

## 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

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The relationship between the *ab initio* quantum mechanically calculated Zunger–Cohen pseudopotential orbital radii,<sup>1</sup>  $r_p$ , 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<sup>2</sup> has been recently investigated.<sup>3</sup> A set of radii  $CR^-$  and  $CR^+$  corresponding to (singly) charged negative and positive ions was related linearly to  $r_{(sp)}$  ( $(r_s + r_p)/2$ ). The interatomic distance,  $d_{M-M}$ , in non-transition-metal elements was found<sup>3</sup> to be given by the sum of  $CR^+$  and  $CR^-$ . In general,

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

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

where the coefficient  $C_l$  and the length scale  $D_l$  have universal values for given  $l$ . When  $l = \langle sp \rangle$ , Ganguly<sup>3</sup> found  $C_{(sp)} \sim 4.52 \text{ \AA}$  and  $D_{(sp)} \sim 0.74 \text{ \AA}$ , 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 ( $D_l$ ).

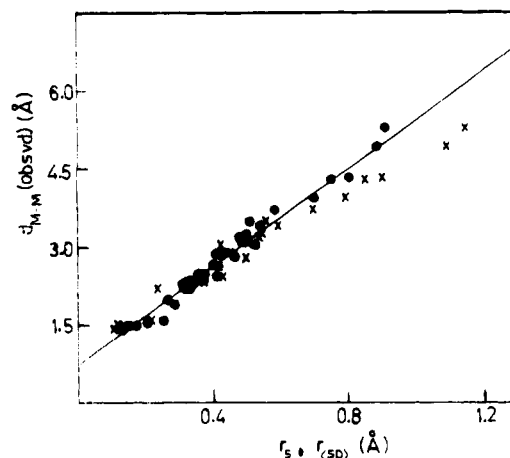
We have fitted the interatomic distances of non-transition-metal elements<sup>4,5</sup> using the nonrelativistic Zunger–Cohen values<sup>1</sup> for  $r_s$  and keeping  $D_l = 0.74 \text{ \AA}$ . The relation

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

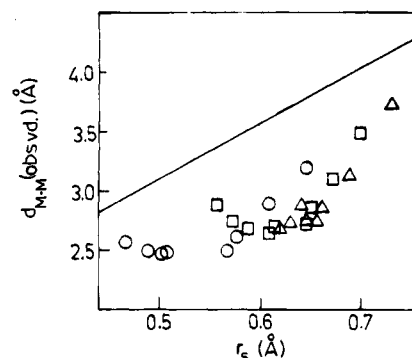
gives the best fit (Figure 1). Only  $r_s$  may be sufficient for the prediction of interatomic distances to a first approximation. Zhang *et al.*<sup>6</sup> have also observed earlier that just  $r_s$  can give important insight into bonding properties and electronegativity scales. Ganguly<sup>3</sup> had noted earlier that  $CR^-$  is close to the van der Waals radii,<sup>7</sup>  $r_{VDW}$ , 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

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

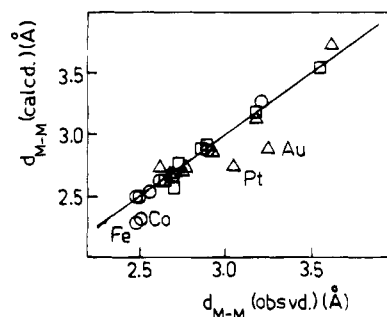
Multiple bond distances in molecules or elements cannot be obtained in a straightforward manner using eq 1 or 2. Moreover, the use of parameters based on density functional approach have also always proved to be inadequate in predicting bonding properties of transition-metal elements.<sup>6,8</sup> We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



**Figure 1.** Plot of  $d_{M-M}(\text{obsvd})$  vs the nonrelativistic Zunger–Cohen orbital radii,  $r_s$  (●) or  $r_{(sp)}$  ( $(r_s + r_p)/2$ ; ×) 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  $\text{\AA}$ ). ○, 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  $d_{M-M}(\text{obsvd})$  vs  $d_{M-M}^S(\text{calcd})$  using eq 4 with  $C(S) = 1.19$  and  $n(S) = 0.08$  and eq 2 for obtaining  $d_{M-M}^S(\text{calcd})$ . The symbols are the same as those given in Figure 2. The line is meant as a guide to the eye for  $d_{M-M}(\text{obsvd}) = d_{M-M}^S(\text{calcd})$ .

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<sup>4</sup> 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.<sup>9</sup> 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  $S$  ( $n/2$ ).

(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.

Thus, the calculated "spin"-dependent interatomic distance,  $d_{M-M}^S(\text{calcd})$ , is obtained by dividing  $d_{M-M}(\text{calcd})$  (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<sup>10,11</sup> (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<sup>12</sup> 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<sup>12</sup> for the first row elements are 1.18 and 1.31, respectively. The values of  $F_S$  for  $n = 1$  ( $\sim 1.16$ ) and  $n = 2$  ( $\sim 1.26$ ) 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.<sup>2</sup> 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,<sup>13-16</sup> 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<sup>a</sup>

compound	bond order <sup>b</sup>	$d_{M-M}$ obsvd	$d_{M-M}^c$ calcd	$d_{(M-M)^+d}$ calcd
[Tc <sub>2</sub> Cl <sub>8</sub> ]	4	2.15	2.76	2.14 (+3,*3)
[Mo <sub>2</sub> Cl <sub>6</sub> ](dippe) <sub>2</sub> <sup>e</sup>		2.76		2.76 (+1,*0)
[Mo <sub>6</sub> Cl <sub>8</sub> ] <sup>4+</sup>		2.61		2.64 (+0,*1)
[Mo <sub>2</sub> (HPO <sub>4</sub> ) <sub>4</sub> ] <sup>2-</sup>		2.22		2.20 (+3,*3)
[Mo <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ] <sup>3-</sup>		2.16		2.16 (+4,*3)
[Mo <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> ] <sup>4-</sup>		2.11		2.13 (+3,*4)
Mo <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>		2.09		2.09 (+4,*4)
Mo≡Mo <sup>f</sup>	3	2.208	2.95	2.20 (+3,*3)
MO <sup>4</sup> Mo <sup>f</sup>	4	2.106	2.82	2.12 (+4,*4)
Re≡Re <sup>f</sup>	3	2.27-2.28	2.89	2.30 (+2,*2)
Re <sup>4</sup> Re <sup>f</sup>	4	2.22	2.76	2.20 (+3,*3)
Re=Re	2	2.47	3.20	2.50 (+1,*1)
W <sup>4</sup> W <sup>f</sup>	4	2.20		2.22 (+3,*3)
Cr-Cr <sup>f</sup>		1.87		1.90 (+4,*4)
Cr <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub> (Et <sub>2</sub> O) <sub>2</sub>		2.54		2.61 (+0,*0)
Pt <sub>3</sub> (CO) <sub>3</sub> (μ-CO) <sub>3</sub>		2.65 <sup>g</sup>		2.66 (+0,*0)
Pt <sub>3</sub> (CO) <sub>3</sub> (μ-CO) <sub>3</sub>		3.05 <sup>h</sup>		3.00 (+0,*0)

<sup>a</sup> 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). <sup>b</sup> The bond order ( $n + 1 = 2S + 1$ ) is taken from that reported in the literature (refs 14 and 15). <sup>c</sup> Calculated using eq 4 for the value of  $S$  corresponding to that given by the bond orders given in the second column. <sup>d</sup> 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. <sup>e</sup> dppe, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>. <sup>f</sup> The values given are the average values from examples given in refs 14 and 15. <sup>g</sup> Intracluster Pt-Pt distance. <sup>h</sup> 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  $CR_{\text{cov}}$  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<sup>13-16</sup> reasonably well. When  $M = \text{Mo}$ , 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 Cr<sub>2</sub> 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<sup>13</sup> such as the insulating K<sub>2</sub>Pt(CN)<sub>4</sub>·3H<sub>2</sub>O, the Pt-Pt distance of  $\sim 3.48$  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 K<sub>2</sub>[Pt(CN)<sub>4</sub>]Br<sub>0.3</sub>·3H<sub>2</sub>O or K<sub>2</sub>[Pt(CN)<sub>4</sub>]Cl<sub>0.3</sub>·3H<sub>2</sub>O have Pt-Pt distances close to 2.88 Å and have higher conductivity than K<sub>1.75</sub>[Pt(CN)<sub>4</sub>]·1.5H<sub>2</sub>O (Pt-Pt distance of 2.96 Å compared to  $\sim 3.00$  Å obtained from eq 2 for  $S = 1/2$ ). An interesting example<sup>13</sup> is Pt<sub>3</sub>(CO)(μ-CO)<sub>3</sub>, in which the intracluster Pt-Pt distance of  $\sim 2.65$  Å is close to that (2.66 Å) obtained from eq 5 with  $S = 0$ , while the intercluster distance of  $\sim 3.05$  Å is close to that ( $\sim 3.00$  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 ( $N = \text{IIIB}$  and  $\text{IB}$ , respectively) or  $n = 4$  for Cr, Mo, W ( $N = \text{VIB}$ ) or Fe, Ru, Os ( $N = \text{VIII A}$ ), 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.