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Bonded and promolecule radii for molecules and crystals

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ABSTRACT

Within the context of the total electron density distribution, a well-defined set of radii known as bonded radii can be derived by measuring, along the bond path, the distance between the center of an atom and the point of minimum electron density. As the properties of a crystal, including its total energy, are determined by its electron density distribution, such radii provide an objective measure of atomic size and a basis for understanding and correlating physical and chemical properties.

Bonded radii observed for chloride and oxide anions are not constant for a given coordination number, as assumed in derivations of lists of ionic and crystal radii, but increase in a regular way with bond length. On the other hand, bonded radii observed for cations show a much smaller increase with coordination number than that reported in studies of ionic and crystal radii. An examination of the electron density distributions observed for the alkali halides, fluorides, oxides, and silicates indicates that the distributions in such crystals can be regarded as largely atomic in nature, despite bond type. Promolecule radii calculated for spherically averaged electron density distributions for corresponding coordinated polyhedra with bond lengths and angles fixed at values observed in crystals reproduce to within ~0.05 Å the Tosi-Fumi radii derived for the alkali halides with the rock salt structure and bonded radii observed for the silica polymorphs, BeO, MgO, CuCl, CaF_2, and CuBr. The close correspondence of promolecule and bonded radii indicates that the electron density distribution of individual atoms in these crystals decreases rapidly with distance. Reliable estimates of bonded radii of atoms in crystals are obtained from a calculated charge density distribution for the corresponding coordinated polyhedra making up such crystals, using Roothaan-Hartree-Fock wave functions.

INTRODUCTION

For more than half a century, crystallographers have recorded X-ray diffraction patterns for thousands of crystals and have been able to account for the scattering of X-rays by such crystals quite satisfactorily with an independent atom or procrystal model that employs spherically averaged atomic scattering factors. Also, in recent years, numerous workers have attempted a mapping of the elusive deformation electron density (e.g., Coppens and Hall, 1982; Tsirelson et al., 1990) and have found that it is very small relative to the total density and difficult to recover even when the diffraction data are precise and massive, particularly when the atoms involved are heavy (atomic number of 10 or greater) (Hirshfeld, 1985). Both of these observations indicate that the electron density distributions in these crystals are largely atomic in nature, particularly when the constituent atoms are heavy. They also corroborate Slater's (1965) conclusions that the atoms in the alkali halides tend to be more nearly neutral than a fully ionic model would indicate and that the electron density differences for a crystal consisting of either ions or atoms would be small and very difficult to measure. They also suggest that the bonded radius of an atom in such crystals, as measured by the electron density distribution, would be largely independent of charge and bond type.

ELECTRON DENSITY DISTRIBUTIONS AND BONDED RADII

Within the context of the total electron density distribution, $\rho(\mathbf{r})$, in a crystal, Gourary and Adrian (1960) and later Slater (1965) have argued that a sensible and well-defined list of radii, referred to as bonded radii by Bader et al. (1971) and Bader (1990), can be derived by measuring, along the bond path, the distance between the center of an atom and the point of minimum electron density. Such a definition of radii is natural because the properties of an atom in a molecule, as well as the total energy of the molecular system, are determined by the ground-state electron density distribution (Hohenberg and

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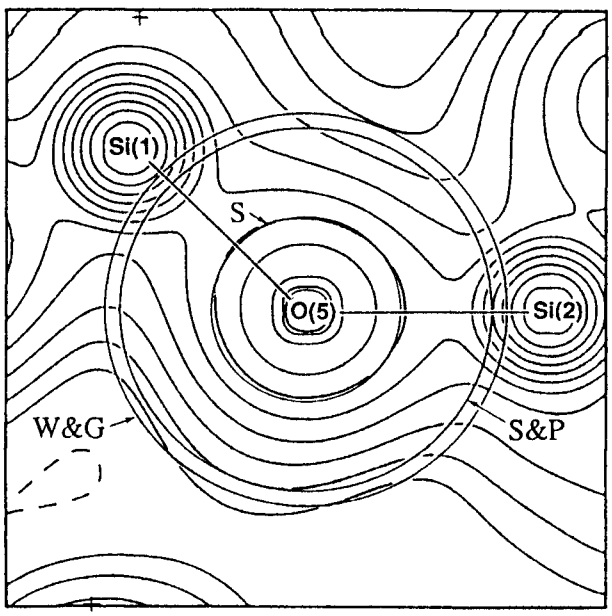

Fig. 1. A map of the static electron density distribution obtained in a pseudoatom model refinement of coesite, calculated through the plane of the Si1-O5-Si2 group. The contour interval is 0.0625, 0.125, 0.250, . . . , e/Å^3. The circle centered on O5 and labeled S (Slater, 1964) defines the outermost limit of the O atom as defined by its atomic radius, and those labeled S&P (Shannon and Prewitt, 1969) and W&G (Wasastjerne, 1923; Goldschmidt et al., 1926) define the outermost limits of the oxide ion as defined by its crystal and ionic radii, respectively.

Kohn, 1964; Reiss and Münch, 1981). Furthermore, the electron density is so distributed that it adopts a configuration that minimizes the total energy of the resulting configuration (Bader, 1981, 1990). It follows, therefore, that the bonded radii provided by such a configuration must be considered as minimum energy features of such a system. As a crystal can be viewed as a molecule of visible dimensions (Slater, 1939), these arguments may be extended directly and without loss of generality to a crystalline system.

Figure 1 shows a map of the electron density distribution obtained in a pseudoatom refinement of a set of X-ray diffraction data observed for coesite, a crystalline form of silica with fourfold-coordinate Si (Geisinger et al., 1987). The bonded radii for the atoms that define the Si1-O5-Si2 angle of the structure were obtained by measuring along the Si1-O5 and Si2-O5 bonds the distances between Si1, Si2, and O5 and the minima in the electron density distribution. The measurement for the Si1-O5 bond yielded the bonded radii, r_b(Si1) = 0.65 Å and r_b(O5) = 0.97 Å, and that for Si2-O5 yielded r_b(Si2) = 0.67 Å and r_b(O5) = 0.95 Å (Buterakos, 1990). Concentric circles of radius 0.60 Å (Slater's atomic radius for O), 1.21 Å (crystal radius for O^{2-} of Shannon and Prewitt, 1969), and 1.32 Å (Wasastjerne-Goldschmidt ionic radius for O^{2-}) are drawn about O5 and compared with the points of minimum electron density as measured along the two bonds. In terms of the electron density distribution, Slater's (1964) atomic radius is much too small, with its outermost extent falling well within the basin of charge density belonging to the O5 oxide ion. On the other hand, the outer limits of the crystal and ionic radii assigned to O5 both fall well within the basins of charge density belonging to the two Si atoms. Actually, the bonded radii of the O atoms in coesite have values that lie about halfway between the atomic and ionic radius of the O atom. Thus, the sizes of the bonded radii obtained for the oxide ion are seen to be quite different from traditional values published for ionic, crystal, and atomic radii. As revealed by Figure 1, it is clear that the electron density distribution of the SiOSi group is compressed along both SiO bonds and is expanded into the empty regions of the coesite structure, rendering a nonspherical distribution for O5. We also note that O5 has two marginally different bonded radii, one toward Si1 and the other toward Si2, with the larger one involving the longer Si1-O5 bond.

A relatively few accurate total electron density maps have been published for crystals over the years from which bonded radii can be measured (Witte and Wölfel, 1955; Krug et al., 1955; Schoknecht, 1957; Weiss et al., 1957; Slater, 1965; Kurki-Suonio and Meisalo, 1966; Meisalo and Inkinen, 1967; Järvinen and Inkinen, 1967; Spackman et al., 1987; Downs, 1991). However, as observed by Slater (1965), when such radii are measured, they do not in general agree, as observed above, either with his atomic radii or with lists of ionic radii. In addition, bonded radii recorded for anions are not approximately constant, as traditionally assumed for ionic and atomic radii. For example, the bonded radius for Cl, r_b(Cl), obtained from experimental electron density maps, increases from 1.25 Å for a CuCl bond length of 2.35 to 1.64 Å for a NaCl bond length of 2.82 to 1.70 Å for a KCl bond length of 3.15 Å (Slater, 1965). More recently, O'Keeffe (1979) observed that the apparent radius of the nitride ion in compounds with the rock salt structure increases from 1.28 to 1.46 Å as the interatomic separation, $R(X\text{N})$, between the metal atom, X, and N increases from 2.05 to 2.65 Å, with the radius of the nitride ion increasing linearly with bond length. As the coordination number of the nitride ion is six in a rock salt crystal, this increase cannot be ascribed to a change in coordination number. In a study of more than 500 experimental $R(X\text{N})$ data, Baur (1987) concluded that the ionic radius of the nitride ion shows a greater dependence on the coordination number than that observed for the oxide ion (Shannon and Prewitt, 1969). However, no attempt was made to test whether a correlation obtains between bond length and the radius of the nitride ion. Evidence has also been presented by O'Keeffe (1977, 1979) that suggests that the apparent radius of the oxide ion also increases with bond length. Such variations in radii support the argument made by Fajans (1941) and Johnson (1973) that anion radii tend to decrease with increasing field strength of the metal atom to which an anion is bonded.

An examination of electron density maps recorded for

coesite and stishovite, a crystalline form of silica with sixfold-coordinate Si, yields an oxide bonded radius, $r_b(O)$, for coesite of 0.95 Å, averaged over eight nonequivalent SiO bonds, and an oxide bonded radius for stishovite of 1.05 Å, averaged over two nonequivalent bonds (Spackman et al., 1987; Geisinger et al., 1987). It is apparent that $r_b(O)$ is 0.10 Å larger in stishovite, where $R(SiO)$ is ~1.78 Å, than it is in coesite, where $R(SiO)$ is ~1.61 Å. Also, the bonded radius of the oxide ion is observed to increase with $R(SiO)$ (Fig. 2) in both coesite and stishovite. In addition, $r_b(O)$ obtained from an electron density map recorded for periclase, MgO, for which $R(MgO)$ = 2.09 Å is even larger: $r_b(O)$ = 1.09 Å. Collectively, these results indicate that there is no such thing as a unique bonded radius for atoms like Cl, N, and O but that the radii of these anions appear to vary with bond length.

In a careful study of the cohesive energies of the alkali halides with the rock salt structure type, Tosi and Fumi (1964), Tosi (1964), and Fumi and Tosi (1964) undertook a derivation of a list of crystal radii, using a generalized Huggins-Mayer form for the repulsive energy, based on experimental isothermal compressibility and thermal expansion data. The resulting crystal radii match bonded radii obtained from electron density maps recorded for the alkali halides significantly better than they match the traditional ionic radii derived by Wasastjerne, Goldschmidt, Pauling, and others (Slater, 1965). Tosi and Fumi (1964) also observed that the crystal radii of the cations are ~0.2 Å larger than ionic radii, whereas those of the anions were ~0.2 Å smaller. For instance, the crystal radius for the fluoride ion was found to be 1.19 Å, a radius that is significantly smaller than values proposed in earlier studies (1.33–1.36 Å).

In their derivation of lists of crystal radii for oxides and fluorides from ~1000 bond length data, Shannon and Prewitt (1969) and Shannon (1976) accepted the Tosi-Fumi radius of 1.19 Å as the sixfold-coordinate radius of the fluoride ion. Assuming a difference of 0.07 Å between the radii of the oxide and the fluoride ions, Shannon and Prewitt (1969) deduced a crystal radius of 1.26 Å for a sixfold-coordinate oxide anion. Using these two radii and following the strategy used by Goldschmidt et al. (1926) to obtain ionic radii from observed bond length data, they undertook a derivation of a list of crystal radii in which the radii were refined to conform with observed bond length data and plots of ionic volumes vs. unit-cell volume (r^3 vs. V). The resulting radii have since been found to reproduce average bond lengths in oxide- and fluoride-coordinated polyhedra in a variety of structure types to within ~0.01 Å when coordination number, electronic spin state, covalency, oxidation, and polyhedral distortions are taken into account. These radii have found wide application, as argued by Prewitt (1985) in his MSA Presidential Address, in the determination of the average bond lengths in oxide and fluoride structure types and cation coordination numbers based on radius ratio arguments. They have also provided a basis for correlating physical properties, generating structure field

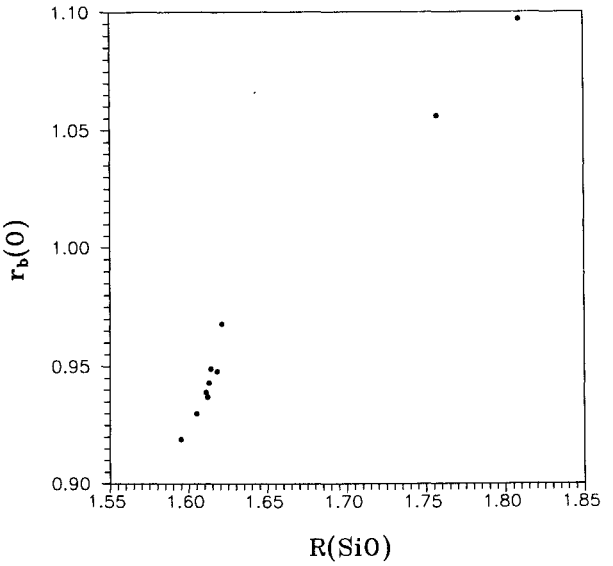

Fig. 2. The bonded radius of the oxide ion, $r_b(O)$, measured from static electron density maps, provided by pseudoatom refinements of observed diffraction data for coesite and stishovite vs. the observed SiO bond length, $R(SiO)$, in angstroms. The pseudoatom refinements were completed by Geisinger et al. (1987) and Spackman et al. (1987), and the bonded radii were measured by Buterakos (1990).

maps, and rationalizing diffusion in solids. Despite such successes, Shannon and Prewitt (1969) did remark that crystal and ionic radii may not be realistic indicators of the sizes of ions, particularly as they relate to easily defined properties of the electronic charge density distribution within a crystal (Slater, 1965). Another problem with the Shannon and Prewitt (1969) crystal radii is their determination of 1.21 Å for the radius of a twofold-coordinate oxide ion. Such a radius requires a negative radius for H^+ of −0.25 Å to reproduce the observed length (0.96 Å) of the OH bond. If radii are additive, then the radius of the oxide ion in the molecule is indicated to be significantly less than 1.0 Å, in conformity with the short OH bond length.

The observation that the Shannon and Prewitt (1969) and the Shannon (1976) radii generate bond lengths that match average values exhibited by coordinated polyhedra in a variety of oxide and fluoride crystals can be taken as evidence that the average separation between the bonded atoms in such polyhedra is largely independent of the forces exerted on the polyhedra by the other parts of the crystal structure, other than those that induced local charge balance. This result suggests that molecules constructed from such coordinated oxide and fluoride polyhedra can serve as useful models for studying bond length and bonded radii variations, provided the molecules are neutralized by attaching H atoms, for example, to the peripheral anions to mimic the local crystal field (Gibbs, 1982). As these molecules are relatively small, molecular orbital calculations have been completed on a wide va-

riety of such molecules, using relatively robust basis sets, to learn whether the resulting bond lengths match observed values reported by Shannon and Prewitt (1969) and Shannon (1976). For example, Gibbs et al. (1987) undertook a calculation of the minimum energy bond lengths in hydroxyacid molecules with fourfold-coordinate $H_{8-n}X^{+n}O_4$ polyhedra and sixfold-coordinate $H_{12-n}X^{+n}O_6$ polyhedra with first- and second-row cations (X = Li through N and Na through S) and found that the resulting bond lengths match those recorded, on average, for similarly coordinated polyhedra in oxide crystals to within ~0.03 Å. In addition, Finger and Gibbs (1985) calculated total electron density maps for these molecules and found, for example, that the bonded radii for Si and O obtained for H_4SiO_4 and H_8SiO_6 match those observed for coesite and stishovite to within ~0.05 Å. The radii also show that r_b(O) increases for fourfold-coordinate X cations from 0.90 Å for the SO bond to 1.22 Å for the NaO bond. Not only did Gibbs and Boisen (1986) observe that r_b(O) increases with $R(XO)$, but they also observed that r_b(O) decreases, for a given bond length, with the row number of the X cation. Total electron density maps calculated for the molecules SO_3, H_2SO_4, $H_2S_2O_7$, and H_6SO_6 show that r_b(S) and r_b(O) both increase linearly with R(SO), with the bonded radii of both S and O increasing at about the same rate (Lindsay and Gibbs, 1988). Similar molecular orbital calculations have been completed on hydrosulfide (Bartelmehs et al., 1989) and hydronitride (Buterakos, 1990; Buterakos et al., 1992) molecules. In these studies, the bonded radii for both the sulfide and the nitride ions were found to increase in a regular way with bond length and to decrease with row number. It is noteworthy that the cation bonded radii obtained in each of these molecular orbital studies correlate with the available crystal and ionic radii, but the slopes of the lines are not 1.0 because the radius of the anion to which a cation is bonded also increases linearly with bond length.

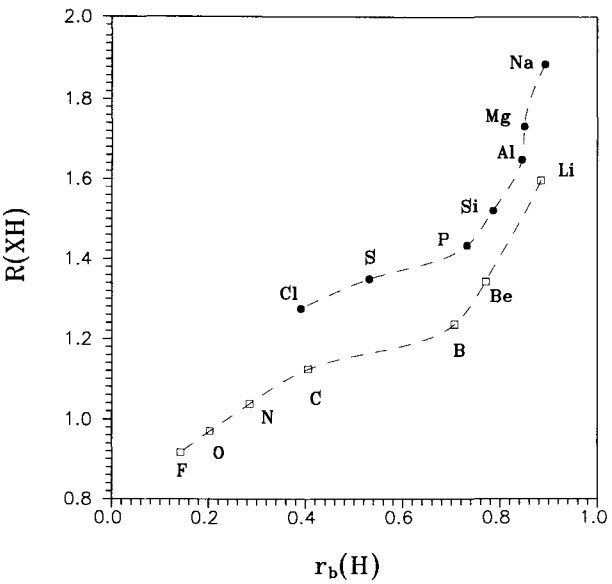

Fig. 3. A plot of the bonded radius for the H atom in XH diatomic molecules calculated from total electron density maps generated with Hartree-Fock wave functions vs. the minimum energy $R(X\text{H})$ bond length in angstroms. The data used to prepare this plot were taken from Table A3 of Bader (1990). The open squares represent X atoms of the first row of the periodic table, and the solid circles represent X atoms of the second.

Promolecule radii

A promolecule is defined to be a model of a molecule where the electron density distributions of each of its atoms have been spherically averaged and placed at their minimum energy positions (Hirshfeld and Rzotkiewicz, 1974). Like the bonded radius of an atom in a molecule, the promolecule radius, r_p, of an atom is defined to be the distance between the nucleus of the atom and the point of minimum electron density between the atom and its nearest neighbors, as measured along the line between the atom and each of its neighbors. Spackman and Maslen (1986) have calculated promolecule radii for 39 diatomic molecules, with bond lengths clamped at the values recorded for these molecules, and have found that the resulting promolecule radii match bonded radii obtained from electron density distributions calculated with accurate Roothaan-Hartree-Fock wave functions with an estimated standard error, ese, of 0.06 Å. As the difference (deformation electron density) between the Roothaan-Hartree-Fock electron density and the promolecule electron density is small, they concluded that bonded radii derived from electron density maps are largely consistent with those calculated in the promolecule and, therefore, appear to be largely atomic in nature, despite bond type. In other words, the deformation electron density, which is very small in comparison with the promolecule electron density, apparently exerts a minor role in determining bonded radii.

A comparison with published lists shows that promolecule radii, just like bonded radii, calculated for diatomics and for the silica polymorphs, correlate with but lie between atomic and ionic radii. Spackman and Maslen (1986) also observed that promolecule radii bear little resemblance to the radii of such anions as F^-, O^{2-}, and so forth, as determined by Pauling (1927). They also observed that bonded radii for a given atom exhibit a relatively wide range of values. An examination of these radii shows, as observed for the hydroxyacid, hydrosulfide, and hydronitride molecules discussed above, that the radii of the nonmetal atoms tend to increase with bond length and to decrease with the row number of the metal atom to which they are bonded (Gibbs et al., 1991). Figure 3 shows, for example, how the bonded radius of the H atom measured for a variety of diatomic hydride molecules varies with bond length. Clearly, for these diatomics, the radius of the H atom is not constant but increases from 0.14 Å when bonded to F to 0.90 Å when bonded to Na. Thus, for H in the hydride diatomics and

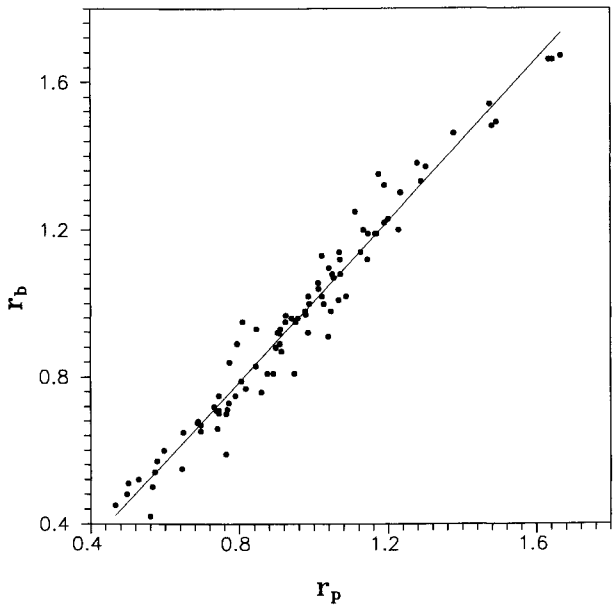

Fig. 4. Bonded radii, r_b, vs. promolecule radii, r_p, calculated for hydroxyacid (Gibbs et al., 1987), hydrosulfide (Bartelmehs et al., 1989), and hydronitride molecules (Buterakos et al., 1992).

for the O, N, and S in hydroxyacid, hydrosulfide, and hydronitride molecules, not only do the bonded radii show a relatively wide range of values, but they also correlate with the length of the bond in which they participate. A calculation of the promolecule radii for the H and O atoms in the H_2O molecule and the OH group yields r_p(H) = 0.20 Å and r_p(O) = 0.76 Å. The promolecule radius for H is positive and ~0.45 Å larger than the crystal radius derived by Shannon and Prewitt (1969), and r_p(O) is, as expected, smaller than it is in coesite and stishovite. The bonded radius of the O atom obtained from a Hartree-Fock structure determination of the electron density of the OH molecule (0.77 Å) is in close agreement (Bader, 1990) with that provided by the calculation on the promolecule.

A COMPARISON OF PROMOLECULE RADII WITH BONDED RADII

Promolecule radii, calculated for the hydroxyacid molecules studied by Finger and Gibbs (1985), for the hydrosulfide molecules studied by Bartelmehs et al. (1989) and for the hydronitride molecules studied by Buterakos et al. (1992), are plotted in Figure 4 against the bonded radii calculated for these molecules with robust 6-31G* basis sets. The charge density distributions for the promolecules were calculated (see Appendix 1) with Roothaan-Hartree-Fock wave functions expressed as a linear combination of Slater-type functions, squared and spherically averaged. A linear regression analysis of the bonded radii as a function of the resulting promolecule radii calculated for the molecules shows that more than 96% of the variation of the bonded radii calculated for these molecules can be explained in terms of a linear dependence on the promolecule radius with an ese of 0.06 Å. This indicates, as observed by Spackman and Maslen (1986) for diatomic molecules, that bonded radii can be regarded as largely atomic in nature.

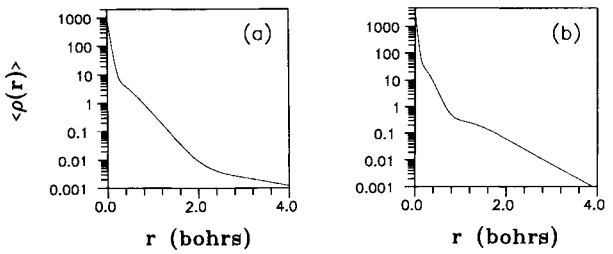

Fig. 5. The spherically averaged electron density, $\langle\rho(r)\rangle$, plotted as a function of r for Na (**a**) and Cl (**b**) atoms. The electron densities were calculated for neutral ground state atoms, using the Roothaan-Hartree-Fock wave functions published by Clementi and Roetti (1974) (1 bohr = 0.529 Å).

Calculations show that the spherically averaged electron density distribution, $\langle\rho(r)\rangle$, of an atom falls off rapidly with increasing distance, r, from its nucleus. This fact is illustrated for both the Na and Cl atoms in Figure 5, where it is seen that $\langle\rho(r)\rangle$ is less than 0.01 e/b^3 for an r value of ~3 bohrs (1 bohr = 0.529 Å). This suggests, because $\langle\rho(r)\rangle$ diminishes rapidly with r, that promolecule radii for atoms making up the coordinated polyhedra in crystals can be accurately estimated by completing a calculation on model polyhedra whose bond lengths and angles are clamped at the values observed for a crystal. We tested this assertion by calculating the promolecule radii of Na and Cl for a NaCl dimer, for a $NaCl_6$-coordinated octahedron, for a $ClNa_6$ octahedron and for a unit cell of NaCl of $Na_{13}Cl_{14}$ composition. In each of these calculations, R(NaCl) was fixed at 2.82 Å, and each ∠NaClNa and ∠ClNaCl was clamped at 90.0°, as observed in the rock salt structure. The calculation for the NaCl dimer yielded promolecule radii of r_p(Na) = 1.168 Å and r_p(Cl) = 1.652 Å, compared with r_p(Na) = 1.169 Å and r_p(Cl) = 1.651 Å calculated for the $NaCl_6$ octahedron, r_p(Na) = 1.165 Å and r_p(Cl) = 1.655 Å calculated for the $ClNa_6$ octahedron, and r_p(Na) = 1.166 Å and r_p(Cl) = 1.654 Å calculated for the $NaCl_6$-coordinated polyhedron centered at ½,½,½ in the unit cell. The values of r_p(Na) and r_p(Cl) obtained for the isolated $NaCl_6$ octahedron and for the one in the NaCl unit cell and those obtained for the $ClNa_6$ octahedron are identical for our purposes. What may be surprising is that the promolecule radii obtained for the $ClNa_6$ octahedron and for both $NaCl_6$ octahedra agree to within 0.003 Å with that calculated for the NaCl dimer, demonstrating that the effect of $\langle\rho(r)\rangle$ is not long-ranged. Witte and Wölfel (1955) calculated electron density maps for a NaCl crystal with observed X-ray diffraction data and reported bonded radii of 1.17 Å for Na^+ and 1.64 Å for Cl^-, radii that agree to within 0.01 Å of the promolecule radii calculated for the $NaCl_6$ octahedra. A map of the promolecule electron

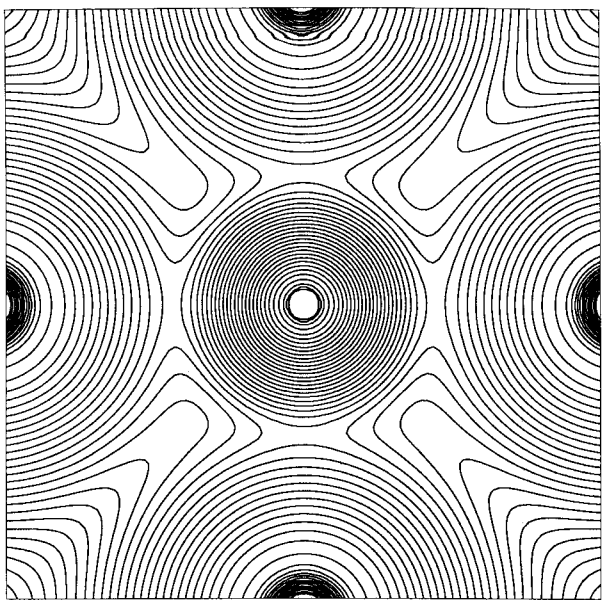

Fig. 6. A total electron density map calculated through a plane defined by Na and four Cl atoms in an $NaCl_6$ octahedron. The map was calculated using the sum of the electron densities from spherically averaged atoms calculated from the Roothaan-Hartree-Fock wave functions (Clementi and Roetti, 1974). The kth contour, counting from the corners of the map, corresponds to the value $(3.0 \times 10^{-4})(1.3^{k-1})e/b^3$. The contours at the atom centers have been omitted.

density calculated through the center of a NaCl octahedron is displayed in Figure 6. Despite the fact that the map was calculated for superimposed spherically averaged Na and Cl atoms, the resulting electron density distribution shows a slight polarization in the direction of the NaCl bond, a feature that might be erroneously ascribed to covalency.

Another test is provided by a careful determination by Downs (1983) of the electron density distribution of bromellite, BeO, using X-ray diffraction data. The bromellite structure can be described as a hcp eutactic array of O atoms in which one-half of the available tetrahedral sites are filled by Be. The term eutactic, as defined by O'Keeffe (1977), means that the centers of the oxide ions in BeO are arranged as those in an hcp metal, but the ions do not make contact with one another as assumed by Bragg and Brown (1926) in their analysis of the structure of forsterite.

As all of the BeO_4 tetrahedra in BeO are equivalent, the corners of each such tetrahedron are shared by four BeO_4-coordinated tetrahedra. Three of the four BeO bonds at the base of each tetrahedron are equivalent and are called basal bonds, whereas the fourth lies along the c axis of the crystal and is called the apical bond. The refinement of the structure shows that the length of the apical bond (1.655 Å) is slightly but significantly longer than that of the basal bonds (1.647 Å). In an excellent review of the electrostatic properties of the mineral, Downs (1991) determined the bonded radii of Be and O in procrystal and the pseudoatom model refinements. Like a promolecule, a procrystal is defined to be a collection of atoms whose electron density distributions have been spherically averaged and placed at their equilibrium positions in the crystal (Coppens and Hall, 1982).

The BeO procrystal electron density distribution measured by Downs (1983) yielded bonded radii for the apical bond [r_b(Be) = 0.579 Å, r_b(O) = 1.076 Å] that are similar to those of the basal bonds [r_b(Be) = 0.577 Å, r_b(O) = 1.070 Å]. These values show close agreement with promolecule radii calculated for a BeO_4-coordinated tetrahedron [apical bond: r_p(Be) = 0.581, r_p(O) = 1.074; basal bonds: r_p(Be) = 0.579, r_p(O) = 1.068 Å] whose bond lengths and angles were clamped at the values observed for the BeO_4 group in BeO. The close agreement between these two lists of radii demonstrates again that promolecule radii calculated for a model coordinated polyhedron with a geometry matching that in a crystal provides a good estimate of bonded radii. The pseudoatom refinement provided bonded radii for the apical bond [r_b(Be) = 0.569 Å, r_b(O) = 1.086 Å] and basal bonds [r_b(Be) = 0.562 Å, r_b(O) = 1.085 Å] that match those obtained in the procrystal refinement to within 0.015 Å, suggesting that charge density distribution in BeO has a dominant atomic component. Despite traditional descriptions of the structure of BeO as a hcp array of large oxide ions with the smaller Be atoms tucked away in the available tetrahedral voids, the bonded radii obtained in Down's (1991) review supports O'Keeffe's (1977) arguments that oxide ions in structures like BeO should be described as eutactic close packed rather than just close packed and making contact (O'Keeffe and Hyde, 1985). A description of such structures with the oxide ions in contact is clearly wrong insofar as the electron density distribution of the crystals is concerned. The close agreement in promolecule and procrystal bonded radii obtained for both NaCl and BeO provides support for the assertion that accurate radii can be obtained for crystals by completing a calculation for coordinated polyhedra with the bond lengths and angles clamped at the observed values.

As observed earlier, Tosi and Fumi (1964) published a list of radii for the alkali halides that match bonded radii obtained from experimental electron density maps significantly better than they match traditional ionic radii. To learn how well the Tosi-Fumi radii agree with promolecule radii, radii were calculated for XY_6 octahedra where X = Li, Na, K, and Rb and Y = F, Cl, Br, and I with $R(XY)$ set at values observed for the alkali halides. The resulting promolecule radii are plotted against the Tosi-Fumi radii in Figure 7. A linear regression analysis of these data shows that 99% of the variation of the Tosi-Fumi radii for the alkali halides can be explained in terms of a linear dependence on the calculated promolecule radii. With the exceptions of NaF and RbCl, whose promolecule radii depart by 0.07 Å from the Tosi-Fumi crystal radii, all the remaining promolecule radii agree with

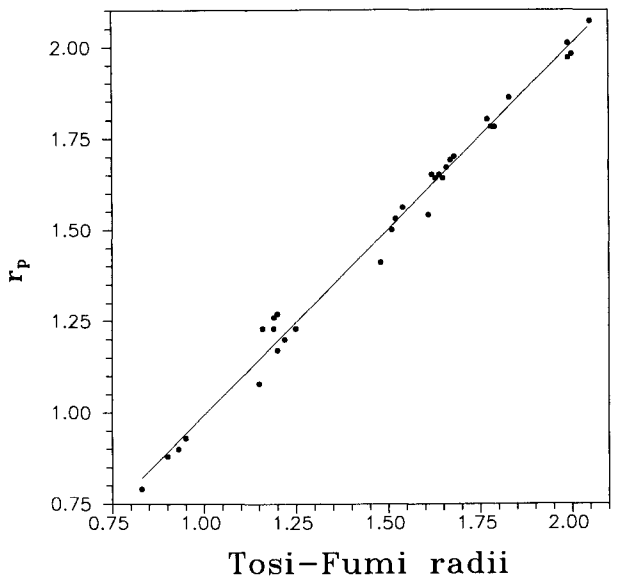

Fig. 7. Tosi-Fumi radii calculated for XY alkali-halide crystals with the rock salt structure vs. promolecule radii calculated for XY_6 coordinated polyhedra with a geometry matching that in the crystal. The Tosi-Fumi radii were taken from Table 3 of Tosi and Fumi (1964).

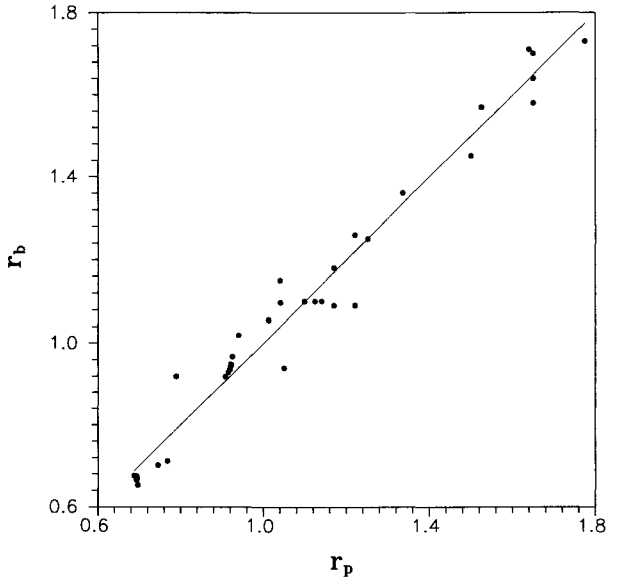

Fig. 8. Bonded radii, r_b, obtained from experimental electron density distributions measured for NaCl, RbCl, LiF, KCl, KBr, coesite, stishovite, MgO, NiO, CuCl, CuBr, BeO, and CaF_2 vs. promolecule radii, r_p, calculated for the nonequivalent coordination polyhedra in each of these crystals with the bond lengths and angles fixed at observed values.

the Tosi-Fumi radii for the alkali halides with an ese of 0.03 Å. This result suggests, as asserted by Slater (1965), that the electron density distributions in the alkali halides have a large atomic component. The observation by Trefry et al. (1987) that the electron density distributions calculated for LiCl and NaF crystals with atomic wave functions are strikingly similar to those calculated for the crystals with ionic wave functions provides additional support for Slater's assertion. That is, that the electron density distributions in each of these crystals can be regarded as similar to that of the procrystal. Trefry et al. (1987) also observed that a calculation of the electrostatic energies for the alkali halides, assuming procrystal models for the electron density distributions, yields energies that match observed cohesive energies with an ese of 0.70 eV compared with those estimated with calculated Madelung energies, which show an ese of 1.38 eV. It is noteworthy that the Madelung energies calculated for the alkali halides systematically overestimate cohesive energies, whereas procrystal electrostatic energies are more randomly distributed around the cohesive energies and provide better estimates.

In an examination of the extent to which promolecule radii correlate with bonded radii obtained from experimental electron density maps in general, promolecule radii were also calculated for the coordinated polyhedra in coesite, stishovite, MgO, NiO, CuCl, CuBr, BeO, and CaF_2, crystals for which experimental total electron density maps have been published. The resulting radii, together with those calculated for the alkali halides with the rock salt structure, are plotted in Figure 8 against the bonded radii obtained from electron density maps. A linear regression analysis of these data shows that 97% of the variation in the bonded radii can be explained in terms of a linear dependence on the calculated promolecule radii. As the ese is 0.05 Å, we conclude that the electron density distribution in each of these crystals is also indicated to have a large atomic component, like that of the procrystal.

In their derivation of a list of crystal radii for the oxides, Shannon and Prewitt (1969) and Shannon (1976) obtained a crystal radius of 0.40 Å for fourfold-coordinate Si and a radius of 0.54 Å for sixfold-coordinate Si, requiring the SiO bond length in an octahedron to be 0.14 Å longer, on average, than it is in a tetrahedron. In contrast, the radius of the oxide ion obtained in their study shows a much smaller increase (0.02 Å) for a change in coordination number from 2 to 3. As observed above, the total electron density maps recorded for the silica polymorphs indicate that the bonded radius of the O atom increases 0.12 Å with an increase in its coordination number from 2 to 3, whereas that of the Si atom is indicated to increase by only 0.04 Å with an increase of coordination number from 4 to 6. In other words, it is the bonded radii of the oxide anion that show the larger increase in size with increasing coordination number, whereas in the case of crystal radii, the reverse seems to be true, with the cations showing the larger increase in size with coordination number. On the other hand, bonded radii recorded for S and O increase at about the same rate in S-containing hydroxyacid molecules with increasing coordination of S and R(SO) (Lindsay and Gibbs, 1988).

As observed earlier, O'Keeffe (1979) has shown that the apparent radius of sixfold-coordinate N correlates linearly with the length of the *X*N bond. A similar result obtains for bonded radii observed for the O atoms in the silica polymorphs, for the O, S, and N atoms in hydroxyacid, hydrosulfide, and hydronitride molecules, and for the H atom in a variety of hydride diatomic molecules. A calculation of the promolecule radii for the nitride anion in VN, CrN, TiN, and ScN yields radii of 1.01, 1.02, 1.03, and 1.09 Å for *X*N bonds of length 2.06, 2.07, 2.12, and 2.22 Å, respectively. Although these radii are ~0.25 Å smaller than those derived by O'Keeffe (1979), they are positively correlated with bond length, as observed, with an r^2 value of 0.99. These results support the observation by O'Keeffe (1977, 1979, 1981) that "it seems quite clear that one should not ascribe a constant radius to an ion, particularly to anions such as O^{2-} and N^{3-}."

Discussion

Despite the successful use of lists of ionic radii in correlating physical and chemical properties and in generating structural field maps, O'Keeffe (1981) argued that these lists are little more than lists of bond lengths for estimating the average separations between bonded atoms in coordinated polyhedra. He continued by asserting that little significance should actually be attached to the values of these radii other than that they are ordinal. It is, after all, the bond lengths that are well known, not the radii. Thus, it is the averaged bond lengths provided by such lists that should be used to ascertain whether one atom will substitute for another in a coordinated polyhedron without destabilizing a structure. For the same reason, such bond lengths, rather than the radii themselves, should also be used to generate structural field maps. Furthermore, the determination of coordination numbers from radius ratio considerations is questionable at best, particularly when the radius of the anion is not constant but shows significant variations.

More than 30 years ago, Mooser and Pearson (1959) showed that the coordination numbers adopted by the atoms in a variety of binary compounds are related to the average principal quantum number of the valence electrons of a pair of bonded atoms and their electronegativity difference rather than to radius ratio considerations. More recently, Phillips (1970) showed that the coordination numbers adopted by cations in a variety of X^nY^{8-n} compounds appear to be governed in large part by the fractional ionic character of their bonds. By plotting the covalent energy gap widths against the ionic energy gap widths for a large number of compounds, he found that fourfold-coordinate compounds could be separated from sixfold-coordinate compounds into disjoint sets, with compounds with large covalent gaps adopting fourfold-coordinate structures. An examination of compounds with the CsCl-structure type with eightfold-coordinate cations shows that these compounds can also be separated from fourfold- and sixfold-coordinate compounds into another disjoint set with large ionic band widths. As radius ratio arguments fail to predict the observed coordination numbers for a number of the alkali halides as well as many others (Phillips, 1974; O'Keeffe, 1977; Tossell, 1979), an effort should be made to purge from textbooks the notion that the coordination number of a cation in a coordinated structure is governed by the relative sizes of the cation and anion that make up the coordinated polyhedra. In fact, Burdett (1982) finds it surprising that the radius ratio rule is still being used as a predictive tool in crystal chemistry, particularly in light of its utter failure to predict the correct coordination number for more than 40% of the alkali halides (Phillips, 1974).

Bonded radii obtained from electron density maps show that it is unreasonable to assume a unique radius for anions like O^{2-}, S^{2-}, and N^{3-} inasmuch as each is observed to increase in a regular way with bond length. As observed by O'Keeffe (1981), the term radius implies that the electron density distribution of an atom is spherical and that it is the same in all directions. However, the bonded radius of an atom, as the term implies, refers to the outer extent of the atom as measured by the minimum in the electron density in the direction of a bond. It does not, however, provide a measure of the outer extent of an atom in other directions. Since the distance to the minimum depends on the nature of the atom to which it is bonded, often the atom is not spherical but may exhibit several different "radii" rather than just one. It is doubtful whether the electron density distribution about an atom in a molecule or a crystal will ever be spherical. Undoubtedly, it will be compressed by the atoms to which it is bonded and extended toward the more empty regions, as observed by Kurki-Suonio and Meisalo (1966) for the fluoride ion in CaF_2. The term radius is clearly unsatisfactory when used in this context, as argued by O'Keeffe, but its niche is so well carved into the parlance of crystal chemistry that it would seem counterproductive to discard it at this late date in favor of another term.

Finally, the determination of accurate bonded radii from the electron density distribution in a crystal using X-ray diffraction data is a nontrivial and difficult undertaking that requires a variety of favorable experimental conditions and utmost care in data reduction (Downs, 1991). Nonetheless, as demonstrated in this study, promolecule radii calculated for the component-coordinated polyhedra in a crystal reproduce bonded radii obtained from experimental electron density maps to within ~0.05 Å. As such radii are easy to calculate, they can be obtained for any coordinated structure, providing the structure is known. In addition to providing a meaningful measure of atomic size, such radii provide a basis for understanding and correlating physical and chemical properties.

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It is a pleasure to dedicate this paper to F. Donald Bloss in honor of his 70th birthday and his pioneering contributions in mineralogy.

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Appendix 1.

The goal of this appendix is to present a strategy for calculating the electron density distribution for a promolecule, i.e., an array of atoms whose electron density distributions have each been spherically averaged and are independent of one another. Suppose that the wave function of an electron on an atom isolated from this array is defined by $R_{nl}(r)Y_{lm}(\theta,\phi)$, then the charge density of the electron, $R_{nl}^2(r)Y_{lm}^2(\theta,\phi)$, can be spherically averaged over the values of the polar angles θ and ϕ for a given value of r by evaluating the integral

$$\langle\rho(r)\rangle = \frac{\int_0^{2\pi}\int_0^{\pi} R_{nl}^2(r)Y_{lm}^2(\theta,\phi)r^2\sin\theta\ d\theta\ d\phi}{\int_0^{2\pi}\int_0^{\pi} r^2\sin\theta\ d\theta\ d\phi}$$

$$= \frac{R_{nl}^2(r)r^2\int_0^{2\pi}\int_0^{\pi} Y_{lm}^2(\theta,\phi)\sin\theta\ d\theta\ d\phi}{r^2\int_0^{2\pi}\int_0^{\pi}\sin\theta\ d\theta\ d\phi}.$$

Since

$$r^2\int_0^{2\pi}\int_0^{\pi}\sin\theta\ d\theta\ d\phi = 4\pi r^2$$

defines the surface area of a sphere of radius r, and since the spherical harmonics, $Y_{lm}(\theta,\phi)$, are normalized

$$\int_0^{2\pi}\int_0^{\pi} Y_{lm}^2(\theta,\phi)\sin\theta\ d\theta\ d\phi = 1.0$$

it follows for a single electron that

$$\langle\rho(r)\rangle = \frac{r^2R_t^2(r)}{4\pi r^2} = \frac{R_t^2(r)}{4\pi}.$$

As the independence of n and l is irrelevant because the charge density has been spherically averaged, both terms can be consolidated into a single term, $t = nl$, where t defines electron type (i.e., 1s, 2s, 2p, etc.). When more than one atom is considered, the R_t associated with an electron of some atom a will be denoted by R_{at}.

According to the discussion in Clementi and Roetti (1974), given an atom a and one of its electrons of type t, R_{at} can be expressed as a linear combination of Slater type orbitals, denoted $(\mathrm{STO})_{\lambda p}(r)$:

$$R_{at}(r) = \sum_{\lambda p} C_{\lambda p}(\mathrm{STO})_{\lambda p}(r)$$

for choices of the parameters λ and p that are appropriate for an atom a and a type of electron t. The expression for $(\mathrm{STO})_{\lambda p}(r)$ is given by (Slater, 1930)

$$(\mathrm{STO})_{\lambda p}(r) = [(2n_{\lambda p})!]^{-1/2}(2\zeta_{\lambda p})^{1/2+n_{\lambda p}}r^{n_{\lambda p}-1}e^{-\zeta_{\lambda p}r}.$$

The values of $\zeta_{\lambda p}$ and $C_{\lambda p}$ were determined in SCF calculations that minimize the total energy of the atom a. The resulting $\zeta_{\lambda p}$ and $C_{\lambda p}$ values used in this study to calculate promolecule charge densities for ground-state neutral atoms with $Z \leq 54$ are given by Clementi and Roetti (1974).

Given an array of independent atoms a with types of electrons t, the promolecule electron density function $\rho(\mathbf{p})$ for this array can be calculated at each point in space, represented by the end point of a vector $\mathbf{p}$ emanating from a chosen origin. This is done with the formula

$$\rho(\mathbf{p}) = \sum_a\sum_t \frac{N_{at}}{4\pi}\{R_{at}[d_a(\mathbf{p})]\}$$

where N_{at} is the number of electrons of type t in atom a and $d_a(\mathbf{p})$ is the distance from the center of any atom a in the promolecule to the end point of $\mathbf{p}$.

To accomplish the calculations presented in this paper, a Fortran 77 program called Promin was written. Given any two atoms, a_1 and a_2, in a promolecule, Promin finds the point along the line between a_1 and a_2 at which $\rho(\mathbf{p})$ is minimum, yielding the promolecule radii of a_1 and a_2. An analytic gradient is calculated at this minimum point to determine whether it qualifies as a $(3,-1)$ or a bond critical point in a three-dimensional ball around the point (Bader, 1990).