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Simple Interrelationship between Crystal Radii, Pseudopotential Orbital Radii, and Interatomic Distances in Elements

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The *angular-momentum-dependent* pseudopotential orbital radii,[1] r_p defined as the radius at which the potential, $V_l(r)$, of the outermost electron crosses over from negative to positive values ($V_l(r_l) = 0$), especially $\langle r_{sp}\rangle$ ($= (r_s + r_p)/2$), have been used as quantum mechanical coordinates (especially $R_o = (r_s + r_p)/2$ and $R_\pi = |(r_s - r_p)|$ for structural discrimination mainly through the efforts of Phillips[2] and Villars.[3] Zunger,[4] using *ab initio* atomic methods, calculated these radii, which were correlated with length scales such as covalent radii or Pauling's tetrahedral or univalent radii[5] derived from condensed matter science. Such core radii have a near invariance with respect to chemical environment.[4] On the other hand, structural refinement procedures[6] often require a matching of interatomic distances obtained from an empirical tabulation of the effective *crystal radii*, CR, for cations and anions. The crystal radii tabulated by Shannon[7] are strongly dependent on the chemical state, including valence, coordination number, spin-state, etc. We have examined the proposition that, since the quantum coordinates such as r_s and r_p may be used to discriminate structures of *AB* compounds refined from distances obtained from crystal radii, the crystal radii may be derived from these quantities. We demonstrate in this communication such a relationship.

In many of the structural delineation plots for binary compounds AB, the crucial quantum mechanical coordinate seems to be R_π, which depends on the difference between r_s and r_p orbitals with their different bonding characteristics. We have plotted in Figure 1 the largest and smallest coordination-number-dependent crystal radii (CR) for the various positively charged non-transition-metal ions (cations) as tabulated by Shannon, *vs* respectively the largest and smallest orbital-angular-momentum-dependent pseudopotential orbital radii r_l ($l = 0$ or 1). Surprisingly, we obtain a fairly linear plot (variance <0.1) obeying the relation

$$\mathrm{CR}^+ = 1.93r_l - 0.289 \qquad (\text{in Å}) \tag{1}$$

Better fits (variance < 0.006) are obtained when we plot r_s *vs* the smallest crystal radii ($\mathrm{CR_{min}}^+$ ($= 2.30r_s - 0.51$ (in Å), Figure 2a) and r_p *vs* the largest crystal radii $\mathrm{CR_{max}}^+$ ($= 1.62r_p - 0.07$ (in Å), Figure 2a). The two relations yield an average value of CR$^+$ which is in agreement with that in eq 1.

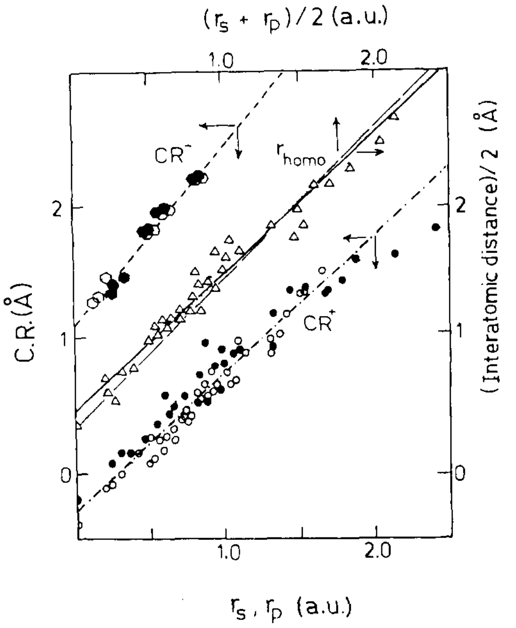

Figure 1. Plots of crystal radii (from ref 7) and half of internuclear distances against pseudopotential orbital radii as calculated by Zunger (ref 4) for non-transition elements. Smallest cation crystal radius $\mathrm{CR_{min}}^+$ (○), *vs* smallest pseudopotential orbital radius. Largest cation crystal radius, $\mathrm{CR_{max}}^+$ (●), *vs* largest pseudopotential orbital radius; dash and dot line gives the best fit. Anion crystal radius, CR$^-$, *vs* pseudopotential orbital radii (○ and ● for r_s and r_p, respectively); dash line gives the best fit. Half internuclear distance in normal state of elements, r_{homo} (△), *vs* $\langle r_{sp}\rangle$ ($= (r_s + r_p)/2$); full line gives the best fit, while broken line corresponds to eq 3.

Similar plots for the anions using the crystal radii as listed by Shannon are shown in Figure 1 (variance <0.001). It may be important to note that the maximum difference is seen for the first row elements such as O and F which have the maximum coordination number dependence of their ionic radii.[7] The best fit is obtained for the relation

$$\langle \mathrm{CR}^- \rangle = 2.56r_e + 1.05 \qquad (\text{in Å}) \tag{2}$$

We have also shown in Figure 1 the plot of $\langle r_{sp}\rangle$ *vs* r_{homo}, half the homopolar bond distances of the elements. The linear plot[8] (variance <0.013) fits well with that expected from an average of $\langle \mathrm{CR}^+\rangle$ and $\langle \mathrm{CR}^-\rangle$ so that

$$r_{\mathrm{homo}} = [\langle \mathrm{CR}^+\rangle + \langle \mathrm{CR}^-\rangle]/2 \tag{3a}$$

$$= 2.23\langle r_{sp}\rangle + 0.38 \tag{3b}$$

The pseudopotential orbital radius of the hydrogen atom is taken as 0 Å. The constant terms in eqs 1–3 are therefore the corresponding radii of hydrogen atom. Thus the radii as well as bond lengths seem to be determined by a term proportional to the pseudopotential core radii, r_p with *all environmental or charge-transfer factors being determined by the constant terms derived from the single electron hydrogen atom*! This explains the transferability of the r_l to various structures as well as the chemical environment dependence of the crystal radii through their r_s and r_p dependence and not their nominal valence.

We show in Figure 2 that the values of the recently calculated radius, r_m, of *mononegative* ions by Sen and Politzer[9] falls on the same line as that of $\langle \mathrm{CR}^-\rangle$ when plotted against $\langle r_{sp}\rangle$. r_m is the radius at which the electrostatic potential $V(r)$ has a minimum

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(1) See: Cohen, M. L.; Bergstresser, T. K. *Phys. Rev.* **1966**, *B141*, 789. Cohen, M. L.; Heine, V.; Phillips, J. C. *Sci. Am.* **1982**, *246*, 82. St. John, J.; Bloch, A. N. *Phys. Rev. Lett.* **1974**, *33*, 1095. See also: Simons, G.; Bloch, A. N. *Phys. Rev.* **1973**, *B7*, 2754. Simons, G.; Parr, R. G. *J. Chem. Phys.* **1971**, *55*, 4197.

(2) Phillips, J. C. *Rev. Mod. Phys.* **1970**, *42*, 317. Phillips, J. C. Universal Aspects of Chemical Bonding. In *Highlights of Condensed Matter Theory LXXXIX Corso*; Soc. Italiana di Fisica: Bologna, Italy, 1985.

(3) Villars, P. *J. Less Comm. Met.* **1983**, *92*, 215; **1985**, *99*, 33; **1985**, *109*, 93.

(4) Zunger, A. *Phys. Rev.* **1980**, *B22*, 5839.

(5) Pauling, L. In *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(6) See, for example: Baur, W. H. In *Structure and Bonding and Crystals*; Academic Press: 1981; Vol. II, p 31.

(7) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. See also: *Structure and Bonding in Crystals*: Academic Press: 1981; Vol. II, p 53.

(8) We find that for *all* transition-metal elements a simple multiplicative factor of $1.2S(S + 1) - 0.08$ reproduces r_{homo} within the scatter in Figure 1, where the spin S is obtained from the nominal d orbital occupancy of the elements. Equation 3 may also be used to predict heteropolar bond distances as we shall show in another communication.

(9) Sen, K. D.; Politzer, P. *J. Chem. Phys.* **1989**, *90*, 4370. These authors have shown that "a mononegative ion has a minimnum in its electrostatic potential, $V(r)$, at a radial distance, r_m, that encompasses a quantity of electronic charge exactly equal to the nuclear charge". At r_m, $V(r)$ is a minimum. For such a potential, r_m is finite only for a negative ion.

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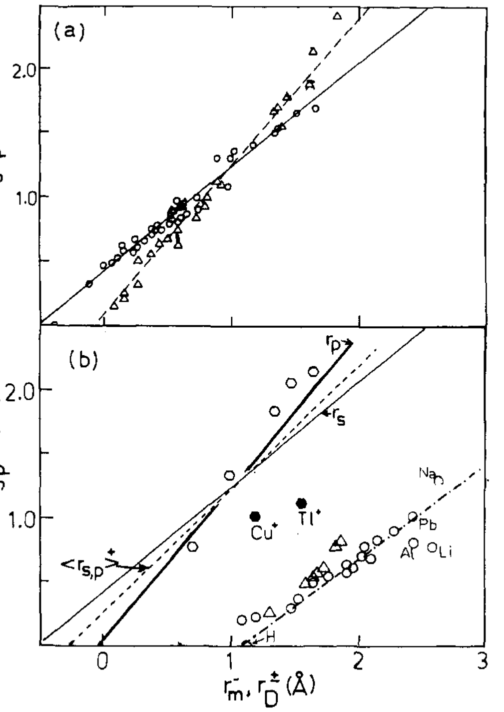

Figure 2. (a) Smallest CR$^+$ (○) *vs* r_s (full line) and largest CR$^+$ (△) (from Shannon, ref 7) *vs* r_p (dashed line, from Zunger, ref 4). (b) Plots of r_D for cations (●) (from Deb *et al.*, ref 11) *vs* $\langle r_{sp} \rangle$ (= $(r_s + r_p)/2$; from ref 4) for alkali metals. The points for Cu$^+$ and Tl$^+$ shows the characteristic disagreement observed with transition metals and other non-octet elements. r_D for singly charged anions (△) (from ref 11) *vs* $\langle r_{sp} \rangle$; plots of r_m (○) (see text; from ref 9) *vs* $\langle r_{sp} \rangle$. The straight lines correspond to those in Figure 1, with dashes (for cations) and dashes and dots (for anions), while the full lines are from Figure 2a.

for these mononegative ions. According to the density functional theory,[10,11] the chemical potential $\mu = -V(r)$ at a radius r_D corresponding to the constant universal one-electron density $\rho(r_D)$ (= 0.008 714) when $(\delta T/\delta \rho) = -(\delta \epsilon_x/\delta \rho) - (\delta \epsilon_c/\delta \rho)$, where $T[\rho]$, $\epsilon_x[\rho]$, and $\epsilon_c[\rho]$ are respectively the kinetic, exchange, and correlation energy functionals. Deb and co-workers[11] have calculated r_D for neutral and singly charged positive and negative ions. The calculated values of r_D for negative ions corresponds closely to the value of r_m and is related to the pseudopotential radii in nearly the same manner as the crystal radii of anions (Figure 2). The values of r_D for alkali metal ions are in good agreement with the plot of largest crystal radii *vs* the pseudopotential orbital radii, r_p (Figure 2b).

The nearly similar behavior of r_m, r_D ($\mu = V(r)$), and CR$^-$ when plotted against $\langle r_{sp} \rangle$ indicates that the former set of radii have probably the same origin, so that the minimum of the electrostatic potential corresponding to r_m is also close to the condition defining the radius r_D at which the function containing the kinetic energy, exchange, and correlation energy contributions cancel each other. The electrostatic potential $V(r_D)$ is equal to the chemical potential μ_D at $r = r_D$. Since the chemical potential μ is a constant throughout the system at equilibrium[12] and the interatomic bond distances are given by the sum of CR$^+$ and CR$^-$, we expect that the chemical potentials for the singly charged cationic ($\mu_D{}^+$) and anionic ($\mu_D{}^-$) components of the homopolar bond should equal each other. The corresponding electrostatic potentials $V^+(r_D)$ and $V^-(r_D)$ for monopositive cations and mononegative and anions, respectively, should also be the same at the point of contact (defined by r_D for the respective ions) of the two ions. Since the effective charges encompassed by the core radii r_D are of opposite sign, $V^+(r_D) = V^-(r_D) = 0$ when this condition is satisfied. The inescapable conclusion, therefore, is that at equilibrium the *covalent bond distances* are determined by the *sum of cationic and anioni radii* defined for a constant zero chemical potential or zero electrostatic potential surface.

Politzer *et al.*[10] have pointed out that the chemical potential $\mu = -(I + A)/2 = -V(r)$ at r_μ or r_{cov} of homopolar M–M bonds, where I and A are the ionization potential of the atom M (required to form M$^+$) and electron affinity of M (or ionization potential of M$^-$), respectively. They were, however, unable to obtain a "fundamental" understanding of their observation. Equation 3a now seems to provide the justification as we require I and A to ionize the atoms and to return to zero potential. It is thus extremely satisfying to note the transparent manner in which empirical experimental observations of many-body science are linked with the transferability of simple theoretical calculations of atomic physics.

Note Added in Proof: The effective crystal radii used in Figures 1 and 2 are the corresponding effective conic radii of Shannon (ref 7).

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(10) Politzer, P.; Parr, R. G.; Murphy, D. R. *J. Chem. Phys.* **1983**, *79*, 3859.

(11) See: Deb, B. M.; Singh, R.; Sukumar, N. *THEOCHEM* **1992**, *91*, 121 and references therein.

(12) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801. Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218.