10}	4.00^{10}
$SbCl_3$	2.35	2.43	2.46	3.58	3.54	3.60
$SbBr_3$	2.51	2.59	2.61	3.78	3.86	3.9p
SbI_3	2.67	2.79	2.81	4.13	4.26	4.30
$BiCl_3$	2.48	2.51^{01}	2.54^{01}	3.80	3.54	3.60
$BiBr_3$	2.63	2.65^{01}	2.67^{01}	4.03	3.86	3.90
As_4O_6	1.78	1.89	1.84	2.70	2.70^{10}	2.80
F_2O	1.42	1.39	1.34	2.22	2.33^{22}	2.14^{22}
Cl_2O	1.70	1.68	1.65	2.79	2.81^{22}	2.86^{22}
ClO_2	1.49	1.50^{01}	1.46^{01}	2.56	2.50^{11}	2.61^{11}
$Cr(OCl)_2$	1.57 (Cr−O)	1.83^{42}	1.77^{42}	2.49 (O−O)	2.50^{11}	2.41^{11}
	2.12 (Cr−Cl)	2.18^{41}	2.21^{41}	3.54 (Cl−Cl)	3.54	3.60
				3.01 (Cl−O)	3.02^{01}	3.01^{01}
$VOCl_2$	1.56 (V−O)	1.86^{32}	1.81^{32}	3.49 (Cl−Cl)	3.54	3.60
	2.12 (V−Cl)	2.13^{22}	2.15^{22}	3.00 (Cl−O)	3.03^{01}	3.01^{01}
SO_2Cl_2	1.43 (S−O)	1.47^{11}	1.43^{11}	2.48 (O−O)	2.50^{11}	2.41^{11}
	1.99 (S−Cl)	2.03	2.06	3.01 (Cl−Cl)	3.05^{11}	3.10^{11}
SO_2	1.43	1.47^{11}				
S_2Cl	1.99	2.01				
$TeBr_2$	2.51	2.57	2.59	3.79	3.86	3.90
SiH_2Cl_2	2.02 (Si−Cl)	2.16	1.94^{01}	3.31 (Cl−Cl)	3.30^{10}	3.35^{10}
	1.46 (Si−H)	1.50	1.50			

[a] Calculated using r_G; the numerals in the superscripts correspond to the number of unpaired electrons, n, requiring a correction of CR^+ or CR^- by the factor F_S as in section II.3.c. Unless otherwise mentioned, X corresponds to the halogen atom. [b] Calculated using r^0_G; the numerals in the superscripts correspond to the number of unpaired electrons, n, requiring a correction of CR^+ or CR^- by the factor F_S as in section II.3.c. Unless otherwise mentioned, X corresponds to the halogen atom. [c] # sign implies that nonbonded distances have been calculated using CR^-_S (eqs 3 and 4).

$$d_{\mathrm{calcd}} \sim d_{\mathrm{obsd}} + 0.04 \text{ (in Å)} \qquad (5)$$

The distances calculated using eq 5 are within 2% of the observed distances in the instances studied. It is as if the inhomogeneous effects due to the surface[28] in such molecular compounds cause a compression of the M−X distance by an average of 0.04 Å.

In the trihalides of the group V elements P, As, Sb, and Bi, we find that as the size of the halogen atom is decreased, the M−*Hal* (*Hal* = halogen atom) bond order increases. This is especially prominent in PF_3. As the size of the *M* ion increase from P to Bi, the *M*−*Hal* distance attains the normal single bond character and the distance between the nonbonded atoms becomes comparable to (when *M* = Sb) or even larger (when *M* = Bi) than the *S* = 0 values of CR^-.

The more interesting development is in the nonbonded *Hal*−*Hal* distances. The F−F distance in AsF_3 is close to only 2.35 Å compared to a value of ~2.70 Å calculated from the van der Waals' radius. Such a short nonbonded F−F distance is found also in AsF_3 and F_2O. The nonbonded F−F distance of ~2.35 Å may be accounted for by the unusual step of using the spin-dependent radii, CR^-_S. Using r_G (or r^0_G), this distance is given by $S = 1$ (or $S = {}^1/_2$). In the case of the arsenic compounds such as $AsCl_3$, $AsBr_3$, and AsI_3, the *Hal*−*Hal* distance is short but requires a value of $S = {}^1/_2$ on only one *Hal* atom. What is satisfying is that, within the uncertainty of the X−X distance, the nonbonded distances correspond quite closely to that given by *integral* values of the number of unpaired valence electron, *n*, for each atom.

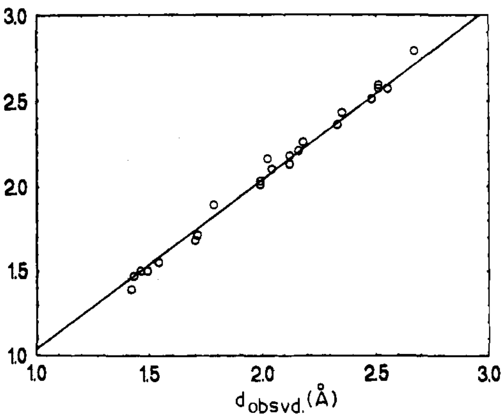

Figure 5. Plot of $d_{M-X,\mathrm{calcd}}$ *vs* $d_{M-X,\mathrm{obsd}}$ (ref 17) in heteropolar compounds using values of r_G in Table 1. The details of the calculation of interatomic distances are the same as in section II.3.b except that r_G has been used instead of r^0_G of Table 1. The line corresponds to $d_{\mathrm{calcd}} = d_{\mathrm{obsd}} + 0.04$ Å.

The shortening of nonbonded *X*−*X* interatomic distances seems to be independent of the bond order in the *M*−*X* bond. The value of *S* for different bonding on the same atom may thus be different. This aspect is familiar to the chemist for several bonding situations as in the ketone group in which the carbonyl group is associated with double-bond character while the C−C linkage of the same carbon has single-bond character.

There seems to be some major discrepancies[29] which are not removed by the correction in eq 5. Thus the Cr−O distance in $Cr(OCl)_2$ or the V−O distance in $VOCl_2$ (see Table 3) cannot be explained for a reasonable value of *S*. The Shannon radii[12] also cannot account for the short distance.

III. Discussion

1. Importance of Radius Ratio. The radii associated with positive and negative charges have more significance when they satisfy a radius-ratio ($R^S_+ = CR^+_S/CR^-_S$) criterion such as those used classically in delineating crystal structures based on the coordination number[30] of the metal ions. We find that the compounds with zinc blende or wurtzite structures, in which the metal ions are in tetrahedral coordination, have $R^S_\pm < 0.41$ as required. The radius ratio criterion for rock-salt structures in which the metal ion is octahedrally coordinated is complicated because of two possible descriptions[31] of this structure. One of these is that the *AX* compounds are based on close-packing of *A* and *X* ions (those in italics in the list in section II.3.c, $R^S_\pm$

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(28) See, for example: Gunnarsson, O.; Jonson, M.; Lundqvist, B. I. *Phys. Rev. B* **1979**, *20*, 3136 and references therein.

(29) In most cases the unaccountable (in this model) shortening is by about 0.3−0.4 Å which is close to the value of CR^+ of the hydrogen atom or the constant term for CR^+ in eq 4, for example. There are very short metal−metal distance in some metal cluster compounds (see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley: New York, 1980; Chapter IV), such as the Mo−Mo distance of ~2.10 Å in $Mo_2(O_2CCF_3)_4{\cdot}2py$ in $(M{-}X)^+$ compared to the minimum possible calculated (Mo−Mo) (4*4*) distance of 2.73 Å (using r_G values of Table 1). The nonbonded Mo−Mo distance obtained from the radius (CR^+) of the Mo atom is 2.10 Å.

(30) See ref 1, Chapter 13.

> 0.732 as required[31]) and another series of BX compounds in which the B ions occupy octahedral interstices derived from close-packing of X ions. For the BX compounds we find $0.41 < R^{S}_{\pm} < 0.732$ as required.

For compounds with CsCl structure, $R^{S}_{\pm}$ is required to be greater than 0.732. In most of the intermetallic compounds, $R^{S}_{\pm} < 0.40$. One may require another description for the radius ratio.[32] From an examination of eqs 4 and 2b it is seen that CR^- is enlarged and CR^+ reduced by half the length scale, D_1. CR^- and CR^+ are thus to be associated with localized effects due to actual charge transfer of electron and hole, respectively. In metallic compounds the valence electrons are itinerant, and it would be more appropriate to use "neutral" radii, $CR^{+}{}_{0}$ and $CR^{-}{}_{0}$, written as

$$CR^{+}{}_{0} = CR^{+}{}_{G}r^{0}{}_{G} + 0.37 \text{ (in Å)} \qquad (6a)$$

and

$$CR^{-}{}_{0} = CR^{-}{}_{G}r^{0}{}_{G} + 0.37 \text{ (in Å)} \qquad (6b)$$

The spin-dependent values $CR_{0,S}$ and $CR^{-}{}_{0,S}$ are obtained in the usual manner by dividing $CR^{+}{}_{0}$ or $CR^{-}{}_{0}$ by the factor F_S. Such a definition of "neutral" radii for metallic compounds still allows the applicability of rule I without contributing significantly to a change in interatomic distances calculated from eqs 1 and 4. The plots of $CR^{+}{}_{0,S}$ *vs* $CR^{-}{}_{0,S}$ of the intermetallic compounds with CsCl structure are given in Figure 6, using the same values of the number of unpaired electrons, n, as assigned in section II.3.c. The condition $0.732 < R_0{}^{S} = CR^{+}{}_{0,S}/CR^{-}{}_{0,S} < 1/0.732$ is required[31] for this structure. The only exceptions are the semiconducting[33] CsAu (01) and RbAu (02) with $R_0{}^{S} = 1.61$ and 1.68, respectively. However, the ionic configurations Cs^+Au^-(01) or Rb^+Au^-(01) have the ratio $CR^{+}{}_{S}/CR^{-}{}_{S} = R_{\pm} = 0.775$ and 0.742, respectively.

2. Ionic Sizes and Electronegativity. Rule I gives another criterion based on atomic sizes for the ordinal listing of the atoms in an electronegativity scale associating the atom with smaller orbital radii with a larger electronegativity. Following Sanderson,[34] we may consider an equalization of chemical potential at equilibrium which takes place not by charge transfer but by a change in the length scales[35] (for constant charge or number of electrons, N), consistent with the direction of virtual charge transfer dictated by rule I. It is in this context that the sizes CR^+ and CR^-, modified by F_S have significance. Just as there can only be integral values of charge being transferred,[36] we seem to have CR^+ and CR^- associated with integral charges.

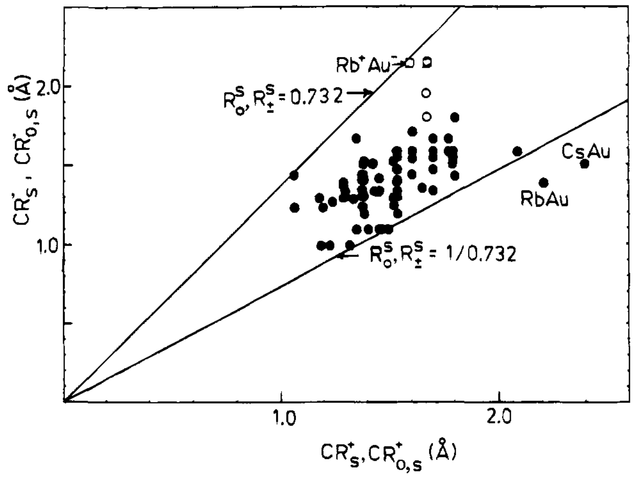

Figure 6. Plots of $CR^{+}{}_{0,S}$ *vs* $CR^{-}{}_{0,S}$ of the intermetallic compounds with CsCl structure (filled circles) as listed in ref 8. The lines are meant as guide to the eye for the limits $0.732 < CR^{+}{}_{0,S}/CR^{-}{}_{0,S} < 1/0.732$. The exceptions are CsAu(01) and RbAu(02) (see section II.3.b for interpretation of symbol within brackets). The ionic radii CR^+ and CR^- satisfies the radius ratio condition for the cesium halides (open circles) and Cs^+Au(01) and Rb^+Au^-(01) (open squares).

Chemical reactions of the elements M and X (M may be equal to X) in their standard state with different individual chemical potentials, μ_M and μ_X, yield a product, MX, with a new chemical potential, $\mu_{MX,\text{equib}}$, which is constant throughout the system at equilibrium.[29] In the process, the M and X species acquire, either *via* charge transfer or change in size,[34,35] an equilibrium charged state which we designate $M^{\$+}$ and $X^{\#-}$ with the radii CR^+ and CR^-, respectively. These charge states exist only in the context of the formation of a bond. The chemical potentials $\mu_{M^{\$+}}$ and $\mu_{X^{\#-}}$ corresponding to these charged states in any $M-X$ bond may now be associated with the surface of spheres of radius CR^+ and CR^-, respectively. It seems to us that given the transferability of length scales, one requires that for *all* $M-X$ bonds, $\mu_{MX,\text{equib}}$ as well as $\mu_{M^{\$+}}$ and $\mu_{X^{\#-}}$ has an universal value. Thus

$$\mu_{M+,\text{equib}} = \mu_{X-,\text{equib}} = \mu_{MX,\text{equib}} = \text{constant} \qquad (7a)$$

$$= \mu_{M+,\text{equib}} + \mu_{X-,\text{equib}} \qquad (7b)$$

Relations 7b and 7a are simultaneously satisfied only when $\mu_{MX,\text{equib}} = 0$. This seemingly Thomas–Fermi-like conclusion requires further investigation.

JA941742T

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(31) Ganguly, P.; Shah, N. *Physica C* **1993**, *208*, 307.

(32) This implies that the metallic elements in intermetallic compounds may be defined by their orbital radii alone. This aspect will be dealt with in another communication.

(33) Sommer, A. H. *Nature* **1943**, *152*, 215. See: Wormuth, R.; Schmutzler, R. W. *Theor. Chim. Acta* **1990**, *160*, 97 and references therein.

(34) Sanderson, R. T. *Science* **1951**, *114*, 670. Sanderson proposed that the radius of the atoms in a heteropolar bond changes so as to have equal attractive potential for the electron implying an equalization of electronegativity in a chemical bond. The atom with the greater attraction for the electron has the larger size.

(35) Hubermann, R. L.; Grimsditch, M. *Phys. Rev. Lett.* **1989**, *62*, 1403. This aspect has been discussed in terms of lattice expansion and contraction in metallic superlattices.

(36) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L., Jr. *Phys. Rev. Lett.* **1982**, *49*, 1691.