Relation between Interatomic Distances in Transition-Metal Elements, Multiple Bond Distances, and Pseudopotential Orbital Radii

P. Ganguly

Physical Chemistry Division
National Chemical Laboratory
Pashan Road, Pune 411008, India

The relationship between the *ab initio* quantum mechanically calculated Zunger−Cohen pseudopotential orbital radii,[1] r_p, of an atom calculated from the classical turning point and the valence- and coordination-number-dependent ionic radii of cations and anions tabulated by Shannon[2] has been recently investigated.[3] A set of radii CR^- and CR^+ corresponding to (singly) charged negative and positive ions was related linearly to $r_{\langle sp \rangle}$ $((r_s + r_p)/2)$. The interatomic distance, d_{M-M}, in *non-transition-metal elements* was found[3] to be given by the sum of CR^+ and CR^-. In general,

$$d_{M-M} = CR^+_l + CR^-_l \qquad (1a)$$

$$= C_l r_l + D_l \qquad (1b)$$

where the coefficient C_l and the length scale D_l have universal values for given l. When $l = \langle sp \rangle$, Ganguly[3] found $C_{\langle sp \rangle} \sim 4.52$ Å and $D_{\langle sp \rangle} \sim 0.74$ Å, which is close to the interatomic distance in the hydrogen molecule. It is satisfying to note that the special case of $r_l = 0$ yields the H−H bond distance in the hydrogen molecule (D_l).

We have fitted the interatomic distances of non-transition-metal elements[4,5] using the nonrelativistic Zunger−Cohen values[1] for r_s and keeping $D_l = 0.74$ Å. The relation

$$d_{M-M} = 4.74 r_s + 0.74 \qquad \text{(in Å)} \qquad (2)$$

gives the best fit (Figure 1). Only r_s may be sufficient for the prediction of interatomic distances to a first approximation. Zhang et al.[6] have also observed earlier that just r_s can give important insight into bonding properties and electronegativity scales. Ganguly[3] had noted earlier that CR^- is close to the van der Waals radii,[7] r_{VDW}, so that we may use r_{VDW} to obtain the relation between CR^- and r_s and subsequently (*via* eqs 1 and 2) that between CR^+ and r_s. We find from this exercise that

$$CR^+ = 2.24 r_s - 0.37 \qquad \text{(in Å)} \qquad (3)$$

Multiple bond distances in molecules or elements cannot be obtained in a straightforward manner using eq 1 or 2. Moreover, the use of parameters based on density functional approach have also always proved to be inadequate in predicting bonding properties of transition-metal elements.[6,8] We show in this

Figure 1. Plot of d_{M-M}(obsvd) vs the nonrelativistic Zunger−Cohen orbital radii, r_s (●) or $r_{\langle sp \rangle}$ $((r_s + r_p)/2$; ×) values obtained from the classical turning point of valence s and p electrons. The straight line corresponds to eq 2 in text.
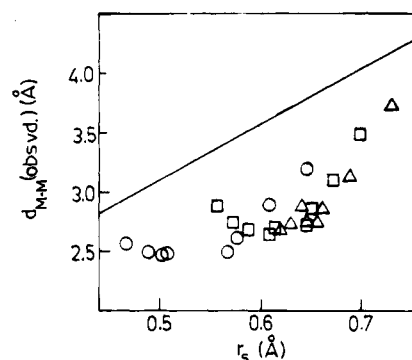
Figure 2. Plot of observed interatomic distances at room temperature (ref 4) in transition-metal elements vs the Zunger−Cohen s-orbital radii, r_s (in Å). ○, 3d; □, 4d; and △, 5d elements. The line is meant as a guide to the eye for the values expected from eq 2.

Figure 3. Plot of d_{M-M}(obsvd) vs d^S_{M-M}(calcd) using eq 4 with $C(S) = 1.19$ and $n(S) = 0.08$ and eq 2 for obtaining d_{M-M}(calcd). The symbols are the same as those given in Figure 2. The line is meant as a guide to the eye for d_{M-M}(obsvd) = d^S_{M-M}(calcd).

(1) (a) Zunger, A.; Cohen, M. L. *Phys. Rev.* **1978**, *B18*, 5449; (b) **1979**, *B20*, 4082; (c) **1980**, *B22*, 5839.

(2) Shannon, R. D. *Acta. Crystallogr.* **1976**, *A32*, 751.

(3) Ganguly, P. *J. Am. Chem. Soc.* **1993**, *115*, 9287.

(4) The interatomic distances have been obtained from *The CRC Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1981; p F-217.

(5) The values of r_s after relativistic correction or other radii such as the nodal radii calculated by Zhang et al. (Zhang, S. B.; Cohen, M. L.; and Phillips, J. C. *Phys. Rev.* **1987**, *B36*, 5861) do not give as good fits.

(6) (a) Zhang, S. B.; Cohen, M. L.; Phillips, J. C. *Phys. Rev.* **1988**, *B38*, 12085. (b) Zhang, S. B.; Cohen, M. L. *Phys. Rev.* **1989**, *B39*, 1077.

(7) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7−20, p 260. *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; pp 3−121.

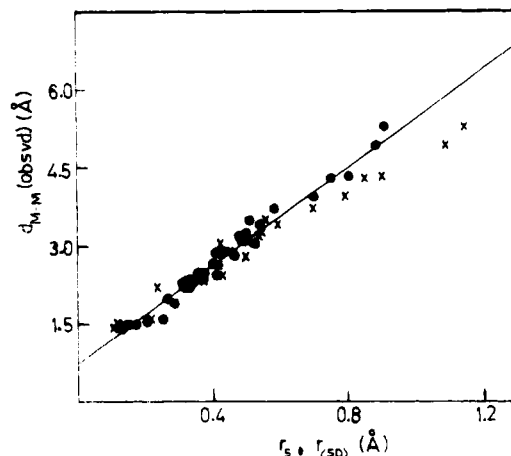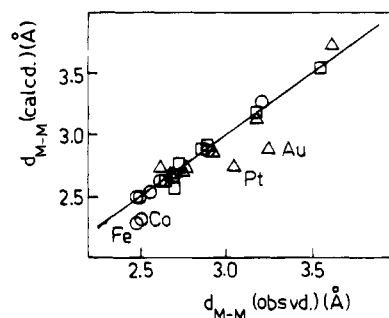(8) Garcia, A.; Cohen, M. L. *Phys. Rev.* **1993**, *B47*, 4221.

Communication that there may exist a simple universal function of the number of unpaired valence electrons, n, which in conjunction with eq 1 *accounts for the variation of interatomic distances in transition-metal elements in the same manner as it explains multiple bond distances in the first row elements.*

The observed interatomic distances in transition-metal elements[4] are always smaller than those calculated using eq 1, as shown in Figure 2. The elements with the maximum deviation in Figure 2 are those elements in which the d orbitals are close to being half-filled.[9] The extent of reduction of the interatomic distance in transition-metal elements may be related to the number, n, of unpaired d electrons or the total spin S $(n/2)$.

Thus, the calculated "spin"-dependent interatomic distance, d_{M-M}^S(calcd), is obtained by dividing d_{M-M}(calcd) (eq 2) by an universal spin-dependent factor, F_S, applicable to *all* transition-metal elements ($S > 0$). Thus we have

$$d_{M-M}(\text{calcd})/d_{M-M}^S(\text{calcd}) = F_S = C(S)[S(S+1)]^{n(S)} \quad (4)$$

The best fit[10,11] (Figure 2) is obtained with $C(S) = 1.19$ and $n(S) = 0.080$ ($\sim 1/4\pi$). The maximum deviations are observed with Fe, Co, Pt, and Au (see Figure 2).

Equation 4 yields $F_S = 1.16, 1.26, 1.32, 1.37,$ and 1.41 for $n = 1, 2, 3, 4,$ and 5, respectively. The ratios of the single-bond distance to the double-bond and triple-bond distances for carbon[12] are 1.16 and 1.28, respectively. The average values of the ratios of double-bond and triple-bond distances to the single-bond distances as tabulated by Pauling[12] for the first row elements are 1.18 and 1.31, respectively. The values of F_S for $n = 1$ (~ 1.16) and $n = 2$ (~ 1.26) obtained from eq 4 correspond closely, therefore, to the ratios of the single-bond to double-bond and triple-bond distances, respectively.

Equation 4 is applicable for rare-earth (4f) systems only when $S = 1/2$, as in Y or Sc. It is not valid when S is calculated from the number of unpaired 4f electrons, thereby emphasizing *the requirement of unpaired outer or valence electrons* for eq 4 to apply. F_S, and hence atomic sizes, may therefore change with the valence state.[2] The influence of unpaired valence electrons is quite distinct from that of the bonding valence electrons, as seen from eq 4, in which d_{M-M}^S does not extrapolate to d_{M-M} when $S = 0$. There need be no restriction for using different values of F_S with the atoms constituting a chemical bond. Moreover, chemical experience, such as the existence of various bond orders for different bonds of the carbon atom in the carbonyl group of a ketone, requires F_S for an atom to be dependent on the environment in the bonding direction. With such an F_S or bond order flexibility, the prediction or interpretation of internuclear distances on the basis of eq 4 requires a judicious choice of F_S, especially in complicated structures.

An important issue in which bond lengths play a crucial role in the identification of the problem is the question of multiple metal–metal bonds in polynuclear complexes,[13–16] some of which are listed in Table 1. The triple-bond or quadruple-bond distances calculated from eq 4 using the Zunger–Cohen r_s are very high (Table 1) and point to another prescription for obtaining intermetallic distances in such clusters. The bonding of a polynuclear clusters of metal, M_p, bonded to ligands, L, with higher electronegativity may be written as $(M_p)^+–L^-$. We have considered the intermetallic M–M distance within this $(M_p)^+$ cluster to be given simply as

Table 1. Observed and Calculated Metal–Metal Distances in Some Polynuclear Cluster Complexes[a]

compound	bond order[b]	d_{M-M} obsvd	d_{M-M}[c] calcd	$d_{(M-M)^+}$[d] calcd
[Tc₂Cl₈]	4	2.15	2.76	2.14 (+3,*3)
[Mo₂Cl₆](dppe)₂[e]		2.76		2.76 (+1,*0)
[Mo₆Cl₈]⁴⁺		2.61		2.64 (+0,*1)
[Mo₂(HPO₄)₄]²⁻		2.22		2.20 (+3,*3)
[Mo₂(SO₄)₄]³⁻		2.16		2.16 (+4,*3)
[Mo₂(SO₄)₄]⁴⁻		2.11		2.13 (+3,*4)
Mo₂(O₂CCF₃)₄		2.09		2.09 (+4,*4)
Mo≡Mo[f]	3	2.208	2.95	2.20 (+3,*3)
Mo≣Mo[f]	4	2.106	2.82	2.12 (+4,*4)
Re≡Re[f]	3	2.27–2.28	2.89	2.30 (+2,*2)
Re≣Re[f]	4	2.22	2.76	2.20 (+3,*3)
Re=Re	2	2.47	3.20	2.50 (+1,*1)
W≣W[f]	4	2.20		2.22 (+3,*3)
Cr–Cr[f]		1.87		1.90 (+4,*4)
Cr₂(O₂CCF₃)₄(Et₂O)₂		2.54		2.61 (+0,*0)
Pt₃(CO)₃(μ-CO)₃		2.65[g]		2.66 (+0,*0)
Pt₃(CO)₃(μ-CO)₃		3.05[h]		3.00 (+0,*0)

[a] The observed distances for the compounds listed are taken from refs 13–16. The r_s values for Mo (1.19 au), Pt (1.09 au), and W (1.20 au) have been calculated from the interatomic distances in the elements using eq 4. For the others, the calculated Zunger–Cohen orbital radii have been used (ref 1). [b] The bond order ($n + 1 = 2S + 1$) is taken from that reported in the literature (refs 14 and 15). [c] Calculated using eq 4 for the value of S corresponding to that given by the bond orders given in the second column. [d] Calculated using eq 5; the figures in parentheses ($+n$,*n') are the numbers of unpaired electrons used to calculate $F_{S,+}$ and $F_{S,\text{cov}}$ in eq 5 so as to obtain the best agreement with observed values. [e] dppe, Ph₂PCH₂CH₂PPh₂. [f] The values given are the average values from examples given in refs 14 and 15. [g] Intracluster Pt–Pt distance. [h] Intercluster Pt–Pt distance.

$$d_{(M-M)^+} = CR^+/F_{S,+} + CR_{\text{cov}}/F_{S,\text{cov}} \quad (5)$$

with CR^+ being given by eq 3 and $2CR_{\text{cov}} = d_{M-M}$ given by eq 3. $F_{S,+}$ and $F_{S,\text{cov}}$ are the values by which CR^+ and CR_{cov} are reduced due to the unpaired valence electrons, n, on the corresponding atoms. The internuclear distances calculated using eq 5 are compared with the observed distances in Table 1. The values of F_S used correspond to the proposed bond orders[13–16] reasonably well. When M = Mo, however, the average proposed Mo–Mo triple-bond and quadruple-bond distances of 2.208 and 2.106 Å, respectively, fit better the quadruple ($S = 3/2$) and quintuple ($S = 2$) bond distances calculated using eq 5. On the other hand, the ratio of the average Mo–Mo triple-bond distance to the average quadruple-bond distance is 1.048, which is almost exactly the expected ratio of $1.32/1.26 = 1.048$ obtained from eq 4. It is interesting to note from Table 1 that the changes in the value of S account for the range of Cr–Cr distances in polynuclear clusters of Cr, with the supershort Cr₂ distance being given by $S = 2$ and the longer Cr–Cr distance by $S = 0$.

Equation 5 seems to be relevant only for intracluster distances of polynuclear clusters. In one-dimensional solids[13] such as the insulating K₂Pt(CN)₄·3H₂O, the Pt–Pt distance of ~ 3.48 Å is obtained from eq 2 for $S = 0$, assuming $r_s \sim 1.09$ au for Pt (this value is used hereafter for all other Pt complexes), obtained by applying eq 2 to the Pt–Pt distance of 2.77 Å in Pt metal, with $S = 1$. Complexes such as K₂[Pt(CN)₄]Br₀.₃·3H₂O or K₂-[Pt(CN)₄]Cl₀.₃·3H₂O have Pt–Pt distances close to 2.88 Å and have higher conductivity than K₁.₇₅[Pt(CN)₄]·1.5H₂O (Pt–Pt distance of 2.96 Å compared to ~ 3.00 Å obtained from eq 2 for $S = 1/2$). An interesting example[13] is Pt₃(CO)(μ-CO)₃, in which the intracluster Pt–Pt distance of ~ 2.65 Å is close to that (2.66 Å) obtained from eq 5 with $S = 0$, while the intercluster distance of ~ 3.05 Å is close to that (~ 3.00 Å) obtained from eq 2 with $S = 0$.

(9) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 11, see especially Figure 11–9. Such a deviation forms the basis of Pauling's discussions on metallic bonding.

(10) The value of S has been obtained nominally from the number N of the row that the element occupies in the periodic table; for example, $n = 1$ for Sc and Cu ($N = $ IIIB and IB, respectively) or $n = 4$ for Cr, Mo, W ($N = $ VIB) or Fe, Ru, Os (N = VIIIA), etc.

(11) Another suitable function is $F_S = d_{M-M}/d_{M-M}^S \sim 1 + (2S + 1)/C'$-$(S)$ ($C'(S) \sim 12.6$), which gives too short values of interatomic distances for high values of S.

(12) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7–5, p 228.

(13) See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley and Sons: New York, 1980; p 1080.

(14) See: Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27 and references therein.

(15) See: Cotton, F. A.; Walton, R. A. *Structure and Bonding*; Springer Verlag: Berlin, 1985; Vol. 62, p 1.

(16) See: Chisholm, M. H. *Acc. Chem. Res.* **1990**, *23*, 419.