A Computational Quantum Chemical Study of the Bonded Interactions in Earth Materials and Structurally and Chemically Related Molecules

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INTRODUCTION

Studies of bond lengths and angles and electron density distributions observed for earth materials and related molecules and those calculated with computational quantum chemical strategies have been a meeting place where experiment has engaged theory in advancing our understanding of bonded interactions. Not only have the calculations provided a physical basis for the proposal that the bond lengths and angles are governed in large part by short-ranged molecular-like forces, but they have also provided a connection between bond length, bond strength and the bond critical point properties of the electron density distributions. They have also provided a basis for Pauling’s (1929) famous definition of bond strength and for the Brown and Shannon (1970) proposal that bond strength can be used as a simple measure of bond character. In addition, extrema in the local charge concentration of the valence electrons of the oxide anion and the electron localization function of electron density distributions calculated for earth materials and related molecules were found to highlight features ascribed to lone-pair and bond-pair domains and to sites of potential chemical reactivity.

In this chapter, a number of properties will be examined including bond length and angle variations, bond strength, crystal and bonded radii, bond “stretching” and “bending” force constants, polyhedral compressibilities, molecular based potential ad hoc energy functions, the generation of new structure types for silica and the bond critical point properties of observed and calculated electron density distributions. Local concentrations and localizations in the distributions (sites of potential electrophilic attack) for several earth materials and related molecules will also be examined and compared.

BOND LENGTH AND BOND STRENGTH CONNECTIONS FOR OXIDE, FLUORIDE, NITRIDE, AND SULFIDE MOLECULAR AND CRYSTALLINE MATERIALS

Bond lengths and crystal radii

With the on-going invention and development since the 1950’s of sophisticated tools and important advances in computer power and software for collecting and processing X-ray, neutron and electron diffraction data and microwave and molecular beam spectra,
thousands of structural analyses of molecules and crystalline materials have been completed and studied. These analyses have provided a wealth of accurate bond length and angle data for a vast array of materials. This resulted in a determination and compilation of large sets of average bond length data, \(<R(MX)\rangle\), for the MX_r-coordinated polyhedra that comprise the structures of a large number of oxide, fluoride, sulfide and nitride crystalline materials (X = O, F, N and S anions), consisting of M-cations from all six rows of the periodic table (Shannon and Prewitt 1969; Shannon 1976; Shannon 1981; Baur 1987). With these bond length data, sets of radii were derived for a variety of coordination numbers and valences for almost all of the M-cations of the table by assuming a given set of radii for the X-anions. The resulting radii have since been used extensively to generate accurate average bond lengths for the coordinated polyhedra of new and potentially viable crystal structures, to construct structural field maps, to study ion mobility, diffusion, leaching and partitioning of trace and minor element distributions among coexisting phases and to serve as a basis for correlating physical properties (Shannon and Prewitt 1969; Shannon 1976; Prewitt 1985; Fisler et al. 2000).

Although a given chemical bond in crystalline materials and molecules exhibits a range of individual bond lengths, it tends to adopt a near-constant average length, \(<R(MX)\rangle\), that depends in large part on a given set of properties (the coordination numbers of the M-cation and the X-anion, the number of valence electrons, the electronic spin state of certain transition M-cations, etc.; cf. Bragg 1920; Goldschmidt et al. 1926; Pauling 1927, 1960; Slater 1964; Shannon and Prewitt 1969; Coulson 1973; Shannon 1976; Baur 1987). Further, for a given M-cation with a given set of properties, \(<R(MX)\rangle\) is largely independent of structure type and nearly constant in value, particularly when the coordination number of the anion is taken into account (Shannon and Prewitt 1969; Shannon 1976). This near-constancy in \(<R(MX)\rangle\) is one of the chief reasons why the average bond lengths of the coordinated polyhedra in many oxide materials can be “reproduced moderately well” with single sets of ionic and crystal radii (Shannon 1976). The near-constancy in \(<R(MX)\rangle\) is the fundamental reason why bond length is such an important property in our quest for understanding the bonded interactions in earth materials (Pauling 1960; Coulson 1973).

**Bonded interactions**

In spite of all that has been said and written about bonded interactions and the chemical bond, these concepts can, in some cases, be elusive as in the case of the SiO bond (Gibbs et al. 1994). Nonetheless, the well-known chemist Jack Dunitz, when referring to the chemical bond, has indicated that he knows one when he sees one. How then does one decide whether a pair of atoms is bonded or not? One tried and more or less proven method is to rely upon experience which has shown that when atoms combine and form the bonds of a coordinated polyhedron, an average bond length is usually adopted that is characteristic of the pair of atoms, their coordination numbers and valences. For instance, when Si and O ions combine and form bonds where each Si cation is bonded to four oxide anions disposed at the corners of a SiO_4 silicate tetrahedral oxyanion and each oxide anion is bonded to valence compensating cations, a characteristic average bond length, \(<R(SiO)\rangle\), of \(~1.62\) Å is adopted. This is true regardless of whether the bond comprises a silicate tetrahedral oxyanion in either gas phase organosiloxane molecules, silicones, siloxane molecular crystals, silicate earth materials or silica glass.

Another more quantitative strategy that has been used to determine whether a pair of atoms is bonded or not is based on the bond critical point properties of the electron density distribution. According to Bader (1998), two atoms are indicated to be bonded if
and only if the pair is connected by a line in the distribution, referred to as a bond path, with the property that the electron density at each point along the line is a local maximum in the plane perpendicular to the bond path at the point. Further, there must exist a single stationary point \( \nabla(r) = 0.0 \) that is a saddle point along the line. This point is referred to by Bader (1990) as a bond critical point, bcp. Hence, regardless of the nature of the pair of atoms involved, the presence of these features is assumed to be an universal indicator of a bonded interaction (Bader 1998). This criterion has not only been used to establish the bonded interactions for a number of molecules and crystals, but it has also been used to establish the existence of bonds and the coordination numbers for the non-framework cations in such earth materials as danburite (7-coordinated Ca; Downs and Swope 1992), low albite (5-coordinated Na; Downs et al. 1996; Gibbs et al., unpublished data) and maximum microcline (6-coordinated K; Allan and Angel 1997; Gibbs et al., unpublished data). This criterion has also been used to explain the adopted planar configuration of the molecules in crystals like Cl\(_2\) in terms of intermolecular bond paths in contrast with a more close-packed configuration expected for a structure governed by a nondirectional van der Waals-type force field (Tsirelson et al. 1995). In addition, bond paths and bonded interactions were reported to obtain between the anions that comprise the polyhedral edges shared in common between the coordinated polyhedra of periclase (Aray and Bader (1996) and related materials (Pendas et al. 1997; Lauña et al. 1997; Recio et al. 1998), a result that has raised questions about the applicability of bond path as an universal indicator of bonded interactions. (cf. Abramov 1997; Bader 1998). For example, paths have been reported between the intertetrahedral oxide anions of the silica polymorphs quartz and coesite (Gibbs et al. 1999b; Gibbs et al. 2000b). However, an examination of the calculated electron density distribution for coesite suggests that the paths between the oxide anions may, in some cases, be related to purely geometrical factors rather than to O-O bonded interactions (Gibbs et al. 2000b).

**Pauling bond strength and bond length variations**

Prior to the advent of computational quantum chemistry, bond length variations for earth materials were usually ascribed to variations in the bond strengths of the bonded interactions between the cations and anions for lack of a better and more accessible measure of bonding power (Pauling 1929). In such studies, the average strength, \(<s>\), of the MX bonds comprising a given MX\(_x\)-coordinated polyhedron was defined to be \(<s> = z/v\) where \(z\) is the valency of the M-cation and \(v\) is its coordination number. According to Pauling’s famous bond valence model, the sum of the average bond strengths, \(\zeta\), to each anion in a stable material was postulated to exactly or nearly equal the negative valency on the anion. For example, consider the Si cation in the high pressure silica polymorph, stishovite, where each cation is bonded to six oxide anions disposed at the corners of an SiO\(_6\)-octahedron and where each oxide anion is bonded to three Si cations disposed at the corners of a triangle. Given that the Si cation has a valency of 4, the average bond strength of the SiO bonds comprising the SiO\(_6\) octahedron is \(z/v = 4/6\). As this bond strength is smaller than that for a silicate tetrahedral oxygenion, \(<s> = 4/4\), the average SiO bond length for the SiO\(_6\) octahedron in stishovite is observed to be substantially longer (\(\approx 1.77\) Å) than that (\(\approx 1.61\) Å) observed for the silicate tetrahedral oxygenion in quartz. This simple example serves to illustrate that \(<s>\) is a measure of the average strength of the bonds in the case of the two silica polymorphs, the greater the value of \(<s>\), the stronger and the shorter the average SiO bond length. Also, as each oxide anion in stishovite is bonded to three Si cations, \(\zeta = 2\), the value of the negative valency of the oxide anion.

In cases such as the silica polymorphs quartz and stishovite, the sum of the average bond strengths, \(\zeta\), to the oxide anions is exactly two, but it is not uncommon in crystalline
materials for $\zeta$ to depart from the valency of the oxide anion by as much as 40% (Baur 1970). Upon re-examining the crystal structure of melilite, a direct connection was found between $\zeta$ and the length of the SiO bonds, the greater the value of $\zeta$, the longer the bonds (Smith 1953; see also Baur 1970). In related studies, Zachariasen (1954, 1963) and Zachariasen and Plettlinger (1954) prepared bond strength vs. bond length curves for the bonded interactions in several uranyl and borate structures and likewise found that the bond lengths decrease as the strength of each the bonds increases. In a similar study, Clark et al. (1969) used a quadratic polynomial to model the correlation between the bond strengths and the individual SiO bond lengths observed for several chain silicates including diopside. Given the well-developed inverse correlation that exists between bond length and bond strength, they concluded that the bonded interactions and the distortions of the silicate tetrahedra in the chain silicates can be rationalized rather simply in terms of an ionic model and bond strengths. The bond lengths in a wide range of materials have since been rationalized either in terms of the Pauling bond strength or some variant of bond strength, despite its simple definition (cf. Baur 1970; Brown and Shannon 1970; Siegel 1978 and references therein).

**Brown and Shannon bond strength and bond length variations**

For MO bonds involving M-cations from the first couple of rows of the periodic table, Donnay and Allman (1970) and more recently Brown and Shannon (1973) observed that they could model the bond strength-bond length connection with the power law expression $s = (R_o/R)^{-N}$ where $s$ is the strength of an individual bond with length $R$ and where $R_o$ and $N$ are constants characteristic of an atom pair. These constants were obtained by Brown and Shannon (1973), Brown (1981) and Brown and Altermatt (1985) for the bond lengths observed for a relatively large number of oxide materials with the constraint that the sum of the bond strengths to each cation and anion in a structure is equal to their valences. Constants were not only obtained for the individual bonds for a relatively large number of different M-cations, but universal constants were also obtained for bonds for cations from the first-, second- and third-rows of the periodic table. In this chapter, Li, Be, B, ..., F are considered to comprise first-row atoms, Na, Mg, Al, ..., Cl to comprise second-row atoms, etc. (cf. Hehre et al. 1986 and others).

One of the notable features of the Brown and Shannon expressions is that the sum of the strengths of the individual bonds to the ions of a structure satisfies the valences of both the cation and the oxide anion regardless of the coordination number and valency of the cation and the irregularity of the coordinated polyhedron. Even though the valence bond model was originally proposed for ionic materials, Brown and Shannon (1973) observed that a single set of parameters is capable of modeling bonded interactions and bond length variations for a wide variety of oxides ranging from closed-shell ionic to shared-electron covalent bonds. With this observation, they concluded that the strength of a bond, as originally defined by Pauling (1929) in his bond valence model, is a direct measure of bond type, the greater the strength, the more covalent the bonded interaction (Brown and Shannon 1973). Support for this conclusion has since been found by Brown and Skowron (1990) who observed that the Brown and Shannon bond strengths obtained for observed structures increase quadratically with Allen’s (1989) spectroscopic electronegativities, $X_{spec}(M)$ of the M-cations. In short, the greater the strength and the shorter an MO bond, the greater the electronegativity of the M-cation and the more covalent the MO bonded interaction (Pauling 1960).

**Bond strength $p$ and bond length variations**

The average bond lengths, $\langle R(MO) \rangle$, observed for a large number of crystalline materials for a variety of MO$_x$-coordinated polyhedra containing main group and closed-
shell transition metal M-cations from all six rows of the periodic table (Shannon 1976), are plotted in Figure 1a against the Pauling average bond strengths, $<s>$, for the MO bonds of the polyhedra. Although the plot displays a relatively wide scatter of data, there is an overall tendency for $<R(MO)>$ to fan out and decrease nonlinearly with increasing $<s>$ with the shorter bond lengths tending to be associated with bonds with larger average bond strengths. In searching for a basis for the trends and the scatter of the data with molecular orbital methods, calculations were completed for the coordinated polyhedra of more than 25 different hydroxycacid and related molecules containing first- and second-row M-cations with coordination numbers, $v$, ranging between three and six. In the calculations, the bond lengths were geometry optimized at the Hartree-Fock 6-31G* level (Gibbs et al. 1987a). When the resulting mean bond lengths, $<R(MO)>$, were plotted against $<s>$, they were found to scatter along two distinct but slightly divergent trends for the row-one and row-two M-cations (Fig. 2a). When the bond length data for the molecules were plotted against the Brown and Shannon bond strengths, they likewise were found to scatter along two distinct trends similar to those calculated for the molecules (see Gibbs et al. 1987a).

In a search for an alternate way of defining the strength of a bond such that it would systematize the bond lengths along a single trend, the data used to construct Figure 1a were examined in a search for some underlying factor that might accomplish this task (Gibbs et al. 1987a). The search revealed that the following bonds, $^{IV}$Be$^{2+}$O, $^{IV}$Si$^{4+}$O, $^{VP}$P$^{5+}$O, $^{V}$S$^{6+}$O, $^{IV}$Cr$^{6+}$O and $^{IV}$Se$^{6+}$O, for example, each has about the same average bond length, $\approx$1.63 Å (the coordination numbers of the cations comprising these bonds are denoted by the Roman numeral superscripts). Accordingly, the average bond strengths, $<s>$, for these bonds exhibit a range of values, 0.5, 1.0, 1.0, 1.5 and 1.5, respectively, rather than exhibiting a single value as one might expect for a set of bonds all of which

![Figure 1](image_url)

**Figure 1.** Average bond length data, $<R(MO)>$, observed for MO$_v$-coordination polyhedra for a large variety of oxide crystalline materials (Shannon 1976) (a) plotted against the Pauling (1960) mean bond strengths, $<s>$, of the bonds in valence units (v.u.) for the MO bonds comprising the polyhedra and (b) plotted against the average bond strength, $p = <s>/r$, where $r$ is the row number of the M-cation comprising the MO bonds ($r = 1$ for Li, Be, B, ...; $r = 2$ for Na, Mg, Al, ...; etc., cf. Hehre et al. (1986) (page 66) for the row number nomenclature used for the M-cations in this chapter).
Figure 2. Geometry optimized MO bond lengths, $R(\text{MO})$, calculated with molecular orbital methods at the HF/6-31G* level for the coordination polyhedra of hydroxyacid and related molecules containing first- and second-row M-cations (Gibbs et al. 1987) plotted (a) against $<s>$ and (b) against $p = <s>/r$. The bond lengths for first-row M-cations are plotted as open circles while those for the second-row M-cations are plotted as solid circles. A regression analysis of the data used to prepare Figure 2b yielded the expression $R = 1.39p^{-0.22}$ which is graphed as a solid line along with the data in the figure. See the legend for Figure 1 for definitions for $<s>$ and $r$.

have the same bond length. When each of the bond strengths was divided by the row number, $r$, of the M-cation, a value of $<s>/r = 0.5$ resulted, conferring the same average bond strength on each of the bonded interactions (Gibbs et al. 1987a). To see how well the resulting average bond strength $p = <s>/r$ systematizes the geometry optimized bond lengths, the $<R(\text{MO})>$-values generated in the molecular orbital calculations were plotted in Figure 2b against $p = <s>/r$. Although not perfect, the data tend to scatter along a single trend described by the regression equation $R = 1.39p^{-0.22}$ (Gibbs et al. 1987a). For purposes of comparison, the $<R(\text{MO})>$ data for crystalline materials used to construct Figure 1a were likewise plotted against $p = <s>/r$ in Figure 1b where they are also seen to scatter roughly along a trend similar to that displayed in Figure 2b. In fact, when the power law expression $R = 1.39p^{-0.22}$ was graphed on the figure, the resulting line was found to fall fairly close, with a few exceptions, to the overall trend of the data.

With the Brown and Shannon equations, individual bond strengths were calculated for each of the non-equivalent MO bond lengths observed for more than 40 bulk silicates and oxide materials (see below). As displayed in Figure 3a, the bond lengths fall along two well-defined slightly divergent trends, as observed for the molecules, when plotted against the individual $s$-values. Perhaps not all that surprising, when the Brown and Shannon bond strengths were each divided by the row number of the cation and $R(\text{MO})$ was plotted against $s/r$, the data were found to scatter along a single trend (Fig. 3b). A regression analysis of the data set yielded the power law expression $R = 1.39(s/r)^{-0.22}$ in exact agreement with the form of the expression obtained in a regression analysis of the molecular data set used to prepare Figure 2.

Bond number and bond length variations

In a graph-theoretic study of bond strengths for the bonds of representative moieties of ten silicate crystals, Boisen et al. (1988) found that the observed nonequivalent bond lengths in these earth materials correlate with the graph-theoretic resonance bond number
of the bonds in much the same way that the bond lengths correlate with the Pauling and Brown and Shannon bond strengths. For the study, the graph-theoretic bond number, \( n \), of an individual MO bond of an MO\(_r\)-coordinated polyhedron was defined to be equal to the average number of electron-pairs that comprise the bonds of a structure averaged over all of the Lewis graphs used to model the representative moieties. A scatter diagram of the resulting bond numbers versus the nonequivalent individual observed R(MO) bond lengths (Fig. 4) was not only found to match the trends discussed above when \( n \) was equated with \( s \), but a regression analysis of the data set generated the power law expression \( R = 1.39(n/r)^{-0.22} \). This expression is in an one-to-one correspondence with the form of the expression obtained for the data used to construct Figures 1 and 2 where again \( r \) is the row number of the M-cation. It is pertinent that the same bond strength-bond length power law relationship obtains, as observed by Brown and Shannon (1973), regardless of whether one considers the bonded interactions to be either predominantly ionic or covalent.

**Nitride, fluoride and sulfide bond strength and bond length variations**

Average bond lengths, \( \langle R(MX) \rangle \), observed for fluoride, nitride and sulfide MX\(_r\)-coordinated polyhedra in crystalline materials and calculated for related molecules have also been found to display similar correlations with \( p \) (Buterakos et al. 1992; Nicoll et al. 1994; Bartelmehs et al. 1989). In each case, the expression was found to be of the same form, \( R = kp^{\beta} \), as observed for oxide crystals and molecules. The \( \beta \)-values obtained in the regression analyses for the three data sets were found to be the same, within the

![Figure 3](image-url)
Figure 4. A scatter diagram R(MO) vs. n/r where R(MO) represents the nonequivalent observed MO bond lengths for diopside, jadeite, acmite, spodumene, NaInSi$_2$O$_8$, NaCrSi$_2$O$_8$, F-tremolite and sillimanite, n is the resonance bond number and r is the row number in the periodic table for the metal cations M.

statistical error, as that obtained for the oxides, ~0.22, but the $\kappa$-values were found to increase in the order 1.37, 1.49 and 1.93, respectively, for fluorides, nitrides and sulfides. These three $\kappa$-values are the average bonds lengths for bonds with a $p$-value of unity. The relative change (per unit interval) in the expression $f(p) = \kappa p^{-\beta}$, as a function of p, is $-\beta/p$. Since $\beta \sim 2/9$ for each of the four types of bonded interactions, it can be concluded that the relative change in $<R(MX)>$ as a function of $p$, for any given bond strength, is indicated to be identical for oxide, fluoride, nitride and sulfide molecules and crystalline materials. Furthermore, the connection between bond strength and the relative change in bond length provided by this relationship is compelling evidence that the forces that govern the bond length variations in nitride, oxide, fluoride and sulfide crystals and molecules are similar and behave as short-ranged and molecular-like.

**Bond strength and crystal radii**

With the power law expression $R(MO) = 1.39p^{-0.22}$, Gibbs et al. (1997b) found that a rough estimate can be made for the crystal radius of a cation with the expression $r(M) = R(MO) - r(O) = 1.39p^{-0.22} - r(O)$, assuming a given radius for the oxide anion, $r(O)$. For example, by assuming that the 3-coordinate crystal radius for the oxide anion is 1.22 Å (Shannon 1976) as in stishovite, they estimated the 6-coordinated crystal radius of Si$^{4+}$ to be $r(\text{Si}^{4+}) = 1.39(1/3)^{-0.22} - 1.22$ Å $= 0.55$ Å, in agreement with the Shannon (1976) crystal radius of the cation, 0.54 Å. Likewise, by assuming a 2-coordinate radius for the anion, 1.21 Å (Shannon 1976) as in quartz, the 4-coordinate radius of the Si cation was estimated to be $r(\text{Si}^{4+}) = 1.39(1/2)^{-0.22} - 1.21$ Å $= 0.41$ Å, again in agreement Shannon’s radius for the cation (0.40 Å).

With the expression $r(M) = 1.39p^{-0.22} - 1.22$ Å, the crystal radii of the M-cations used to construct the average bond lengths, $<R(MO)>$, in Figure 1 were estimated. These
radii are plotted against the Shannon’s (1976) crystal radii in Figure 5 where it is seen that the two sets of radii are highly correlated \( (r^2 = 0.99) \) as expected. It is also seen that the radii estimated for the smaller cations are in better agreement with Shannon’s (1976) crystal radii, on average, than those estimated for the larger cations. Given that the expression was obtained for molecules with first- and second-row M-cations, the better agreement for the smaller cations is expected. Also, given that the radius of an oxide anion in a structure with a preponderance of large cations is necessarily larger (by as much as 0.03–0.05 Å) than it is in one with a preponderance of small cations, the departure of the estimated radii for the larger cations from the 45° line in Figure 5 is expected as well (Shannon and Prewitt 1969)

**FORCE CONSTANTS, COMPRESSIBILITIES OF COORDINATED POLYHEDRA, AND POTENTIAL ENERGY MODELS**

**Force constants and bond length variations**

Quadratic bond “stretching” force constants, \( f_c(MX) \), have been calculated at the Hartree Fock 6-311++G** level for the MX bonds (\( X = N, O \) and \( S \)) comprising the coordinated polyhedra for a series of geometry optimized oxide, nitride and sulfide molecules, using a finite difference method (Hill et al. 1994; Hill 1995). When the \( f_c(MX) \)-values were plotted against the geometry optimized bond lengths, \( R(MX) \), the data were found to scatter along three separate power law trends that can also be related to the row numbers of the cations and anions that comprise the MX bonded interactions (Fig. 6). The trend defined by the triangles in the figure involves bonded interactions between only row-one atoms like C and O, that defined by the squares involves bonded interactions between row-one and row-two atoms like O and Si and that defined by the circles is for bonded interactions between only row-two atoms like Si and S. When force

![Figure 5](image-url)

**Figure 5.** A scatter diagram of Shannon’s crystal radii \( r(M) \) for main group and closed-shell transition metal M-cations, \( r(M) \), plotted against a set of radii estimated with the expression \( r(M) = 1.39p^{-0.22} - r(O) \) where \( r(O) = 1.22 \) Å is the crystal radius for the 3-coordinate oxide anion (Shannon 1976). The line superimposed on the data set is regression line \( (r^2 = 0.99) \) fit to the two data sets.
constants and bond lengths are compared, as in the case of bond length-bond strength variations, the row numbers of the cation and anion serve to systematize the trends. Not only do the data in Figure 6 indicate that the force constants increase exponentially with decreasing bond length, but it also indicates that they increase, for a given bond length, with increasing row numbers of the cations and anions.

**Force constants and polyhedral compressibilities**

In a study of compressibility data observed for cubic metals and binary compounds, Waser and Pauling (1950) observed, more than half a century ago, that the bond “stretching” force constant – compressibility relationships for the crystalline materials are not appreciably different from those observed for related molecules. With compression and expansion data measured for MO_x-coordinated polyhedra in crystals, Hazen and Prewitt (1977) have since established that the compressibility, \( \beta = 3.7((<R(MO)>)^3/z) \times 10^{-4} \) GPa\(^{-1} \), of the polyhedra in crystals depends on the average bond length, \(<R(MO)>\), of a coordinated polyhedron and the valence \( z \) of the M-cation. With the force constant-bond length data generated for the coordinated polyhedra of the molecules, Hill et al. (1994) found a connection between the polyhedral compressibilities and the quadratic force constants of the bonds that comprise the polyhedra. Using the geometry optimized bond lengths, the compressibilities of the polyhedra for the molecules were estimated with the Hazen and Prewitt expression (1977). The resulting compressibilities, when plotted against \( f_c(MX) \) (Fig. 7), follow a trend given by the Morse (1929) power law expression \( f_c(MX) = (2.18 \times 10^3)R^{-0.96} \), similar to that established earlier by Waser and Pauling (1950) for crystals. The fact that the “stretching” force constant data calculated for the molecules scatter fairly uniformly along the line suggests that the compressibilities of the coordinated polyhedra in crystals are not that different from those
in chemically and structurally related molecules. In other words, as observed by Waser and Pauling (1950), nearest neighbor molecular-like interactions account for much of the variation in the force field that govern the force constants of the bonded interactions in crystalline materials.

**Force fields and bond length and angle variations**

Further insight into the values and the variation of the bond lengths and angles and force constants observed for earth materials has been provided by potential energy curves and surfaces calculated for representative molecules (Geisinger and Gibbs 1981; Gibbs 1982; Geisinger et al. 1985; Gibbs and Boisen 1986; Hess et al. 1986, 1988; O'Keeffe and MacMillan 1986; Gibbs et al. 1987b; Tsuneyuki et al. 1988a,b; MacMillan and Hess 1990). For example, in the case of the silica polymorphs, the observed SiOSi angles display a relatively wide range of values between ~135° and 180° with an average value of ~145° while the observed SiO bond lengths, R(SiO), display a much smaller range of values between ~1.58 Å and ~1.63 Å with an average value of ~1.61 Å (Boisen et al. 1990). The wide range of angles and the small range in bond length suggest that the “bending” force constant of the SiOSi angle in these materials is very small relative to the “stretching” force constant of the SiO bond. To learn whether this difference is consistent with the force field of a relatively simple yet related molecule, the geometry of the H₆Si₂O₇ disilicic acid molecule was partially optimized and a potential energy surface was generated with a minimal basis set at the STO-3G level (Gibbs 1982). Despite the crude level of the calculations, the resulting surface was found to conform relatively well with the bond length-angle data observed for the silica polymorphs. However, for a given SiOSi angle, the observed bond lengths were found to be ~0.02 Å longer than that calculated for the molecule.
In a recent study of SiO and GeO bonded interactions, the geometry of $H_6Si_2O_7$ was re-optimized, assuming $C_{2v}$ point symmetry, and a potential energy surface was calculated (Fig. 8) at a more robust Becke3LYP/6-311G(2d,p) level (Gibbs et al. 1998a). The bond length and angle data observed for the silica polymorphs were plotted on the surface as a function of the bridging SiO bond length and SiOSi angle. The geometry optimized bridging bond length (1.611 Å) and SiOSi angle (145.2°) for the molecule were found to be in close agreement with the observed average values given above for the silica polymorphs. Also, the majority of the observed data fall within the 2 kJ/mol level line contour with the trend of the data conforming with the region outlined by the level line with the longer bond lengths tending to involve the narrow angles (Gibbs et al. 1977; Newton and Gibbs 1980; Boisen et al. 1990). In short, the overall topography of the potential energy surface is consistent with a framework structure with relatively rigid silicate tetrahedral oxyanions linked together by much “softer” SiOSi intertetrahedral angles. The topography of the surface is not only consistent with the relatively large compressibilities of the silica polymorphs like quartz and cristobalite (Levien et al. 1980; Downs and Palmer 1994) but also with the variety of structure types exhibited by silica, silicates, silicones and siloxanes in general (Chakoumakos et al. 1981; Gibbs 1982).

Given that the bulk of the polymorphic, zeolitic, mesoporous and amorphous forms of silica have similar enthalpies that lie within 15 kJ/mol of that of quartz, Navrotsky (1994a) has gone a step further and concluded that the rich polymorphism of silica can be ascribed in large part to the low energy costs expended in distorting the SiOSi angles to produce the large variety of amorphous and crystalline tetrahedral framework structure types exhibited by silica (see also Geisinger and Gibbs 1981; Gibbs 1982; Gibbs and Boisen 1998). It is noteworthy that the unscaled force constant calculated for the bridging SiO bonds of the $H_6Si_2O_7$ molecule ($\partial^2E/\partial R^2 = 615$ N/m, $R = R(SiO)$) is larger, as expected, than that observed for quartz (597 N/m) by Etchepare et al. (1974) and it is

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**Figure 8.** SiO bond lengths, $R(SiO)$, and SiOSi angles, $\angle SiOSi$, observed for silica polymorphs with 4-coordinated Si plotted on a potential energy surface for the bridging SiOSi dimer calculated for the $H_6Si_2O_7$ molecule with a Becke3LYP/6-311G(2d,p) basis set. The level line contour interval is 2 kJ/mol. The level lines are defined assuming that the total energy of the geometry optimized molecule is 0.0 kJ/mol.
roughly one order magnitude larger than that calculated for the $\phi = \text{OSiO}$ angle ($1/R^2 \partial^2 E/\partial \phi^2 = 50 \text{ N/m}$) and two orders of magnitude larger than that calculated for the $\theta = \text{SiOSi}$ angle ($1/R^2 \partial^2 E/\partial \theta^2 = 5 \text{ N/m}$) (see also Hill et al. 1994; Hess et al. 1986; O'Keeffe and MacMillan 1986; Hess et al. 1988; MacMillan and Hess 1990; Lazarev and Mirgorodsky 1991). The force constants given in this chapter were obtained from the Hessian matrix of second derivatives calculated at the optimized geometry of the $\text{H}_2\text{Si}_2\text{O}_7$ molecule. In particular, it is noteworthy that these force constants are consistent with the accompanying changes in the bond lengths and angles that occur when, for example, a silica polymorph like quartz is compressed. With increasing pressure, the oxide anions becomes roughly “closed-packed” with the “soft” SiOSi angle decreasing rather dramatically whereas the “stiffer” SiO bond lengths and the OSiO angles remain relatively unchanged (Levien et al. 1980). However, in other earth materials in which the SiO bond lengths correlate with the OSiO angles with the shorter bonds tending to involve the wide angles, the OSiO angles are more distorted and exhibit a larger range of values (Boisen and Gibbs 1987).

**Generation of new and viable structure types for silica**

Given the extent to which the observed bond lengths and angles of the silica polymorphs conform with the potential energy surface displayed in Figure 8, an *ad hoc* potential energy function was constructed for silica using a representative block of the Hessian force constant matrix calculated for the molecule. Employing a penalty function based on the optimized bond lengths and angles, a model of the O-O non-co-dimer nonbonded interactions and the force constants, a large number of structure types for silica were generated using simulated annealing and quasi-Newton optimization strategies (Boisen et al. 1994, 1999). The derivation was completed starting with either 2, 3, 4 or 6 formula units of SiO$_2$ randomly distributed in a unit cell of variable geometry and P1 symmetry. In the calculations, more than 40 low energy structures were derived, including quartz, cristobalite and mixed stacking sequences of tridymite and cristobalite. The tridymite structure type of silica was conspicuously absent in the derivation, casting some doubt on whether it is a stable phase for silica (cf. Flörke 1967). Despite the short-ranged nature of the potential, the translational and space groups symmetries of quartz and cristobalite were reproduced. In addition to generating model structures that match or are related to zeolite and other aluminosilicate framework structures, model structures were also generated that match a number of framework structures that had been cleverly deduced by Smith (1977) and O’Keeffe and Brese (1992). In addition to the known silica polymorphs, the structures of several of the viable structures have since been geometry optimized, using a first-principles pseudopotential method (Teter et al. 1995). The cohesive energies of the viable structures were found to be the same as those calculated for quartz and cristobalite, but they were found to be substantially lower than that calculated for stishovite.

With other *ad hoc* molecular potential energy functions including those based on SiO$_4$, Si$_2$O$_4$, H$_4$SiO$_4$, H$_2$Si$_2$O and H$_{12}$Si$_5$O$_{16}$, the structures and volume compressibilities for quartz, coesite and other known silica polymorphs together with viable high pressure polymorphs were generated with varying degrees of success (cf. Anderson 1980; Tsuneyuki et al. 1988a,b, 1990; Tse et al. 1992). In addition, their elastic, vibrational and piezoelectric properties together with the photon spectra, volume compressibility and elastic constants were likewise generated with varying degrees of success. The functions were also found to serve as a basis for generating and interpreting the X-ray absorption, photoemission and magic-angle and dynamic-angle spinning NMR spectra, phase transformations, defects and the Poisson ratio. (cf. DeJong and Brown 1980; Lasaga and Gibbs 1987, 1988, 1991; O’Keeffe and MacMillan 1986; Gibbs et al. 1988; Stixrude and
CALCULATED ELECTRON DENSITY DISTRIBUTIONS FOR EARTH MATERIALS AND RELATED MOLECULES

The electron density distribution of a molecule or a crystal in a stationary state adopts a configuration wherein the total energy of the resulting distribution is minimized. A grasp of the connection between such a distribution and the bonded interactions that bind the ions together is fundamental to our understanding of the properties of earth materials. In this section, the bond lengths and bond strengths for the bonded interactions in a number of earth materials and related molecules will be examined in terms of their electron density distributions with the goal of establishing a connection between these properties and $\rho(\mathbf{r})$ and improving our understanding of molecule and crystal chemistry.

A mapping of an electron density distribution in a plane passing through the nuclei of any pair of bonded atoms in an earth material usually displays two well-defined maxima connected by a relatively low lying ridge of electron density. The two maxima define the positions of the atoms and the top of the ridge tends to follow the bond path in the distribution along which $\rho(\mathbf{r})$, at each point on the path, is a local maximum, as observed above, in the plane perpendicular to the path at that point. Between the two maxima, $\rho(\mathbf{r})$ tends to decrease along the path until it reaches a minimum value at the bond critical point, $\mathbf{r}_c$. The distances between $\mathbf{r}_c$ and the nuclei of the two bonded atoms were defined by Bader (1990) to be the bonded radii of the two atoms as measured in the direction of $\mathbf{r}_c$. Generally, the greater the electronegativity of an M-cation comprising an MX bonded interaction, the shorter the bond and the smaller the bonded radii of both the cation and the anion (Bader 1990; Feth et al. 1993; Etschmann and Maslen, 2000). However, with decreasing bond length, the bonded radius of an anion decreases substantially more than that of a cation. In addition, the value of $\rho(\mathbf{r})$ evaluated at $\mathbf{r}_c$ has been taken as a measure of the strength of a bonded interaction, the greater the value of $\rho(\mathbf{r}_c)$, the greater the bond strength and the shorter the bond (Feynman 1939; Berlin 1951; Bader 1982; Cremer and Kraka 1984a; Knop et al. 1988; Gibbs et al. 1997a).

Bond critical point properties and electron density distributions

The bond critical point properties of an electron density distribution are evaluated at the bond critical point, $\mathbf{r}_c$, of a bonded interaction. Collectively, they consist of the curvatures and the Laplacian of the distribution, the value of $\rho(\mathbf{r}_c)$ and the bonded radii of the bonded atoms. The curvatures of $\rho(\mathbf{r}_c)$ determine the local concentration or local depletion of the electron density distribution in the vicinity of the bond critical point measured in three mutually perpendicular directions. As observed by Bader and Essén (1984), the curvatures in these directions are found by evaluating the eigenvalues and eigenvectors of the Hessian matrix of $\rho(\mathbf{r}_c)$, $H_{ij} = \frac{\partial^2 \rho(\mathbf{r}_c)}{\partial x_i \partial x_j}, (i,j = 1,3)$. The three
eigenvalues of the matrix are denoted $\lambda_i (i = 1,3)$, where the Laplacian of $\rho(r_c)$, $\nabla^2 \rho(r_c) = \lambda_1 + \lambda_2 + \lambda_3$. Both $|\lambda_1|$ and $|\lambda_2|$ define the curvatures of $\rho(r_c)$ measured in two mutually perpendicular directions perpendicular to the bond path and $\lambda_3$ measures the curvature at $r_c$ parallel to the bond path. Hence, the larger the values of $|\lambda_1|$ and $|\lambda_2|$, the sharper the local maximum of $\rho(r)$ at $r_c$ in the plane perpendicular to the bond path. Likewise, the larger the value of $\lambda_3$, the sharper the minimum of $\rho(r)$ along the bond path. According to Bader (1990), if the negative curvatures dominate in a region ($\nabla^2 \rho(r)$ is negative), it is called a region of local concentration of $\rho(r)$. Otherwise, it is called a region of local depletion. A point in a region of local concentration has a $\rho(r)$-value that is above the average of the $\rho(r)$-value at points in its immediate vicinity. On the other hand, a point in a region of local depletion has a $\rho(r)$-value that is below the average of the $\rho(r)$-value at points in its immediate vicinity. It is important to note that this information about the curvatures of $\rho(r)$ at $r_c$ is independent of the magnitude of the actual value $\rho(r_c)$. Indeed, for the majority of the MO bonds examined in this chapter, as bond length decreases, $\rho(r_c)$ increases while the region in the vicinity of $r_c$ becomes (or becomes more) locally depleted (that is, $\nabla^2 \rho(r_c)$ increases in value).

The value of $\rho(r_c)$ and the value and the sign of $\nabla^2 \rho(r_c)$, in particular, have been used to classify a bonded interaction. As proposed by Bader and Essén (1984), a bonded interaction qualifies as a shared-electron covalent interaction when the value of $\rho(r_c)$ is large (greater than $\sim 1.5 \text{ e/Å}^3$), $|\lambda_1 + \lambda_2| > \lambda_3$ making $\nabla^2 \rho(r_c)$ large in magnitude and negative in sign. On the other hand, when $\rho(r_c)$ is small (less than $\sim 0.5 \text{ e/Å}^3$, Kuntzinger et al. 1998), $\lambda_3 > |\lambda_1 + \lambda_2|$ and $\nabla^2 \rho(r_c)$ is positive, a bonded interaction is said to qualify as a closed-shell ionic interaction (Bader 1998). Bonds with intermediate $\rho(r_c)$- and $\nabla^2 \rho(r_c)$-values between these two extremes are said to be intermediate in character. A calculation of the bond critical point properties for a series of geometry optimized diatomic hydride MH molecules (optimized at the Becke3lyp 6-311G(2d,p) level) containing first and second row M cations revealed that as $\rho(r_c)$ increases in value and the MH bonds decrease in length, the sign of $\nabla^2 \rho(r_c)$ changes from positive, $\sim 5 \text{ e/Å}^3$, for the closed-shell ionic interactions to negative and becomes progressively larger in magnitude for shared-electron covalent interactions, $\sim 80 \text{ e/Å}^3$. Thus, for the hydride molecules, the Bader-Essén (1984) criteria serve to classify a spectrum of bond types ranging between close-shell ionic to intermediate to shared-electron covalent rather well.

**Bond critical point properties calculated for molecules**

In a study of the bonded interactions for a variety of MO bonds (M = Li, Be, ..., N; Na, Mg, ..., S), the electron density distributions and bond critical point properties were calculated for ~40 hydroxyacid and oxide molecules (Hill 1995; Hill et al. 1997). The geometries of the molecules were optimized at the RHF 6-311++G** level with GAUSSIAN92 software (Frisch et al. 1993). The software PROAIM/AIMPAIC (Bader 1990) was used to walk the bond paths, to find the bond critical points and to evaluate the bond critical point properties for each bond. The MO bonded interactions were examined in terms of bond lengths and the *in situ* electronegativities of the M cations (Allen 1989), $\chi_M = 1.31 \times F_M^{0.23}$, where $F_M = (z \times \rho(r_c))/r_b(O)$, $r_b(O)$ is the bonded radius of the oxide anion bonded to the M-cation, $z$ is the number of valence electrons on the M-cation and $\rho(r_c)$ is the value of the electron density at $r_c$ (Boyd and Edgecombe 1987; Hill et al. 1997). According to this expression, $\chi_M$ increases as the valence of the M-cation and the value of $\rho(r_c)$ both increase and as the bonded radius of the oxide anion decreases in value. The calculations revealed that $\rho(r_c)$ and the average curvature of $\rho(r_c)$, $\lambda_{1,2} = (|\lambda_1| + |\lambda_2|)/2$ measured perpendicular to the bond path, each tend to increase with increasing $\chi_M$ and decreasing R(MO) (Hill et al. 1997). With a few exceptions, $\nabla^2 \rho(r_c)$ was found to increase and become positive in value with increasing $\chi_M$. These trends suggest that the
shared-electron covalent interaction of a MO bond tends to increase with increasing \( V^2 \rho(r_e) \) contrary to the trend exhibited by the hydrides. Thus, in the case of the oxides, as the bonded interactions change from predominantly ionic to predominantly covalent, both \( \rho(r_e) \) and \( V^2 \rho(r_e) \) tend to increase in value accompanied by systematic decrease in bond length.

For this chapter, the electron density distributions and the bcp properties for a number of geometry optimized hydroxyacid molecules were calculated at the Becke3lyp/6-311G(2d,p) level, a hybrid method that includes a mixture of Hartree-Fock exchange with density functional theory and exchange-correlation. The calculations were completed with the hybrid method because the bcp properties calculated for Si\(_2\)O\(_{16}\) moieties of the coesite structure were found to be in better agreement with those calculated for silica polymorph than those generated at RHF 6-311++G** level (Gibbs et al. 1994; Rosso et al. 1999). When plotted against \( \rho(r_e) \), the geometry optimized bond lengths, R(MO), calculated for the hydroxyacid molecules were found to decrease with increasing values of \( \rho(r_e) \) along separate yet roughly parallel trends (Fig. 9), as observed by Hill et al. (1997). Likewise, bonds of a given length involving second row cations tend to have larger \( \rho(r_e) \) values than those involving first-row cations. Each bond tends to display a distinct trend with R(MO) decreasing regularly with increasing \( \rho(r_e) \) in parallel echelon fashion. For a given decrease in bond length, the bonds involving the more electronegative cations tend to display a larger increase in \( \rho(r_e) \)-value than those involving the more electropositive cations. As, \( \lambda_{1,2} \) increases with decreasing bond length, the maxima in the electron density distribution perpendicular to the bond path in the vicinity of \( r_e \) becomes progressively sharper. Also, as \( \rho(r_e) \) and \( \lambda_{1,2} \) both increase, \( \lambda_3 \) likewise increases and the minimum in the electron density distribution along the bond path becomes progressively sharper. For each MO bond, because \( \lambda_3 \) tends to be larger than \( |\lambda_1 + \lambda_2| \), \( V^2 \rho(r_e) \) tends to increase in a regular way with decreasing R(MO). With the

![Diagram](image.png)

**Figure 9.** Geometry optimized MO bond lengths, R(MO), calculated for hydroxyacid and related molecules containing coordination polyhedra vs. the calculated value of the electron density, \( \rho(r_e) \), evaluated at the bond critical point along each bond. The MO bond length data for first-row M-cations are plotted as open symbols while those for second-row cations are plotted as solid symbols.
exception of the NO bond, the values of both $\rho(r_c)$ and $\nabla^2 \rho(r_c)$ both increase and R(MO) decreases as $\chi_M$ increases in value. Also, the bonded radius of the oxide anion, decreases linearly for each bond with decreasing bond length and increasing $\rho(r_c)$. The observation that bonds involving second-row M-cations (for a given bond length) exhibit larger $\rho(r_c)$-values is consistent with the observation that bonds (for a given bond length) involving second-row ions tend to exhibit larger force constants.

**Bond critical point properties calculated for earth materials**

In exploring whether the trends in the bcp properties calculated for the molecules are similar to those calculated for chemically related earth materials, the electron density distributions and bcp properties were computed for the bonded interactions observed for more than 40 bulk silicates and oxide materials (Gibbs et al., unpublished data). The earth materials for which the calculations were completed included the silica polymorphs quartz, coesite, cristobalite and stishovite, the framework structures beryl, danburite, low albite, maximum microcline, the chain silicates tremolite, diopside, jadeite and spodumene, the orthosilicates forsterite, topaz and pyrope and the oxides include calcite, magnesite, natratine, corundum, vanthoffsite, anhydrite, berlinite, bromellite and crysoberyl (Gibbs et al., unpublished data). The wave functions and electron density distributions for these materials were generated with CRYSTAL98, using the space group symmetries, cell dimensions and coordinates of the atoms observed for each crystal. The bcp properties of the electron density distributions were generated with TOPOND (Gatti 1997). CRYSTAL98 is a periodic ab initio code that uses Gaussian basis sets to expand the wave function for crystalline systems (Dovesi et al. 1996). It is capable of treating systems at the Hartree-Fock or Kohn-Sham level. All of the crystalline calculations mentioned herein were performed using the local density approximation. The Gaussian basis sets used in molecular orbital calculations are too diffuse to serve as basis sets in crystal orbital calculations in that their use often results in an over-estimate of the orbital overlap and numerical instability. To avoid this problem, we used basis sets that were specially developed and optimized for CRYSTAL98. The strategies used to find the bcp properties are basically the same as those used to calculate the properties for the molecules (Gatti 1997).

The trends between the observed bond lengths and the $\rho(r_c)$-values calculated for the earth materials (Fig. 10) are similar to those calculated for the molecules (Fig. 9). The MO bond length data fall along separate and divergent trends for first- and second-row cations, as observed for the molecules, with the second-row bonds exhibiting larger $\rho(r_c)$-values for a given bond length than first-row bonds. With the exception of the R(PO) vs. $\rho(r_c)$ trend, the trends for both the molecules and earth materials are similar. Although the R(PO) vs. $\rho(r_c)$ trend for the molecules parallels that for the crystals, the $\rho(r_c)$-values for the former are $\sim 0.02$ e/Å$^3$ larger for a given PO bond length (Fig. 10). As observed for the molecules, the R(MO) vs. $\rho(r_c)$ trends also tend to be unaligned in parallel echelon form. Likewise, with decreasing R(MO), $\rho(r_c)$ and the curvatures $\rho(r_c)$, both perpendicular and parallel to the bond paths, each increase non-linearly (Figs. 11b and 11c). For a given bond length, the curvatures of $\rho(r_c)$ for bonds involving second-row M-cations tend to be larger than those for first-row cations. This is not surprising given that $\rho(r_c)$ and $\lambda_{1,2}$ are positively correlated. With the exceptions of the NO and CO bonded interactions, $\nabla^2 \rho(r_c)$ is positive in value which indicates, according to the Bader and Essén (1983) criteria, that the remaining bonded interactions are either intermediate or closed shell ionic interactions (Fig. 11d). As observed for the molecules, as R(MO) decreases in value, $\rho(r_c)$ and $\nabla^2 \rho(r_c)$ both increase non-linearly in roughly parallel echelon form. As observed for the molecules, the family of bonds associated with each pair of atoms has bcp properties that exhibit distinct trends. For a given bond length, bonds
involving first-row cations not only exhibit smaller $\rho(r_c)$-values compared with bonds involving second-row cations but also smaller $\lambda_{1,2}$, $\lambda_3$ and $\nabla^2\rho(r_c)$ values. As the value of $\rho(r_c)$ increases, R(MO) decreases while $\lambda_{1,2}$, $\lambda_3$ and $\nabla^2\rho(r_c)$ increase. Thus, with decreasing bond length and increasing covalent character, the value of $\rho(r_c)$ increases while the sharpness of the maximum perpendicular to the bond path and the minimum parallel to the bond path at $r_c$ both increase. With a few exceptions, similar results have been reported for nitride and sulfide molecules (Feth et al. 1998; Gibbs et al. 1999a).

Contrary to the negative correlation that exists between $\rho(r_c)$ and $\nabla^2\rho(r_c)$ for the diatomic hydrides, $\nabla^2\rho(r_c)$ is positively correlated with $\rho(r_c)$ for the earth materials. Hence, a determination of the bond character on the basis of the sign of $\nabla^2\rho(r_c)$ can lead to disparate results when applied in general. Considering the available information, it would appear that the character of a bonded interaction in oxides, nitrides and sulfides is directly related to the values of $\rho(r_c)$, $\lambda_{1,2}$, $\lambda_3$ and the bond length, the shorter the bond and the greater the values of $\rho(r_c)$, $\lambda_{1,2}$ and $\lambda_3$, the more covalent the bond. Indeed, in an assessment of the electron density distributions obtained for a number of molecules, Cremer and Kraka (1984) and later Coppens (1997; 1998) and Gibbs et al. (1999) have indicated that the Bader-Essén (1983) classification may require some revision particularly, as observed in this chapter, for bonded interactions for which $\lambda_3$ is large relative to $|\lambda_1 + \lambda_2|$ and $\nabla^2\rho(r_c)$ is necessarily positive in sign.

**Variable radius of the oxide anion**

In earth materials, the crystal radius of the oxide anion exhibits a relatively small range of values depending on the number of MO bonds that it forms, the greater the number of bonds, the larger its radius (Brown and Gibbs 1969; Shannon and Prewitt 1969). In contrast, the bonded radius of the anion exhibits a relatively large range of values depending on both the electronegativities of M-cations bonded to the anion and
Figure 11. The observed MO bond length used to prepare Figure 3 plotted against the bond critical point properties (a) the bond radius of the oxide anions, \( r_b(O) \), (b) \( \lambda_{1,2} \), the average curvatures of \( \rho(r_c) \) measured perpendicular to the bond paths, (c) \( \lambda_3 \), the curvature \( \rho(r_c) \) measured parallel to the bond paths and (d) \( \nabla^2 \rho(r_c) \), the Laplacian of \( \rho(r_c) \). The open symbols denote bonds involving first-row M-cations and the solid symbols denote bonds involving second-row M-cations.
the MO bond lengths. As observed above, the greater the electronegativity of the M-cation and the shorter the bond, the smaller the value of $r_b(O)$ (Feth et al. 1993). In this context, it is important to recall that the bonded radius of the anion is only defined in the direction of a bonded atom; it is undefined in all other directions. The value of $r_b(O)$ calculated for a MO bond in an earth material (Fig. 11a) is virtually the same as that calculated for a representative molecule or procrystal (Gibbs et al. 1992). For each case, $r_b(O)$ decreases linearly along separate trends with decreasing R(MO) and increasing electronegativity of the M-cation for each of the bonds. The $r_b(O)$-values calculated for the first- and second-row MO bonds form distinct parallel trends when plotted against R(MO). In addition, the $r_b(O)$-values calculated for first-row MO bonds are ~0.1 Å larger for a given bond length than those for the second-row bonds. However, for both rows, as the electronegativity of the M-cation increases and R(MO) decreases, $r_b(O)$ decreases regularly, as observed for the molecules, from the ionic radius of the oxide anion, ~1.4 Å, when bonded to a Na cation to the atomic radius, ~0.65 Å, of the oxygen atom when bonded to a N cation. As the $r_b(O)$-value for each bond increases with decreasing bond length, the value of $r_b(O)$ decreases as the M-cation distorts the electron density distribution of the oxide anion; the greater the electronegativity of the cation, the shorter the bond, the smaller the value of $r_b(O)$, the greater the penetration of the cation and the more distorted and polarized the oxide anion (Bader 1990). It is noteworthy that Shannon and Prewitt (1969) observed that if one assumes that the radius of the oxide anion is taken to be the distance between the nucleus of the anion and the bcp, then the radius of the anion would be expected to vary depending on the nature of the cation to which it is bonded and the character of the bonded interaction.

It is notable that the oxide anions in an earth material like danburite, CaB$_2$Si$_2$O$_8$, (Downs and Swope 1992; Gibbs et al. 1992) are each observed to exhibit several different bonded radii with a radius of 0.96 Å in the direction of Si, 0.98 Å in the direction of B and 1.22 Å in the direction of Ca. Actually, within this context, the term “radius” has little or no meaning in that the electron density distribution of the oxide anion is distorted rather dramatically from spherical symmetry (cf. Gibbs and Boisen 1986; Cahen 1988; Gibbs et al. 1992; 1997b). In such a case, the bonded radii of the anion serve as a measure of the distortion and polarization of its electron density distribution induced by the bonded interactions. For example, in the case of the nitride mineral, nitratine, NaN0$_3$, each of the oxide anions is bonded to two 6-coordinated Na cations at a distance of 2.40 Å and a 3-coordinated N cation at 1.24 Å. As such, the oxide anion is highly polarized in a plane with a bonded radius of 0.64 Å in the direction of the N cation and a radius of 1.32 Å in the directions of the two Na cations. In effect, the oxygen atom exhibits its atomic radius in the direction of N and its ionic radius in the direction of the Na cations. Actually, the physical importance of the pronounced polarization of the oxide anion relates to its capacity to act as a Lewis base when bonded to Si, for example. On the other hand, when the anions in a structure are bonded to one kind of cation coordinated by a given number of anions, the radii of the anion will display much less variation. For example, in the case of quartz where each oxide anion is bonded to two 4-coordinated Si cations, the bonded radius of the anion varies slightly between 0.94 and 0.95 Å.

Given that the bonded radius of the oxide anion typically varies substantially, ~0.3 Å, even for a single choice of M-cation (see Fig. 11a), the question naturally follows “Why can a set of radii like Shannon’s (1976) crystal radii reproduce average bond lengths within 0.04 Å for a given set of conditions, assuming that radii are strictly additive?” For example, in the case of AlO bond, $r_b(O)$ varies between ~0.95 and ~1.25 Å. Crystal radii were found to be successful because the average bond length is nearly constant in value for the given set of properties (see above). Thus, if a given rigid
radius is assumed for the oxide anion and the additive rule is applied, then a set of M-cation radii can be generated for a given set of properties, using the strategies of Shannon and Prewitt (1969). In short, when used with a given radius for the oxide anion, these spherical radii can be expected to reproduce near-constant average bond lengths, despite the length of the bond and the bonded radius of the anion. However, as observed by Cahen (1988), “the use of spherical radii, while more or less accurate quantum-mechanical theoretical or experimental electron density maps are available, is somewhat of an anachronism.”

**BOND STRENGTH, ELECTRON DENSITY, AND BOND TYPE CONNECTIONS**

The well-developed correlation between \( \langle R(MO) \rangle \) and \( p = \langle s \rangle / \langle r \rangle \) displayed in Figure 1b indicates that \( p \) is a measure of the average strength of the bonds for a given \( MO_v \)-coordinated polyhedron, regardless of the row number of the cation, the greater the value of \( p \), the shorter the average MO bond length (Gibbs et al. 1998b; 2000a). As the bond lengths for bulk crystals and representative molecules decrease in a regular way with the increasing value of \( \rho(r_c) \), \( \langle R(MO) \rangle \) was plotted in Figure 12 against \( \langle \rho(r_c) \rangle / r \) (where \( \langle \rho(r_c) \rangle \) is the average value of \( \rho(r_c) \) for the bonds of a given coordination polyhedron) for the values of \( \langle \rho(r_c) \rangle \) calculated for the molecules and bulk crystals used to construct Figures 9 and 10, respectively, and for the values observed for a variety of crystalline materials (bromellite, danburite, L-alanine, coesite, Li bis(tetramethylammonium hexanitrocobaltate (III), citrinin, natrolite, mesolite and scolecite (Gibbs et al. 1998b). A regression analysis of the combined data set yielded the expression \( R = 1.47(\langle \rho(r_c) \rangle / r)^{-0.18} \). As the scatter of the data along the trend is relatively small, it is apparent that a close connection exists between \( \langle R(MO) \rangle \), \( \langle s \rangle \) and \( \langle \rho(r_c) \rangle \) for crystalline materials and molecules and that the bonded interactions for a given

**Figure 12.** The grand mean MO bond lengths \( \langle R(MO) \rangle \) observed and calculated for crystals and calculated for molecules vs. the grand mean value of \( \rho(r_c) \), \( \langle \rho(r_c) \rangle \), averaged over all of the different coordination polyhedra.
coordinated polyhedron, whether in a molecule or a crystal, are virtually the same, as observed above, despite the large size difference between a crystal and a molecule. These results serve to demonstrate that the average strength of the bonds for a coordinated polyhedron is a direct measure of the average value of $\rho(r_c)$, the greater the value of $\langle \rho(r_c) \rangle$, the smaller the value of $\langle R(MO) \rangle$ and the larger the value of $\rho$. It is noteworthy that when the MH bond lengths, optimized at the Becke3LYP/6-311G(2d,p) level, for the hydride molecules studied by Bader and Essén (1984), are plotted against $\rho(r_c)/r$, a single trend likewise obtains. A regression analysis of the data set yielded the power law expression, $R = 1.20(\rho(r_c)/r)^{-0.19}$, with an exponent that is statistically identical with that obtained for the MO bonds. This result suggests that if a given cation in an oxide or a hydride molecule forms bonds with a given $\rho(r_c)/r$ value, and if the cation is replaced by another cation, then the relative change in the bond length (per unit interval) is indicated to be the same, regardless of whether the cation forms a bond in either type of molecule or crystal. As observed above, a similar connection was made between $p$ and bond length, a connection that likewise suggests the $p$ and $\rho(r_c)$ are related in a similar way.

The average values of $\rho(r_c)$ calculated for each of the MO bonds for all of the coordinated polyhedra used to prepare Figures 3 and 11 are plotted in Figure 13 against the spectroscopic electronegativities of the M-cations, $\chi_{\text{spec}}(M)$ (Allen 1989). With the exception of the CO bond, $\langle \rho(r_c) \rangle$ increases in a systematic way with increasing $\chi_{\text{spec}}(M)$. Etschmann and Maslen (2000) have reported a similar connection between electronegativity and electron density for a large set of diatomic molecules. From electronegativity considerations, it can be concluded, given Pauling's (1960) arguments, that the character of an MO bonded interaction is directly related to the value of the electronegativity of the M-cation, the greater the value of $\rho(r_c)$, the more covalent the bonded interaction. With the change in bond character from a closed shell ionic to a shared-electron covalent interaction, $R(MO)$ and $r_s(O)$ each decreases and $\lambda_{12}$, $\lambda_3$ and $\nabla^2 \rho(r_c)$ each increases in value as displayed in Figure 11. Hence, short MO bonds with

![Figure 13](image_url)

**Figure 13.** The grand mean value of $\rho(r_c)$, $\langle \rho(r_c) \rangle$, for the MO bonds in the crystals used to prepare Figure 3 irrespective of the coordination number of the M-cation vs. the spectroscopic electronegativity of the M-cation, $\chi_{\text{spec}}(M)$ comprising the MO bonds.
large $\rho(r_c)$, $\lambda_{1,2}$ and $\lambda_3$-values and small $r_d(O)$-values tend to be more covalent than long bonds with typically smaller $\rho(r_c)$, $\lambda_{1,2}$ and $\lambda_3$-values and larger $r_d(O)$-values.

As observed above, Brown and Shannon (1973) and Brown and Skowron (1990) have argued that the bond strength $s$ can also be used to characterize MO bonded interactions and bond type. According to their arguments, bond strength is a measure of bond type, the greater the value of $s$, the shorter the bond and the more covalent the bonded interaction. The correlations presented here between $<R(MO)>$ and $<\rho(r_c)>/r$, $<R(MO)>$ and $<s>/r$, $R(MO)$ and $s/r$ and $\rho(r_c)$ and $\chi_{\text{spec}}(M)$ provide a physical basis for their arguments. These correlations show that the value of $<R(MO)>$ for a given MO bond increases as $<s>$ and $\chi_{\text{spec}}(M)$ both increase and as $<R(MO)>$ decreases. Albeit simple, the strength of an individual bond, as argument by Brown and Shannon (1973), can be used as a measure of the nature of the bonded interactions that comprise a MO$_v$-coordinated polyhedron, the larger the value of $s$, the more covalent the bonded interaction.

**SITES OF POTENTIAL ELECTROPHILIC ATTACK IN EARTH MATERIALS**

**Bonded and nonbonded electron pairs**

It is well-known that the electron density distribution of an isolated atom consists of a single maximum from which the value of the electron density decays exponentially with distance. In contrast, the corresponding $-\nabla^2\rho(r)$-distribution consists of a series of concentric shells that define regions where the electron density is alternately locally concentrated and locally depleted, a distribution that reflects the shell structure of the atom. The outer most valence shell of the distribution can be divided into an inner region where $-\nabla^2\rho(r)$ is negative in sign and an outer one where it is positive (Bader et al. 1984). Further, the region of the shell where the distribution is positive has been called the valence-shell charge concentration, VSSC, of the atom (Bader et al. 1984). When two atoms combine and a bond is formed, the VSSC of the atoms is distorted to one degree or another, depending on the nature of the atoms and the bonded interaction, with a concomitant formation of maxima in the VSSC that define domains of local concentrations of electron density. In an important step in developing a theory of chemical reactivity based on electron density distributions, Bader et al. (1984), Bader and MacDougall (1985) and MacDougall (1984) discovered that the number, the location, and the relative sizes of the maxima provide a faithful representation of the bonded and nonbonded electron pairs of the Lewis (1916) and Gillespie (1963) models of electronic structure. With this connection, Bader and his colleagues went on to ascribed the maxima to domains of bonded and nonbonded of electron-pairs of the VSEPR model. In support of this connection, they observed that the number and locations of the domains for a variety molecules showed a close correspondence with the number and arrangement of the domains predicted by the model (Gillespie and Hargittai 1991). Equally important, they found that the domains correspond in a number of cases with sites of potential electrophilic attack.

In particular, their study of the H$_2$O molecule ($C_{2v}$ point symmetry) revealed that the VSSC of the oxide anion displays four maxima that correspond with the two lone pair, lp, and the two bond pair, bp, domains as predicted by VSEPR model (Gillespie and Hargittai 1991; Bader and MacDougall 1984). The two bp domains were found to be symmetrically disposed in the plane of the HOH angle (105.6°) on the same side of the anion as the two H atoms whereas the two lp domains were found to be disposed on the opposite side of the molecule in a perpendicular plane that bisects the HOH angle. Each
lp domain was found to be located 0.33 Å from the anion, making an lpOlp angle of 141.0° and each bp domain was found to be 0.37 Å from the anion, making a bpObp angle of 102.8°. The four equivalent lpObp angles were found to be each 102.0°. As predicted by the VSEPR model, the lpOlp angle was found to be appreciably wider than the bpOlp angle and the lp domain was found to be closer to oxide anion than the bp domain. Contrary to the model, however, the bpObp angle was found to be wider than the lpOlp angle. As noted, the bp domains were found to be located close to the OH bonds on the interior of the HOH angle with each bpO vector making an angle of 1.4° with a OH vector (Gibbs et al. 1998a).

To appreciate the extent and overall shape of the features ascribed to the lp and bp domains of local concentrations of electron density for the molecule, wave functions calculated at the Becke3lyp/6-311G(2d,p) level, were used to construct three-dimensional representations of the VSCC for the oxide anion. Figure 14 displays a medial cut through a set of envelopes of the distribution that bisects the HOH angle (the features displayed by this figure are easier to appreciate by studying the color version of the figure displayed on the back cover of this volume; see Beverly, 2000). The innermost spherical envelope centered on the anion defines the 0 e/Å²-isosurface where \( \rho(r) \) is neither locally concentrated nor locally depleted. To illustrate the geometric features of the VSCC in the vicinity of the domains ascribed to the lone pairs, a few isosurfaces have been drawn. The 44 e/Å²-isosurface was found to provide a good representation of these geometric features. The two crescent-shaped surfaces comprising this isosurface are drawn and labeled in the figure. This figure shows that \( \rho(r) \) becomes progressively more locally concentrated as one moves from the 0 e/Å²-isosurface toward the maxima occurring inside the crescent-shaped branches depicted for the 44 e/Å²-isosurfaces. These two regions of concentric isosurfaces not only highlight the maxima in the VCSS where the electron density is locally concentrated, but they also occur in the vicinity where these features are predicted to occur by the VSEPR model. A similar representation of the VSCC, cut along the HOH plane, likewise was found to display concentric crescent-shaped isosurfaces along each of the OH bonds, ascribed to bp domains. However, these domains were found to be somewhat smaller than those ascribed to the lp domains. As predicted by the VSEPR model, the lp domains are larger and more electron rich than the bp domains (Bader et al. 1984; Bader and MacDougall 1984).

Figure 14. A three-dimensional representation of the VSCC isosurfaces for the oxide anion of the water molecule. The central white sphere represents the oxide anion. The H atoms are not shown but are in the directions of the two line segments radiating from the oxide anion. The lines connecting the spheres represent the OH bonds. The spherical envelope centered at the position of the oxide anion represents the 0 e/Å² isosurface. The two crescent shaped 44 e/Å² isosurfaces represent local concentrations of electron density centered on the lone pair electrons of the molecule as predicted by the VSEPR model. (See back cover for color figure.)
In general, the more electron rich the lp domains, the more susceptible they are to electrophilic attack, the greater they repel one another, the greater their separation, the wider the lpOlp-angle and the closer they are to the nucleus of the atom (Gillespie and Hargittai 1991). As observed by Hendrickson et al. (1970), lp electrons act as sites of electrophilic attack that seek positively charged and electron deficient sites like, for example, the H atoms of adjacent water molecules (cf. Chakoumakos and Gibbs 1986).

**Bonded and nonbonded electron lone pairs for a silicate molecule**

In a search for the sites of the local concentrations in the electron density distribution for the H_6Si_2O_7 molecule, VSCC-isosurfaces were constructed for the bridging and nonbridging oxide anions of the molecule using wave functions generated at a Becke3LYP/6-311G(2d,p) level. The VSCC for the bridging oxide anion, O_{br}, was found to display a long, crescent-shaped 25 e/Å^3-isosurface ascribed to a single lp domain located 0.35 Å from O_{br}, rather than two lp domains as found for the H_2O molecule. A 3D representation of the VSCC-isosurfaces for the anion, cut in a perpendicular plane that bisects SiOSi angle of the molecule, is displayed in Figure 15. The isosurfaces selected for this figure range in value from 0 to 25 e/Å^3, the latter centered on a set of concentric crescent-shaped isosurfaces ascribed to an lp. Unlike the oxide anion in the water molecule, which has features ascribed to two lps, the VSCC for the bridging oxide anion of the H_6Si_2O_7 molecule exhibits a single, highly elongated crescent-shaped domain that is wrapped approximately one half the way about the anion (see color version of Fig. 15 on back cover of this volume and Beverly 2000).

Like the oxide anion of the H_2O molecule, however, bp domains were found to reside along each of the SiO and OH bonds of the H_6Si_2O_7 molecule. In contrast, the nonbridging oxide anions, O_{nbr}, in addition to being bonded to an Si and an H cation, were each found to exhibit two concentric crescent-shaped lp domains and two bp domains of electron density along the SiO and OH bond vectors. The two lp domains and the H and Si atoms were found to be disposed in a nearly tetrahedral array about O_{nbr} with the lp domains located 0.35 Å from O_{nbr}. The angles formed at O_{nbr} between the two lp domains, the H and Si were found to agree within ~5°, on average, with the ideal tetrahedral angle (<lpO_{nbr}lp = 113°, <lpO_{nbr}Si = 108° (2x), <lpO_{nbr}H = 105° (2x), <SiO_{nbr}H = 117°).

Figure 16 displays a 3D representation of the VSCC for the nonbridging oxide anion (see back cover of this volume for color version and Beverly 2000). The VSCC map
shows concentric crescent-shaped isosurfaces displayed along each SiO and OH bond. An examination of the 25 e/Å²-isosurface reveals that it is not only crescent-shaped, but that is split into a crescent dumb-bell shaped feature that extends part way around the anion. As such, it indicates that the electron density is locally concentrated in two lp domains connected by an intervening region where the electron density is locally concentrated but to a much lesser degree. Thus, the oxide anion, when bonded to an H and Si atom, exhibits two lone pair domains rather than an elongate one as found when it is bonded to two Si atoms.

The VSCC for the oxide anion in quartz has also been mapped and evaluated (Gibbs et al., unpublished data). It was found to exhibit three maxima ascribed to one lp and two bp domains as observed for the bridging anion of the H₂Si₂O₇ molecule. The lp domain was located 0.36 Å from the anion, compared with 0.35 Å obtained for H₂Si₂O₇, with the lp making a lpO₄BrSi angle of 109.2°, compared with 108° obtained for the H₂Si₂O₇ molecule. Despite the great size difference between the crystal and molecule, the location of the lp domain and the site of potential electrophilic attack on the bridging oxide anion for the molecule were found to be very similar to that found for quartz. The similarity of the distribution of the lp and bp domains in quartz and the molecule provide a basis for understanding why transition state calculations on small molecules can provide considerable insight into adsorption and hydrolysis reactions involved in the interaction of water with silica (cf. Lasaga and Gibbs 1990).

**Localization of the electron density for the silica polymorphs**

The electron localization function (ELF) is another tool that has been used with considerable success in highlighting domains in ρ(r) of strong electron localization (Becke and Edgecombe 1990). These domains, like those defined by the maxima in VSCC, have likewise been associated with the bonding and nonbonding electron-pairs of the VSEPR model (Becke and Edgecombe 1990; Bader et al. 1996; Bader et al. 1996; Savin et al. 1997). The ELF has also been found to reveal the shell structure of an atom in a clear and faithful fashion.

ELF values for the valence electron distributions for quartz, coesite and stishovite have been calculated at an isosurface ELF level of 0.844 (Gibbs et al. in prep). For each of these silica polymorphs, localized domains of electron density were found along each...
of the SiO bond vectors about one third the way from the oxide anion. With the exception of the straight SiOSi dimer in coesite, a single sausage-shaped localization was found on each of the oxide anions in quartz and coesite, similar to the crescent-shaped features found for the H₆Si₂O₇ molecule. A similar sausage-shaped feature has been reported for the bridging oxide anion of the COC dimer of methyl acetate molecule (Savin et al. 1997). In a classification of chemical bonds in terms of ELF distributions, Silvi and Savin (1994) have asserted that a covalent shared-electron bonded interaction generally results localized domains of electron density between the bonded atoms as found for quartz, coesite and stishovite. In the case of closed-shell ionic bonded interaction like that of the NaF bond, the bond attractor domains were found to be absent between the two ions.

For illustration purposes, a three-dimensional representation of the ELF isosurface calculated for the silicate tetrahedron in quartz is displayed in Figure 17. Localized bp domains are displayed along each of the SiO bond vectors about one-third the way along the vector from the oxide anion. As observed above, a larger sausage-shaped lp domain is situated on the apex side of the SiOSi angle. The shape and location of the feature not only corresponds fairly well with the $-\nabla^2 \rho(r)$-features displayed for the H₆Si₂O₇ molecule, but they also serve as evidence that a close correspondence exists between the SiO bonded interactions of H₆Si₂O₇, quartz and coesite. It is apparent from this evidence that when, for example, the H atom of a water molecule attacks the lp domain of an anion of either quartz or coesite, it may be expected to approach the anion in a variety of pathways rather than along a single well-defined pathway (cf. Lasaga and Gibbs 1990). Further, a lp domain, because of its larger size relative to a bp domain, is expected to be more susceptible to electrophilic attack than a bp domain. In contrast, the absence of a lone pair feature on the O(5) oxide anion involved in the straight angle in coesite indicates that the anion may be less susceptible to electrophilic attack than the other oxide anions in the structure.

In stishovite, each oxide anion is bonded to three Si cations and lies in the plane defined by the cations. The anion was found to be coordinated by five well-defined domains of electron localization (Gibbs et al., unpublished data). Of these, three were found to be displaced slightly off the SiO bond vectors toward the exterior of the shared edges as observed in deformation maps (Spackman et al. 1987) The remaining two were

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Figure 17. Three-dimensional representation of the electron localization function evaluated for the valence electrons at an ELF level of 0.844 for a silicate SiO₄ anion in quartz. The valence electron density distribution was obtained for a geometry optimized model of the quartz structure (Gibbs et al. 1999b). The silicate anion is viewed along a line closely parallel to one of the two rotation axes. The black sphere at the center of the figure represents Si and the four gray spheres linked to central sphere by rods represent the oxide anions (The sizes of the spheres have no significance). The localization domains of electron density ascribed to lone- and bond-electron pair features are displayed in shades of gray. Note that each oxide anion is coordinated by two-bond pair features and a sausage-shaped lone-pair. The bonds to the four adjacent silicate tetrahedra in quartz are not shown but their bond pairs point in the direction of the Si cations of these tetrahedra.
found to be calotte-shaped domains located directly above and below the oxide anion. These features are in one-to-one correspondence with the peaks reported in experimental and theoretical deformation maps generated for stishovite (Spackman et al. 1987; Cohen 1994). Observed and calculated deformation maps for coesite have also been found to show peaks along each of the SiO vectors but peaks were found to be absent in the lone pair region except for O(5) oxide anion where a well-defined peak was found (Geisinger et al. 1987; Downs 1995). On the basis of these results, it would appear that deformation maps do a better job in delineating bp domains than lp domains for materials with silicate tetrahedra.

**Nonbonded lone pair electrons for low albite**

The critical point properties of the $-V^2\rho(r)$-maps for the bridging oxide anions of the alkali-feldspar low albite have also been determined (Gibbs et al. in prep). Unlike quartz, low albite contains oxide anions bonded either to two Si cations or to a Si and an Al cation or, in some cases, also to one or two Na cations. Of the four oxide anions bonded to two Si cations, three (O$_{Bm}$, O$_{Cm}$ and O$_{Dm}$) are bonded only to Si cations and exhibit only one lp domain at $\sim$0.35 Å, as found for both the H$_8$Si$_2$O$_7$ molecule and quartz, whereas the fourth (O$_{A2}$) is bonded to two Si cations and a Na cation and exhibits two lp domains at a distance of 0.36 Å. In this case, it appears that the NaO$_{A2}$ bonded interaction has split the crescent-shaped lp domain into two separate well-defined domains; the two are 0.50 Å apart with the lpO$_{A2}$lp angle (89°) roughly bisected by the NaO$_{A2}$ bond. Of the four remaining oxide anions bonded to Si and Al, O$_{B0}$ and O$_{C0}$ exhibit two lp domains, O$_{D0}$ exhibits one and O$_{Al}$ exhibits none. Of these anions, O$_{Al}$ is bonded to two Na cations at 2.54 Å and 2.66 Å, O$_{B0}$ and O$_{D0}$ are each bonded to one Na cation at 2.459 Å and 2.438 Å, respectively, and O$_{C0}$ forms no NaO bonds. The latter anion exhibits two lp domains at 0.355 Å and 0.371 Å. The oxide anion O$_{Al}$, which is bonded to Si, Al and two Na cations, exhibits no lp domains while O$_{B0}$ which bonded to Si, Al and Na exhibit two lone pair domains bisected by a NaO bond. O$_{D0}$ is also bonded to Si, Al and Na, but it only exhibits one lp domain such that O$_{D0}$lp vector is roughly perpendicular to the NaAlSi plane. The relatively wide lpO$_{C0}$lp angle, 117.4°, between the lp domain on O$_{C0}$ is taken as evidence that the domains are larger and better developed than those on remaining anions. When considered with the observation that O$_{C0}$ is the most highly underbonded anion in low albite, it is indicated not only to be the most electron rich oxide anion in the structure but also the site most susceptible to electrophilic attack. On the other hand, O$_{Al}$, which is bonded to Al and Si and two Na cations and lacks lp domains, is probably the site least susceptible to attack.

In a careful study of the structure of low albite, Downs et al. (1994) have argued that the O$_{C0}$ oxide anion plays a central role in governing the behavior of H atom in promoting the interdiffusion of Al and Si in the structure at high pressures (Goldsmith 1986). Unlike the other oxide anions in the structure, O$_{C0}$ is underbonded, $\zeta < 2.0$, with a $\zeta$-value of 1.75 and two well-developed lone pair domains, making it an ideal site for potential attack by H. Therefore, if present, H would very likely be attracted and bonded to the anion as suggested by Downs et al. (1994) because of the excess electron density on the anion and its two lone pair domains. With the formation of an OH bond, this would result in an overbonded anion ($\zeta > 2.0$) with a $\zeta$-value of 2.75 accompanied by an appreciable lengthening and weakening of the SiO and AlO bonds. The end-result would be a structure that would be susceptible to rupture and cation diffusion. The analysis of the properties of the VSQC for the anions of low albite given above provides support for the Downs et al. (1994) picture by demonstrating that O$_{C0}$ is not only the most electron-rich anion in the structure but also the site most susceptible to electrophilic attack.
The SiO bond lengths and the SiOSi angles observed for a quartz crystal (1.61 Å; 144°) are practically the same as those observed for the tiny gas phase molecule, disilylether, H₂SiOSiH₃ (1.63 Å; 142°). Correspondingly, the bond lengths and angles observed for the silica polymorphs including quartz comply in close agreement with the topography of a potential energy surface calculated for the SiOSi group of the disilicic acid (HO)₂SiOSi(OH)₃ molecule. Also, the positions of the maxima displayed by the VSCE of the bridging oxide anions in both quartz and the molecule are virtually identical. Collectively, these results provide a basis for the claim that a quartz crystal can be pictured as a giant molecule bound together by the same forces that bind together the Si and O atoms of a tiny molecule (Gibbs 1982). In effect, it is apparent that the forces that govern the bond lengths and angles in the silica polymorphs behave as if short-ranged and molecular-like. By the same token, the experimental and computational evidence presented in this chapter indicates that a similar picture can be crafted for a number of oxide, sulfide, nitride and fluoride crystals and molecules. Despite their different compositions, the bond lengths in these materials were found to be connected to bond strength by a set of similar short-ranged power law expressions. As the exponents of the expressions were found to be statistically identical, it follows that if a cation forms a bonded interaction with strength \( p \) and if the cation is replaced by another cation, then the relative change (per unit interval) in bond length is indicated to be the same, regardless of whether the cation resides in a coordinated polyhedron in a molecule or a crystal or whether the coordinated polyhedron consists of oxide, nitride, fluoride or sulfide anions (Gibbs and Boisen 1998). Accordingly, inasmuch as the exponent \( p \) of the power law expressions is a measure of the power of the bonded interactions in both molecules and crystals, the bond lengths in these materials can also be pictured, like the silica polymorphs, as governed in large part by molecular-like, short-ranged bonded interactions (cf. Bragg 1930; Burdett and Hawthorne 1993).

Equally important, the bond critical point properties of the electron density distributions for a large number of earth materials and related molecules have also been shown to be similar, on average, in spite of their great differences in size. Where experimental data are available, the value of the electron density at the bond critical points and the bond radii of the oxide anions have similar values for the two materials and vary in a similar way with bond length. Bond strength was found to correlate with \( \rho(\mathbf{r}_c) \) for bonds in both molecules and earth materials, the greater the value of \( \rho(\mathbf{r}_c) \), the greater the indicated strength and the power of a bonded interaction. These results indicate that a fundamental connection exists between the bonded interactions in earth and molecular materials to the extent that the local properties such as bond length and the bond critical properties of the electron density can be pictured as governed in large part by nearest neighbor interactions. They also provide a basis for understanding the success that has emerged in the generation of volume compressibility curves, the properties and the structures of known and new structure types for silica, using molecular based \textit{ad hoc} potential energy functions.

In his classic study on the nature of bonded interactions, Pauling (1939) proposed that the difference in the electronegativities, \( \Delta \chi = \chi_M - \chi_X \), for a pair of bonded atoms M and X can be used as a measure of the bond character for the pair, the smaller the value of \( \Delta \chi \), the greater the shared-electron covalent character of the bonded interaction. In addition to providing a measure of bond type, electronegativity has played a pivotal role over the years in systematizing the properties of a vast range of materials. In a derivation of a set of spectroscopic based electronegativities, Allen (1989; 1994) has since identified electronegativity as the third dimension of the periodic table because of its connection...
with the average one-electron energy of the valence-shell electrons in a ground state free atom. The well-developed correlation observed in this chapter between \( \langle \rho(r_0) \rangle \) and \( \chi_{\text{spec}} \) for the bonded interactions in crystals is consistent with the assertion that \( \Delta \chi \) is a measure of bond character, the larger the value of \( \chi \), the greater the shared-electron covalent character of a bonded interaction. With increasing \( \rho(r_0) \), the values of \( \lambda_1, \lambda_2 \) and \( \nabla^2 \rho(r_0) \) each increase. Accordingly, as the value of electron density increases in the vicinity of the bond critical point, the curvatures of \( \rho(r) \) at the maxima perpendicular to the bond path and at the minimum along the bond path each sharpens with increasing covalent character. Concomitant with these changes, the bond length and the bonded radius of the oxide atom decrease progressively with the latter decreasing from the ionic radius of the oxide anion, when bonded to a highly electropositive cation like Na\(^+\), to the atomic radius of the oxygen atom, when bonded to a highly electronegative atom like N. With these changes, bond strength increases progressively in support of the picture that it is also a rough measure of bond type, the greater the value of \( \rho(r_0) \), the shorter the bond and the more powerful and the more covalent the bonded interaction.

As \( \nabla^2 \rho(r_0) \) increases in value and changes sign from negative to positive for the oxide molecules and earth materials, \( \rho(r_0) \) increases in value. However, in the case of the diatomic hydrides, the opposite is true; as \( \nabla^2 \rho(r_0) \) increases in value and changes sign from negative to positive, \( \rho(r_0) \) decreases in value. Also, the curvature of the electron density perpendicular to the bond path actually flattens rather than sharpens as \( \rho(r_0) \) increases in value. The decrease and change in sign of \( \nabla^2 \rho(r_0) \) from positive to negative for the hydride molecules with increasing \( \rho(r_0) \) does not appear to hold in general for oxides, nitrides and sulfides. Thus, as suggested by several other workers, the classification scheme forged by Bader and Essén (1983) appears to be more restrictive in its application and needs some revision particularly for those systems where \( \nabla^2 \rho(r_0) \) and \( \rho(r_0) \) both increase in value as the bond lengths decrease.

Given the wide variety of bonded interactions in nature, the SiO bond is one of the most common and important interactions in the Earth binding together the bulk of the materials of the crust. Despite its great abundance and the large number of papers that have been written about the bond and silicates, the nature of the bonded interaction still remains a subject of debate (Gibbs et al. 1994, 1999b). From electronegativity considerations, Pauling (1960) proposed that the interaction is intermediate in character, a proposal that is consistent with the observed and calculated \( \rho(r_0) \)-values reported in this chapter and the connection that obtains between \( \langle \rho(r_0) \rangle \) and \( \chi_{\text{spec}} \). However, Garvie et al. (2000) recently concluded from an examination of the projected local densities of the orbital valence states for the Si and O atoms for quartz that the SiO bond is markedly ionic. Cohen (1994) and Gillespie and Johnson (1997) reached similar conclusions, asserting that the bond consists of a pair of nearly fully charged Si\(^{4+}\) and O\(^{2-}\) ions. On the other hand, on the basis of the domains of electron localization along the SiO bonds for quartz, coesite and stishovite, the Silvi and Savin (1994) criteria would classify the bond as a covalent shared-electron interaction. However, inasmuch as the domains are located about one-third rather half-way along the bonds toward the Si cations, the location of the domains suggests that the bond is more intermediate in character than a covalent shared-electron interaction (Savin et al. 1997). Likewise, Gibbs et al. (1999b) concluded from a model study of the structure and the electron density distribution of quartz, that the relatively high compressibilities of quartz and cristobalite and the electron density distributions observed for several other minerals that the bond is more intermediate in character. In a study of the electronic structure of quartz, Binggeli et al. (1991) likewise concluded that the bond is more intermediate in character “characterized as a mix of covalent and strong ionic bonding.”
Given that the energy of a system is a unique functional of its electron density distribution, Tossell and Vaughan (1992) have argued that bond type can, in principle, be defined in terms of the total electron density distribution. Thus, on the basis of the observed and calculated $\rho(r_c)$-values reported in this chapter, the evidence indicates that the SiO bond ($\rho(r_c) \sim 1.0$ e/Å$^3$) is more covalent than KO, NaO, LiO, CaO, MgO, BeO, AlO bonds that involve more electropositive cations and have appreciably smaller $\rho(r_c)$-values (0.1–0.5 e/Å$^3$). On the other hand, it is indicated to be more ionic in character than PO, SO, CO, NO bonds that involve more electronegative cations and have larger $\rho(r_c)$-values (1.2–3.2 e/Å$^3$). In short, these results indicate that the SiO bond is intermediate character between these two sets of bonded interactions rather than being markedly ionic as indicated by the “considerable charge transfer” from Si to O suggested by the band-structure calculations completed for quartz (Garvie et al. 2000).

By locating the domains of local concentrations of electron density in the valence shells of the atoms for earth materials and structurally and chemically related molecules, sites of potential electrophilic attack have been identified. The positions of the maxima in the VSCC ascribed to lp domains for the bridging oxide anions in both quartz and H$_2$Si$_2$O$_7$ are strikingly similar and consist of a crescent-shaped lp domain next to the bridging oxide anion. The oxide anions bonded to two Si atoms in low albite show features similar to those calculated for quartz and the H$_2$Si$_2$O$_7$ molecule. An analysis of the distribution, the location and the number of the lp domains for the oxide anions comprising SiOAl angles in the feldspar provides support for the Downs et al. (1994) interpretation of Al/Si diffusion in the mineral at high pressures. Albeit redundant, the close connection between the positions of the domains of the local concentration of electron density for earth materials and molecule is further evidence that the bonded interactions in earth materials behave in large part as molecular-like.

Finally, given the close connection in structure and electron density distributions, crystal chemists would do well, as ably done by Alex Navrotsky (1994b), to restore to the lore of crystal chemistry a chapter on the close connection that exists between the properties of crystals and molecules. With few exceptions, the coverage devoted to such materials was dropped early last century from crystal chemistry texts (cf. Stillwell 1938) when the Born-Landé (1918) lattice energy model was found to be a successful aid in the interpretation and understanding of physical properties, the generation of the energetics of a variety of crystalline materials (cf. Sherman 1932) and the derivation of a set of ionic radii (Pauling 1927). However, the great solid state physicist John C. Slater (1939) was a notable exception. He included in his elegant book on chemical physics a chapter on the similarities of the structures and properties of molecules and crystals and the perspective that a crystal like diamond can be viewed as a giant molecule bound together by the same forces that bind the carbon atoms together in a tiny cyclohexane molecule. More recently, Noll (1968) observed in his book on the chemistry and technology of silicones that a close connection exists between the properties of silicone molecules and silicates. He not only observed that the bond length and angles in silicates and silicones are virtually the same, but also that the structure of a silicone molecule can be classified with the same rules used by Bragg (1930) to classify a silicate crystal. Clearly, both of these workers understood the close connection that can exist between the properties of certain chemically and structurally related crystalline and molecular materials.

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