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Atomic Radii from Electron Densities

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Abstract

Bond lengths for diatomic molecules are predicted from atomic radii derived from free atom one-electron densities by postulating shielding factors for their valence electrons that depend on orbital angular momentum and on the bond order. The predicted values are closer to spectroscopically measured bond lengths than those based on earlier atomic radii inferred from a wider range of structural evidence. The bond lengths predicted by the sum of the atomic radii are corrected by a reduction that allows for charge transfer and by an extension associated with exchange repulsion of the overlapping electrons in the inter-nuclear region. Both corrections are related to free atom one-electron densities.

1. Atomic Radii from Structural Data

The distance between atoms is a measure of the nature and strength of the interactions between them, and thus a bond length should be predictable if the corresponding bond strength is known. Conversely, detailed information on atom–atom interactions can be inferred from known structural geometry. Geometrical data on crystal structures have been provided by diffraction analyses at an increasing rate since the pioneering experiment of von Laue in 1912 (Friedrich *et al.* 1912).

By 1920, W. L. Bragg (1920) had ascertained that many crystal structures could be approximated by tightly packed assemblies of spherical atoms, each of which was assigned a radius characteristic of that particular element. To first order those interatomic distances within crystals could be approximated by sums of radii for spherical model atoms. Using the relatively limited data available, Bragg derived radii from which it was possible to determine interatomic distances for several hundred crystals to within an average deviation of 0.06 Å. Some individual discrepancies however, were as large as ~10%.

Extensive work on the theory of ionic compounds prior to 1920 made it seem logical to seek better agreement between calculated and measured bond lengths for ionic crystals by developing separate ionic radii. Ionic radii were first determined by Landé (1920), and were subsequently adjusted in a long sequence of progressively more elaborate modifications, aimed at bringing the predictions

* Deceased.

into closer agreement with experiment. A detailed history of atomic/ionic radii can be found in Pauling (1960), Slater (1965) and Shannon and Prewitt (1969).

Pauling (1927) noted that bond lengths are a function not only of the electron distribution of the atoms (which extends infinitely), but also of the crystal structure, and on the nature of the bonding, being ionic, covalent, metallic or somewhere in between, and realised that it was not possible to assign a single unique radius to an atom or ion. For example, the O atom size implied by the bond length of 1.21 Å for O₂ (Spackman and Maslen 1986) is substantially smaller than that indicated by the O–O distance of 1.49 Å in H₂O₂ (Wyckoff 1963).

Similarly, Zachariasen (1931) derived a set of radii which could be corrected for coordination number, bond type (i.e. single, double ..., which he referred to as valence) and for radius ratio. He noted that the agreement of his radii with those of Goldschmidt and Pauling, though excellent for small valences, was not so good for multiply charged ions. He stated: 'This lack of agreement in the latter case may be due to the fact that the conception of ionic bindings cannot be maintained for such ions.'

With increasing refinements, ionic radii applicable to selected groups of interatomic distances can indeed be predicted more reliably, but the improved precision incurs a high cost in reduced generality. For example, cation radii appropriate for oxides do not predict accurate bond lengths for nitrides and sulfides (O'Keeffe and Hyde 1981). Such radii often lack clarity or uniqueness in their definition, e.g. some are obviously un-physical, such as the negative radii sometimes assigned even to such regularly behaved atoms as carbon (O'Keeffe and Hyde 1981).

Fumi and Tosi (1964) determined a set of ionic radii for the alkali halides. Their most significant conclusion was that r_c/r_a , where r_c is the cation radius and r_a the anion radius, is much larger than that in all the other traditional sets of radii, r_c being ~ 0.2 Å larger, and $r_a \sim 0.2$ Å smaller than the traditional radii. As traditional radii refer to free ions, it is physically reasonable that ions in a crystal will be distorted from the free state.

Wavefunctions calculated for ions in crystals show a tightening of the electron density for anions, and relaxation for cations, compared with free ions (Seiler and Dunitz 1986). Smaller anions have the advantage of eliminating any need to assume negative radii for ^{III}C⁴⁺ in the carbonate group and ^{III}N⁵⁺ in the nitrate group. However, Shannon and Prewitt (1969) noted that, even using the Fumi and Tosi radii, it is not possible to achieve a completely positive set of crystal radii, e.g. for HF, $r(\text{F}^-) = 1.199$ Å, implying that $r(\text{H}^+)$ must be -0.28 Å.

Slater (1964, 1965) noted that: '... atoms in a crystal tend to be more nearly neutral than a straight ionic interpretation would suggest.' He extended Bragg's original values to include data for 1200 diatomic molecules. With no elaborate corrections for coordination number (CN) or other effects such as radius ratio or ionic charge, those radii determine interatomic distances for elements, inter-metallic compounds and other non-ionic compounds as well as ionic compounds to an average accuracy of 0.12 Å. Some Slater radii differ significantly from Bragg's, mainly because they were optimised to fit many more interatomic distances, some of which were revised after Bragg's paper was published. Slater's radii are within a few hundredths of an angstrom of the tetrahedral covalent values determined by Pauling and Huggins (1934). As the latter were calibrated against half the

elemental interatomic distance by principles similar to those used by Slater, that is not surprising (Slater 1964, 1965; Pauling 1960). Pauling and Huggins also determined covalent radii for other coordination numbers which, along with the metallic radii by Pauling (1960), also resemble Slater's values.

The bond valence model (BVM), which originates from Pauling (1929), relates bond lengths to bond strengths explicitly. In the resulting principle of local charge balance, the sum of the strengths of the bonds from cations must neutralise the charge of the anion on which they terminate. The ultimate aim in the BVM approach is to identify empirical $d_{AB}(s)$ functions which allow bond lengths in new structures to be predicted accurately when the bond strengths are known. It would also allow bond strengths to be evaluated when the bond lengths are known. The BVM, by avoiding the need for individual radii, requires no *a priori* assumptions regarding the nature of the bonds. The BVM, while not affected by bonding character, is strongly constrained by such electronic effects as Jahn–Teller distortion and the stereo-chemical role of lone pairs of electrons (Brown 1992; Urusov 1995).

Bonded radii have been defined as the distance from the centre of an atom to the minimum in the total electron density (e.g. Gibbs *et al.* 1992). As the electron density distributes itself in such a manner as to minimise the total energy of the configuration, such a definition should provide physically reasonable radii. It would also be consistent with the Hohenberg and Kohn (1964) theorem. Bonded radii differ from standard crystal and ionic radii in that they are not constant for a given coordination number. As the definition depends on, for example, bond length and the anion to which each cation is bonded, such radii are not unique. However, the Fumi and Tosi (1964) radii match the Gibbs' values better than they match more traditional ionic radii.

Taking the saddle points as the dividing points in theoretical electron density studies yields ionic charges that are significantly less than the formal values. Attempts to derive experimental ionic radii by dividing experimental electron density maps into regions of integral charge, while subject to large experimental uncertainties, also support the view that early sets of radii were too large for anions, while the values for cations were too small. Although it is often assumed that attraction between charges of opposite sign reduces the bond lengths in polar compounds, that argument may be over-simplified and contrary opinions have been expressed. O'Keeffe (1981) pointed out that it is a mistake to divide bonds in ratios proportional to properties of free ions where the electrostatic potential expands cations and contracts anions. This is a mistake because it does not fit the evidence and it is intrinsically erroneous.

Spackman and Maslen (1986) determined diatomic promolecular radii, with a minimum number of pre-conceptions on the chemical nature of the bonding involved, by evaluating the distance from the nucleus to the minimum in the promolecule electron density $\rho_{\text{pro}}(\mathbf{r})$ along the internuclear vector. The radii derived for promolecules were closely similar to those evaluated from molecular electron densities in the same way. Deformation of the electron density by bonding thus has little effect on the radii derived from electron distributions, which are largely determined by the promolecule.

No single set of uncorrected radii can reproduce bond lengths in all different types of molecules and crystals accurately. As Slater (1964, 1965) and Gibbs *et al.*

(1992) have pointed out, the deformations of atoms in crystals are small, indicating that radii determined from promolecular densities would be an ideal starting point. These radii can then be corrected for first-order two-atom interactions such as exchange and charge transfer, to estimate bond lengths. This follows the idea of Pauling, but the initial radii are for neutral atoms rather than ions.

2. Atomic Radii from Electron Densities

The precision with which interatomic distances can be predicted is limited ultimately by the understanding of the component interactions that, taken together, constitute inter-atomic forces. That understanding can be improved by relating the interatomic distances d_{AB} to electron densities by formulae that reflect the physical nature of the interactions between the atoms A and B. Atomic radii that closely approximate the experimental bond lengths $d_{AB} \sim r_A + r_B$ are derived from the atomic electron densities used to calculate a standard set of atomic form factors (Mann 1988; Mann and Waber 1973). The interatomic distances predicted by those radii are then modified to allow for charge transfer and exchange effects related to the bonding scenario. The formulae for predicting molecular geometry emphasise physical principles, precision in the predictions being secondary to clarity of understanding.

Atomic radii for limiting cases that serve as upper and lower bounds are readily calculated from electron densities. The systematic deviations of the measured bond lengths from the predictions of these limiting models are a guide to the factors responsible for the deviations. A core radius r_c can be defined by

$$4\pi \int_0^{r_c} r^2 \rho(r) dr = Z - nv, \quad (1)$$

where nv is the number of valence electrons and the atomic number is

$$Z = 4\pi \int_0^{\infty} r^2 \rho(r) dr. \quad (2)$$

The lower bounds to the bond lengths derived from the r_c values for fluorides are shown in Fig. 1.

The true bond lengths correlate well with sums of r_c values, but are systematically larger, by amounts that are proportionately greater for the lighter anions. The extreme outlier is the H atom, which has no core, and thus r_c is zero. An expectation value for the valence electron radius, defined by

$$\langle r_v \rangle = \frac{\int_{r_c}^{\infty} r^3 \rho(r) dr}{\int_{r_c}^{\infty} r^2 \rho(r) dr} \quad (3)$$

sets an upper bound to bond lengths and, as seen for fluorides in Fig. 2, gives moderately reliable radii for anions. It has serious deficiencies as a measure of cation radii, for which the averages over their very diffuse valence distributions are too large.

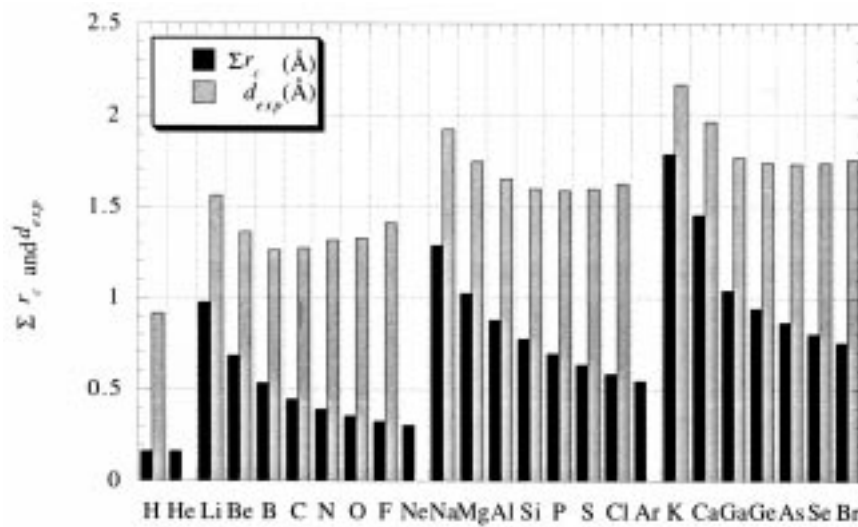


Fig. 1. Comparison of Σr_c versus the experimentally measured bond lengths for the fluorides.

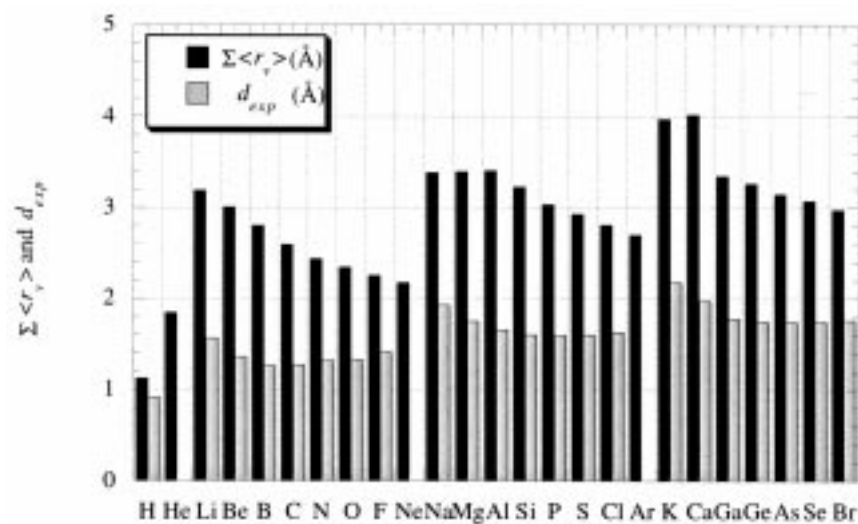


Fig. 2. Comparison of $\Sigma \langle r_v \rangle$ versus the experimentally measured bond lengths for the fluorides.

A best valence shielded atomic (VSA) radius r_{VSA} for the atom with electron density $\rho(r)$ can be defined by

$$4\pi \int_0^{r_{VSA}} r^2 \rho(r) dr = Z - nv + N_v, \quad (4)$$

where the number $N_v = \sum_s w_s N_s$ of valence electrons that shield the neighbouring nucleus from the electrostatic field of each atom is determined by a weighted sum over the valence electron subshells, each containing N_s electrons.

The weights w_s that measure the impenetrability of the valence subshells depend both on the number and electronic states of the electrons as well as on their involvement in bonding. Each subshell's valence electrons, subdivided into bonded and non-bonded categories, are assigned the weights, which were empirically determined to give the best fit for the largest number of compounds, indicated in Table 1. These values are consistent with bonding 'ability', e.g. the singly bonded p electron's low weight reflects the p state's effectiveness in bonding. Although d electrons are not involved strongly in chemical bonding (see e.g. Harrison 1980), it is known from the change in effective radii for metals, when undergoing transitions from low to high spin states, that interatomic distances between atoms with unpaired d electrons are affected significantly by their electron spin configurations (e.g. van Santen and van Wieringen 1952; Blasse 1965).

Table 1. Valence electron weights

| Valence electron type | w_s |
|-------------------------------------|-------|
| Singly bound s electron | 0.16 |
| Doubly or triply bound s electron | 0.21 |
| Unbonded s electron | 0.55 |
| Singly bound p electron | 0.10 |
| Doubly or triply bound p electron | 0.20 |
| Unbonded p electron | 0.64 |

Unbound s and p electrons are in the outer subshells where the overlap is less, and hence have large weights. For a small number of d electrons the d subshell is extended. Its properties are closer to those of valence electrons than those for d subshells which are more nearly complete. Heavily occupied but incomplete d subshells resemble core electrons more closely. In contrast with s and p subshells, where the simple weights in Table 1 suffice, the d electron weights postulated depend on the d subshell occupancy according to the formulae:

$$N_s(d) = \sum_s [w \uparrow_s N \uparrow_s + w \downarrow_s N \uparrow \downarrow_s], \quad (5)$$

where $w \uparrow = wt_{d1} \uparrow + wt_d \uparrow \times N \uparrow \downarrow$, and $w \downarrow = wt_{d1} \downarrow + wt_d \downarrow \times N \uparrow \downarrow$ and $wt_{d1} \uparrow = wt_{d1} \downarrow$, $wt_{d2} \uparrow = wt_{d2} \downarrow$.

Here $N \uparrow$ is the larger of the numbers of d electrons in the up or down spin configurations, and $N \uparrow \downarrow$ is the number of spin paired electrons. The bond lengths involving atoms with paired d electrons on the right-hand side of the transition series may also involve factors additional to those encountered for the first half of the transition series. The d electron contribution to N_v ideally requires two sets of weights, but for the limited number of diatomic molecules for which accurate spectroscopic bond lengths are available it suffices to choose the empirically optimised weights, $wt_{d1} = 0.6$ and $wt_{d2} = 0.078$. Applying Hund's maximum multiplicity rule, five or fewer d electrons all occupy the same spin state. In such cases $N_v(d) = \sum_s w_s N_s$ resembles the form used for s and p electrons.

Table 2. VSA single bond radii in Å compared with values by Slater (1964, 1965)

| Element | Slater (Å) | VSA radii (Å) | Element | Slater (Å) | VSA radii (Å) |
|---------|------------|---------------|---------|------------|---------------|
| H | 0.25 | 0.36 | K | 2.20 | 1.88 |
| Li | 1.45 | 1.24 | Ca | 1.80 | 1.73 |
| Be | 1.05 | 1.01 | Sc | 1.60 | 1.45 |
| B | 0.85 | 0.88 | Ti | 1.40 | 1.32 |
| C | 0.70 | 0.76 | V | 1.35 | 1.28 |
| N | 0.65 | 0.66 | Cr | 1.40 | 1.13 |
| O | 0.60 | 0.59 | Mn | 1.40 | 1.40 |
| F | 0.50 | 0.53 | Fe | 1.40 | 1.21 |
| | | | Co | 1.35 | 1.11 |
| Na | 1.80 | 1.40 | Ni | 1.35 | 1.08 |
| Mg | 1.50 | 1.28 | Cu | 1.35 | 1.32 |
| Al | 1.25 | 1.26 | Zn | 1.35 | 1.18 |
| Si | 1.10 | 1.17 | Ga | 1.30 | 1.23 |
| P | 1.00 | 1.07 | Ge | 1.25 | 1.20 |
| S | 1.00 | 0.98 | As | 1.15 | 1.14 |
| Cl | 1.00 | 0.90 | Se | 1.15 | 1.08 |
| | | | Br | 1.15 | 1.02 |

Although most of the resulting VSA radii listed in Table 2 are within a few hundredths of an angstrom of those determined by Slater (1964), differences for some alkali and transition metals range up to a few tenths of an angstrom. In so far as the accuracy of bond length predictions is limited mainly by our restricted understanding of two-atom contributions, there is little point in trying to evaluate the atomic radii more precisely. If our understanding of the two atom effects progresses to a degree such that the errors in their prediction are reduced, more elaborate specification of the valence electron weights would be justified.

3. Diatomic Molecule Bond Lengths from Atomic Radii

The diatomic molecules are an archetypal set of compounds suitable for testing an electron density approach to predicting interatomic distances. Spectroscopically measured bond lengths (Huber and Herzberg 1979) for diatomic fluorides, hydrides and oxides are compared with the sum of the VSA radii in Tables 3 to 5. The r.m.s. discrepancies between the sum of the VSA radii and the experimental bond lengths for the first, second and third row hydrides, fluorides and oxides, is 0.12 Å, compared with 0.24 Å for the sum of Slater's atomic radii for the same set of 72 diatomic molecules. The former is the same as Slater's value of 0.12 Å reported for a more extensive set of compounds. The r.m.s. deviation for the sum of the Bragg (1920) radii for the relevant subset of these compounds is 0.32 Å.

The best atomic values for most first, second and third row hydrides approximate spectroscopic measurements within 0.05 Å, with the exceptions being d_{NaH} (0.12 Å), d_{MgH} (0.08 Å), d_{CaH} (−0.09 Å) and d_{GaH} (0.07 Å). The best atomic values for the first, second and third row fluorides are poor approximations to spectroscopic measurements, being approximately 10% longer at the electropositive end of the third row, and 34%, 14% and 8% too short at the electronegative end of the first, second and third rows respectively. The best atomic values for the oxides are too large at the electropositive end of the third row (11%), and too short at the electronegative end (19%, 6%, 5%), but the discrepancies are less serious than those for the fluorides.

Table 3. Bond lengths for fluorides

Experimental (Huber and Herzberg 1979), \sum VSA radii, \sum VSA radii corrected for charge transfer, \sum VSA radii corrected for exchange and \sum VSA radii corrected for both charge transfer and exchange

| | d_{exp} (Å) | $d_{\sum \text{VSA}}$ (Å) | d_{ct} (Å) | d_{exch} (Å) | $d_{\text{ct+exch}}$ (Å) |
|----|----------------------|---------------------------|---------------------|-----------------------|--------------------------|
| H | 0.916808 | 0.8892 | 0.8022 | 0.9564 | 0.8694 |
| Li | 1.563864 | 1.7616 | 1.5615 | 1.7627 | 1.5626 |
| Be | 1.3610 | 1.5391 | 1.3494 | 1.5449 | 1.3552 |
| B | 1.26259 | 1.4071 | 1.2524 | 1.4227 | 1.2680 |
| C | 1.2718 | 1.2885 | 1.1896 | 1.3241 | 1.2251 |
| N | 1.31698 | 1.1902 | 1.1408 | 1.2666 | 1.2172 |
| O | 1.326 | 1.1132 | 1.0937 | 1.2727 | 1.2532 |
| F | 1.41193 | 1.0519 | 1.0519 | 1.4119 | 1.4119 |
| Na | 1.925947 | 1.9288 | 1.7763 | 1.9298 | 1.7772 |
| Mg | 1.7500 | 1.8087 | 1.6444 | 1.8119 | 1.6477 |
| Al | 1.654369 | 1.7839 | 1.6007 | 1.7899 | 1.6068 |
| Si | 1.6011 | 1.6952 | 1.5321 | 1.7067 | 1.5437 |
| P | 1.5897 | 1.5940 | 1.4716 | 1.6163 | 1.4939 |
| S | 1.600574 | 1.5025 | 1.4188 | 1.5455 | 1.4618 |
| Cl | 1.628313 | 1.4227 | 1.3712 | 1.5145 | 1.4630 |
| K | 2.171457 | 2.4019 | 2.2327 | 2.4025 | 2.2332 |
| Ca | 1.967 | 2.2542 | 2.0473 | 2.2558 | 2.0489 |
| Ga | 1.774369 | 1.7558 | 1.6168 | 1.7634 | 1.6245 |
| Ge | 1.7452 | 1.7212 | 1.5874 | 1.7329 | 1.5991 |
| As | 1.7360 | 1.6647 | 1.5553 | 1.6842 | 1.5748 |
| Se | 1.7408 | 1.6040 | 1.5188 | 1.6381 | 1.5529 |
| Br | 1.75894 | 1.5455 | 1.4820 | 1.6124 | 1.5489 |

However, it is important to note that the oxides differ from the fluorides and hydrides in that a number of them contain double bonds. This requires N_s (the number of valence electrons) to change from one to two. The double bond O–O calculated is 10.6% too short.

Hydrides differ from oxides and fluorides, in that hydrogen does not have a core. Obviously, the agreement between calculated and experimental bond lengths can be improved if the weights in Table 1 are made dependent on quantum number. The agreement can, in fact, be made almost perfect by using a sufficiently large set of empirically determined parameters.

Although judgement of the reliability of the model bond lengths for transition metal diatomics is impeded by a paucity of data, the consistent accuracy of the predictions for the first, second and third row hydrides and oxides encourages confidence in the transition metal radii. The densities used to predict bond lengths for Cr (in CrO) and for Cu (in CuH and CuO) are those for $3d^4 4s^2$ and $3d^9 4s^2$ configurations (Abdallah and Mann 1995), whereas the free atom ground state configurations are $3d^5 4s^1$ and $3d^{10} 4s^1$ for Cr and Cu respectively. The $3d^n 4s^2$ and $3d^{n+1} 4s^1$ states are almost degenerate (Maslen and Trefry 1988), and thus the use of a non ground-state configuration is an acceptable approximation. The longer bond lengths calculated using the $3d^5 4s^1$ and $3d^{10} 4s^1$ densities were anomalous, producing discordant peaks in the plots of calculated versus experimental bond lengths. Those determined from the $3d^4 4s^2$ and $3d^9 4s^2$ densities fit more smoothly on to the curve defined by the experimental bond lengths for the remaining diatomic transition hydrides and oxides.

Table 4. Bond lengths for hydrides

Experimental (Huber and Herzberg 1979), \sum VSA radii, \sum VSA radii corrected for charge transfer, \sum VSA radii corrected for exchange and \sum VSA radii corrected for both charge transfer and exchange

| | d_{exp} (Å) | $d_{\sum \text{VSA}}$ (Å) | d_{ct} (Å) | d_{exch} (Å) | $d_{\text{ct+exch}}$ (Å) |
|----|----------------------|---------------------------|---------------------|-----------------------|--------------------------|
| H | 0.74144 | 0.7265 | 0.7265 | 0.7390 | 0.7390 |
| Li | 1.5957 | 1.5989 | 1.5356 | 1.5991 | 1.5358 |
| Be | 1.3426 | 1.3764 | 1.3330 | 1.3775 | 1.3341 |
| B | 1.2324 | 1.2444 | 1.2259 | 1.2473 | 1.2288 |
| C | 1.1199 | 1.1258 | 1.1196 | 1.1325 | 1.1262 |
| N | 1.03621 | 1.0275 | 0.9932 | 1.0418 | 1.0074 |
| O | 0.96966 | 0.9505 | 0.8887 | 0.9803 | 0.9184 |
| F | 0.916808 | 0.8892 | 0.8022 | 0.9564 | 0.8694 |
| Na | 1.8874 | 1.7661 | 1.7117 | 1.7663 | 1.7119 |
| Mg | 1.7297 | 1.6460 | 1.5997 | 1.6466 | 1.6003 |
| Al | 1.6478 | 1.6212 | 1.5763 | 1.6223 | 1.5774 |
| Si | 1.52010 | 1.5325 | 1.4988 | 1.5346 | 1.5009 |
| P | 1.42234 | 1.4313 | 1.4160 | 1.4355 | 1.4201 |
| S | 1.3409 | 1.3398 | 1.3359 | 1.3478 | 1.3439 |
| Cl | 1.274552 | 1.2600 | 1.2366 | 1.2771 | 1.2537 |
| K | 2.2425 | 2.2392 | 2.1813 | 2.2393 | 2.1814 |
| Ca | 2.0025 | 2.0915 | 2.0304 | 2.0918 | 2.0307 |
| Sc | | | | | |
| Ti | | | | | |
| V | | | | | |
| Cr | | | | | |
| Mn | 1.7311 | 1.765 | 1.7246 | 1.7705 | 1.7306 |
| Fe | | | | | |
| Co | | | | | |
| Ni | 1.4756 | 1.4396 | 1.4071 | 1.4491 | 1.4166 |
| Cu | 1.46263 | 1.4591 | 1.4312 | 1.4681 | 1.4402 |
| Zn | 1.59490 | 1.5424 | 1.5167 | 1.5501 | 1.5244 |
| Ga | 1.6630 | 1.5931 | 1.5583 | 1.5945 | 1.5598 |
| Ge | 1.5880 | 1.5585 | 1.5291 | 1.5607 | 1.5313 |
| As | 1.5344 | 1.5020 | 1.4865 | 1.5056 | 1.4901 |
| Se | 1.475 | 1.4413 | 1.4388 | 1.4477 | 1.4451 |
| Br | 1.414435 | 1.3828 | 1.3727 | 1.3953 | 1.3852 |

For the transition metal hydrides the sum of the VSA radii is a good approximation to the experimentally determined bond lengths, the discrepancies being within 0.05 Å. In comparison, for the transition metal oxides, sums of the VSA radii poorly approximate the bond lengths, especially for the metals of lower atomic number. The predicted bond length for ScO is 14% longer than the experimental value.

All calculated transition metal oxide bond lengths are larger than the experimental values, except for the case of CuO (1.55 Å calculated versus 1.72437 Å experimental). This discrepancy raises the remote possibility that the CuO bond is single, which is reinforced by the fact that Cu is the only heavy transition metal for which a stable diatomic oxide has been reported. The possibility that the properties of CuO differ from those of the oxides for Co, Ni and Zn was explored by *ab initio* calculations. Attempts using Spartan 3.1.4d (1994) failed to converge. Similar calculations using Gaussian 92/DFT (1993) with methods

Table 5. Bond lengths for oxides

Experimental (Huber and Herzberg 1979), \sum VSA radii, \sum VSA radii corrected for charge transfer, \sum VSA radii corrected for exchange and \sum VSA radii corrected for both charge transfer and exchange

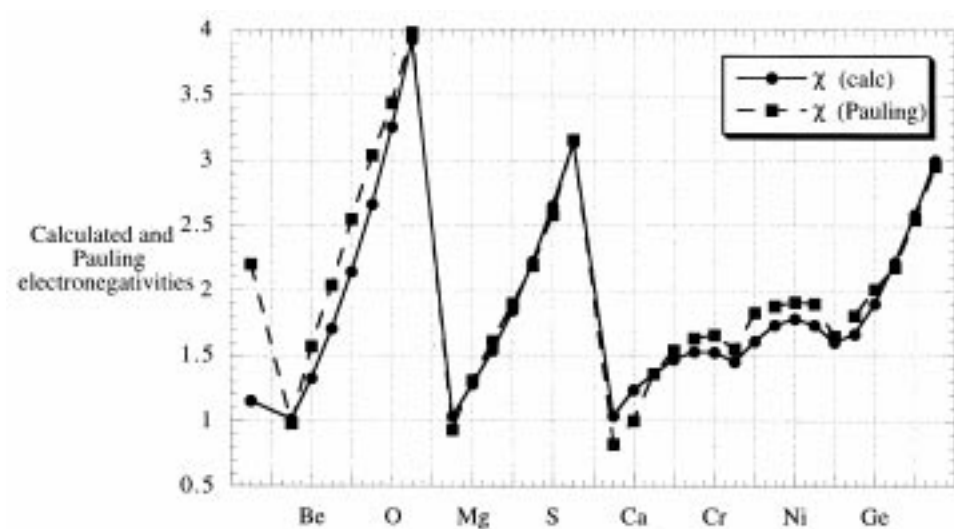
| | d_{exp} (Å) | $d_{\sum \text{VSA}}$ (Å) | d_{ct} (Å) | d_{exch} (Å) | $d_{\text{ct+exch}}$ (Å) |
|----|----------------------|---------------------------|---------------------|-----------------------|--------------------------|
| H | 0.96966 | 0.9505 | 0.8887 | 0.9803 | 0.9184 |
| Li | 1.728 | 1.8230 | 1.6619 | 1.8234 | 1.6624 |
| Be | 1.3309 | 1.4482 | 1.2691 | 1.4519 | 1.2728 |
| B | 1.2045 | 1.2938 | 1.1490 | 1.3056 | 1.1608 |
| C | 1.128323 | 1.2298 | 1.1306 | 1.2551 | 1.1560 |
| N | 1.15077 | 1.1546 | 1.1138 | 1.2073 | 1.1665 |
| O | 1.20752 | 1.0913 | 1.0913 | 1.1986 | 1.1986 |
| F | 1.326 | 1.1132 | 1.0937 | 1.2727 | 1.2532 |
| Na | 2.07 | 1.9902 | 1.8627 | 1.9906 | 1.8631 |
| Mg | 1.7490 | 1.7085 | 1.5550 | 1.7106 | 1.5571 |
| Al | 1.6179 | 1.6379 | 1.4618 | 1.6424 | 1.4664 |
| Si | 1.509739 | 1.6123 | 1.4468 | 1.6204 | 1.4548 |
| P | 1.4759 | 1.5401 | 1.4144 | 1.5550 | 1.4293 |
| S | 1.481087 | 1.4664 | 1.3833 | 1.4944 | 1.4113 |
| Cl | 1.56963 | 1.4840 | 1.4432 | 1.5247 | 1.4839 |
| K | 2.22 | 2.4633 | 2.3056 | 2.4635 | 2.3058 |
| Ca | 1.8221 | 2.1412 | 1.9166 | 2.1422 | 1.9177 |
| Sc | 1.66826 | 1.9029 | 1.6693 | 1.9542 | 1.7206 |
| Ti | 1.62022 | 1.7885 | 1.5658 | 1.8529 | 1.6301 |
| V | 1.58932 | 1.7502 | 1.5393 | 1.8210 | 1.6101 |
| Cr | 1.615 | 1.7752 | 1.5860 | 1.8449 | 1.6556 |
| Mn | 1.769 | 1.8671 | 1.7215 | 1.9289 | 1.7834 |
| Fe | 1.6395 | 1.6924 | 1.5369 | 1.7719 | 1.6164 |
| Co | | | | | |
| Ni | | | | | |
| Cu | 1.72437 | 1.5883 | 1.4784 | 1.6819 | 1.5721 |
| Zn | | | | | |
| Ga | 1.7436 | 1.6452 | 1.5140 | 1.6513 | 1.5201 |
| Ge | 1.624648 | 1.6461 | 1.5058 | 1.6545 | 1.5142 |
| As | 1.6236 | 1.6114 | 1.4991 | 1.6246 | 1.5123 |
| Se | 1.6484 | 1.5661 | 1.4836 | 1.5884 | 1.5059 |
| Br | 1.7172 | 1.6069 | 1.5533 | 1.6365 | 1.5829 |

such as UHF, MP2 and QCISD and with basis sets such as lanl1dz and lanl1mb, converged slowly to anomalously long bond lengths ranging from 1.86 to 2.02 Å. Other investigators have achieved somewhat shorter bond lengths for CuO, such as 1.79 Å (Moriarty 1995), which while being a closer approximation to the experimental bond length, is still too long.

The alkali diatomics provide a further comparison of VSA radii with Slater's (1965) values (shown in Table 6) that is particularly definitive because two-atom corrections for charge transfer and exchange effects should be very small for these molecules. The bond lengths calculated using Slater's atomic radii are on average about 0.42 Å too large for these compounds. The VSA radii infer bond lengths that are on average 0.22 Å too small. Slater's predictions of diatomic bond lengths for diatomic molecules are too large, mainly because they were derived from data that include the longer bond lengths that occur in solids. In this electron density approach it is expected that the increased bond lengths for solids will be described by the two-atom contributions.

Table 6. Comparison of Slater and VSA radii bond lengths for the alkali diatomics

| | d_{exp} (Å) | d_{Slater} (Å) | Δ Slater (Å) | $d_{\Sigma \text{ VSA}}$ (Å) | $\Delta \Sigma \text{ VSA}$ (Å) |
|-----------------|----------------------|-------------------------|---------------------|------------------------------|---------------------------------|
| Li ₂ | 2.6729 | 2.90 | 0.23 | +2.471 | -0.20 |
| Na ₂ | 3.07887 | 3.60 | 0.52 | +2.806 | -0.27 |
| K ₂ | 3.9051 | 4.40 | 0.49 | +3.752 | -0.15 |
| LiNa | 2.81 | 3.25 | 0.44 | +2.639 | -0.17 |
| LiK | 3.27 | 3.65 | 0.38 | +3.112 | -0.16 |
| NaK | 3.589 | 4.00 | 0.41 | +3.279 | -0.31 |

**Fig. 3.** Comparison of the calculated and Pauling electronegativities for the hydrides.

4. Electron Density and Electronegativity

The relationship between electron density and electronegativity was previously reported by Sanderson (1952, 1954). Similarly, in these studies, a strong correlation is noted between χ_{Pauling} and the electron density at the VSA radius, ρ_b . This correlation follows from the empirically determined relationship

$$\chi_{\text{calc}} = 0.88 + 0.30\rho_b. \quad (6)$$

The close agreement between χ_{calc} and χ_{Pauling} is shown in Fig. 3. The r.m.s. discrepancy between the χ_{calc} and χ_{Pauling} for first row atoms is 0.27. There is closer agreement for the second row (r.m.s. deviation = 0.06) and for the latter half of the third row (r.m.s. deviation = 0.09). While following the general shape given by the Pauling electronegativities, the electronegativities calculated for the transition metals are generally lower by a factor of 0.1, the r.m.s. deviation being 0.13 for those elements. The largest difference between χ_{calc} and χ_{Pauling} is for H, and could be the extreme case of the tendency for χ to increase beyond what is allowed for in equation (6) at low atomic radius. Hydrogen, due to its lack of a core, tends to be an outlier in chemical bonding theory generally.

The consequences for bond length prediction are minor, because the exchange corrections for the hydrides are small.

5. Two Atom Components

The experimental values deviate from the first order approximations obtained by summing atomic radii partly because of effects that depend on the nature of the bonding interactions involved. Thus changes in bond length originate in the transfer of electrons between atoms with different electronegativities. Electron transfer from atom A to atom B is expected to reduce d_{AB} because of Coulomb attraction between opposite charges that involve integrals over electron densities. The promolecule charges ΔQ_{pro} (Maslen and Etschmann 2000, present issue p. 299) determined by partitioning overlapping atomic electron density in proportion to atomic potentials are approximately proportional to real charges. A charge transfer correction, arbitrarily calibrated on LiF which has a large ΔQ_{pro} , has the form

$$\Delta d_{\text{ct}} = -\Delta d_{\text{LiF}} \left| \frac{\Delta Q_{\text{pro}}}{\Delta Q_{\text{pro}}(\text{LiF})} \right|, \quad (7)$$

where Δd_{ct} is the change in the bond length due to the charge transfer correction, $\Delta d_{\text{LiF}} = 0.20 \text{ \AA}$ is the difference between the experimental bond length and that calculated from the sum of the VSA radii, and $\Delta Q_{\text{pro}}(\text{LiF}) = 0.975e$.

For the same set of the first, second and third row hydrides, fluorides and oxides, the r.m.s. bond length deviation, corrected for charge transfer increases slightly to 0.13 \AA . The charge transfer correction has the effect of shortening d_{AB} and thus reducing the bond lengths at the electropositive end of the row which are too long in most cases. Discrepancies between predicted and observed bond lengths for the strongly hetero-nuclear diatomics such as the alkali halides are generally brought to within 5%. The exceptions contain Na or Mg, for which all calculated bond lengths are consistently too short.

Bond lengths at the electronegative end that are already too short decrease further. The charge transfer correction improves the agreement between calculated and experimental bond lengths for electropositive third row fluorides significantly (Table 3), but mildly impairs the agreement for hydrides (Table 4). It also improves the agreement for the electropositive third row oxides (Table 5). A slight improvement wrought by the charge transfer correction for MnH was offset by slight deteriorations for the other transition metal hydrides. The charge transfer correction improves the agreement markedly for the first half of the transition metal oxides, but agreement for CrO, FeO and CuO deteriorates. Although the charge transfer correction effectively introduces a discontinuity at FeO, lack of experimental data for the heavier transition metal oxides precludes the development of more reliable corrections for those compounds.

The largest systematic discrepancies between measured and predicted bond lengths corrected for charge transfer are the under-estimated lengths of bonds between strongly electronegative atoms such as F_2 , for which the experimentally measured bond lengths exceeds the predicted value by 0.36 \AA . Those discrepancies are the expected consequence of exchange depletion of the electron density in the inter-nuclear region that increases the effective repulsion between the nuclei. Exchange terms in electron wavefunctions are due to the antisymmetrising of

the atomic wavefunctions. Exchange concentrates density in the overlap region for paired electrons with antisymmetric spin states, and reduces electron density in overlap regions for electron pairs with symmetric spin states. If electron distributions for which \uparrow and \downarrow spins have equally probable overlap, exchange reduction for overlap of symmetric spin state electrons outweighs the exchange concentration due to overlap of paired spin electrons. Exchange depletion of the electrons is strongest in bonds between atoms with nearly filled valence electron subshells, for which the number of \uparrow and \downarrow spins involved are nearly equal. Exchange thus increases bond lengths for diatomic molecules containing electronegative atoms.

As the bond length correction for exchange should be affected by both atoms, a correction is sought that is proportional to the product of the ρ_b for the two atoms in the bond. An exchange correction

$$\Delta d_{\text{ex}}^{\text{AB}} = \frac{\Delta d_{\text{ex}}^{\text{F}_2}}{\rho_b^{\text{F}} \rho_b^{\text{F}} \sqrt{h_A h_B}} \rho_b^{\text{A}} \rho_b^{\text{B}}, \quad \Delta d_{\text{ex}}^{\text{F}_2} = 0.36 \text{ and } \rho_b^{\text{F}} = 2.92 \quad (8)$$

can be calibrated on F_2 which has the largest exchange correction. The additional factor $h_A h_B$, where h is the number of holes in the valence shell, has the effect of minimising the exchange correction for the left-hand side of the periodic table compared to the right, where exchange considerations are more important.

By incorporating the vacancies in the valence shell, the electron-hole approach to bonding is emphasised. Compounds involving high coordination numbers can be better explained by the electron-hole bond, i.e. we regard a bond as an electron-hole pairing. This can explain 'standard' bonds, as well as electron deficient bonds. Thus vacancies (holes) are essential to bond formation. Electrons are shared between atomic states with the same spin and comparable energies, one of which is occupied, and the other is empty.

The limited effect of the exchange correction on the first, second and third row hydrides is shown in Table 4. The r.m.s. deviation for bond lengths with only the exchange correction applied is 0.098 Å, which is an improvement on the r.m.s. value with only the charge transfer correction applied. The exchange corrections for the transition metal hydrides improve some bond lengths slightly, at the expense of others. For the transition metal oxides, the exchange correction lengthens all bond lengths, causing the agreement between most calculated and experimental bond lengths to deteriorate.

The r.m.s. deviation for bond lengths including both charge transfer and exchange corrections is 0.097 Å. The fluoride bond lengths, for which the sums of VSA radii are generally too long at the electropositive end and too short at the electronegative end, improve considerably in the first row, when both corrections are applied, although the systematic nature of the residual discrepancies in Table 3 indicates that there may be scope for further improvement. For the latter half of the second and third row fluorides, simply using the sum of the VSA radii proves to be a better predictor of actual bond lengths than when both corrections are applied. NaF and GaF are outliers. On the whole, the hydrides are actually predicted better by simply summing VSA radii, the r.m.s. deviation changes from 0.044 with no correction to 0.062 with both corrections applied. There is no improvement for the transition metal hydrides or alkali

metal diatomics, for which bond lengths are predicted equally well by summing atomic radii without applying two-atom corrections. The alkali diatomics, having minimal charge transfer and only one valence electron, are unaffected by the charge transfer and exchange corrections. The application of both corrections improves half of the oxides to the detriment of the other half. Although the charge transfer correction introduced the anomaly at Fe, a paucity of data for both the transition oxides and hydrides does not permit the development of a more reliable model.

6. Conclusions

The electron density approach presented here attempts to predict interatomic distances with as few ad hoc assumptions on the nature of bonding as possible. The interatomic distances are related to the electron density either directly, or via physical properties evaluated simply from that density. Bond lengths for diatomic molecules are typically 0.8 to 0.9 Å longer than the sums of the core radii, estimated by setting an integral of the electron density within the core to the expected number of core electrons. For each bonded *s* and *p* electron, about $\frac{1}{10} \sim \frac{1}{5}$ are effective in screening the nuclei from their mutual repulsion. About $\frac{1}{2}$ of each non-bonded *s* valence electron and about $\frac{2}{3}$ of each non-bonded *p* electron is effective in screening the nuclei. The *d* electron screening factor of 0.678 when there is only one electron in the partly filled *d* subshell increases to 0.954 (per electron) when that subshell is nine-tenths occupied. In alkali metal diatomics where the two-atom effects of charge transfer and exchange corrections are negligible, the calculated bond lengths are up to 10% shorter than the experimentally determined values. The accuracy of most other bond lengths predicted from atomic radii is limited by charge transfer and exchange. Charge transfer corrections can be estimated from promolecular charges, calculated by partitioning overlapping atomic densities based on the free atom potentials. Exchange corrections can be estimated from products of the atomic electron densities at the 'best' one-atom radii. Whereas applying either the charge transfer correction or the exchange correction alone increases the r.m.s. deviations between calculated and experimental bond lengths slightly, applying both corrections simultaneously reduces the r.m.s. discrepancy. Bond lengths for some diatomic molecules, notably all hydrides and the alkali metals are not much affected by the corrections, but others, especially those for all fluorides and the transition metal oxides improve appreciably. The corrections also improve agreement for the third row oxides. The close relationship between the experimental bond lengths and the values predicted from atomic electron densities using a limited number of physically reasonable parameters, justifies confidence that those parameters have some physical significance. The bond length formulae in the model may indeed describe cause and effect relationships.

Although Bragg (1920) regarded adding atomic radii as simply a 'working approximation, an aid to the analysis of complex structures', interatomic distances can convey far more information. Deviations of interatomic distances from the values predicted should be indicators of unexpected characteristics of the atom-atom interactions. The dependence of the effective radii on the nature of the other atoms with which it combines is exemplified by the dependence of diatomic molecule bond lengths on the electronegativities of the constituent

atoms. To the limited extent to which interatomic distances are sensitive to deformation of atomic electron densities, they will be related to electronegativity. Electronegativities can indeed be related to the electron densities at standard radii. By expressing electronegativity in terms of atomic electron densities, it was possible to express those changes in bond length that are related to electronegativity differences in terms of the atomic densities.

Although the present model is relatively successful, some aspects are not yet explained. All bond lengths for diatomics containing Na or Mg as one of the constituent atoms are consistently too short. That is most likely to be due to limitations of the model, but the strong contrast with the success for chemically similar atoms raises the possibility that the underlying densities or wavefunctions might be responsible.

Further improvements in these formulae relating electron density to bond lengths are certainly feasible. Additional data for the transition metal hydrides and oxides would allow bond length defining formulae involving d electrons to be refined. Extensions to f electron systems could be envisaged. The two atom terms could be tested further and possible three atom contributions investigated if more extensive structural information were available on triatomic molecules. Because of strong evidence that charge transfer is exchange dependent, combining the charge transfer and exchange corrections should be considered. Extension of this philosophy for predicting bond lengths from electron densities from molecules to solids should also be productive.

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