

An orbital approach to the theory of bond valence

JEREMY K. BURDETT

Department of Chemistry and James Franck Institute, The University of Chicago, Chicago, Illinois 60637, U.S.A.

FRANK C. HAWTHORNE*

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, U.S.A.

ABSTRACT

Molecular orbital ideas, by means of a perturbation expansion of the orbital interaction energy, are used to probe the origin of the bond-valence sum rule that is used extensively in crystal chemistry. It is shown that regular octahedral and tetrahedral coordination geometries have an electronic stabilization arising through interactions between cation (A) orbitals and the $2p$ orbitals on O. The lowest energy structure occurs when the coordination environment is such that all three p orbitals are involved in equal interactions with their environment. Similar perturbation ideas are used to derive an expression analytically for the A-O bond length in terms of the H_{ij} elements of the Hamiltonian matrix and the energy separations between the orbitals involved. A simple extension of this result shows how the equilibrium bond length is dependent on the coordination number of the atom concerned. Using these results with the bond-valence concept leads to the interesting result that the sum of the bond valences at an atomic center is a constant and thus provides the first analytical derivation of the bond-valence sum rule. The rule that the bond valences at an atomic center will be as equal as possible (Brown, 1981) is a natural consequence of this result, and one that is directly comparable with the conclusions concerning the electronic factors stabilizing regular octahedral and tetrahedral geometries. The relationship of the results to Curie's rule (1894) is discussed.

INTRODUCTION

Over the past 50 yr or so, Pauling's second rule (Pauling, 1929, 1960) has been used extensively to interpret and aid in the solution of complex mineral and inorganic crystal structures: In a stable ionic structure, the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations. As noted by Burdett and McLarnan (1984), Pauling's rules were initially presented as ad hoc generalizations, rationalized by qualitative arguments based on an electrostatic model. This has led to an association of these rules with the ionic model, and there has been considerable criticism of the second rule as an unrealistic model for bonding in most solids. Despite the apparent defects of the approach, it was too useful to be discarded and, in various modifications, continues to be used to the present day.

Bragg (1930) considered Pauling's second rule to be of great importance and produced an interesting argument to justify it. He considered the (nearest neighbor) forces that bind together atoms in a coordination polyhedron, modeling the interactions by lines of force. Bragg noted that atoms that are closer together have more lines of force between them, atoms that are farther apart have

fewer lines of force, and next nearest neighbor atoms can only interact through their nearest neighbors. Thus the charge of the bond strength was associated with the bond between the two atoms, and the amount of charge was inversely related to the bond length. This sounds much more like a covalent description than an ionic description, with allowances for the unconventional vocabulary used in the argument. Nonetheless, the perception of this rule as a part of the ionic model continued as the general view.

The great improvements in crystallographic technique that took place in the 1960s have produced a large amount of accurate and precise information on interatomic distances in crystalline solids. These data have led to various modifications of Pauling's second rule (see summary by Allmann, 1975), in which bond strengths are inversely related to bond length; such bond strengths are hereafter called bond valences (Brown, 1978) to distinguish them from Pauling's bond strengths. Of particular interest is the scheme first produced by Brown and Shannon (1973) and subsequently extensively developed by Brown (1981). A single equation of the form

$$s = \left(\frac{r}{r_0} \right)^{-N} \quad (1)$$

where s is the bond valence, r_0 and N are fitted parameters, and r is the observed bond length, is sufficient to

* Permanent address: Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada.

describe relations between bond valence and bond length for an isoelectronic series of ions. Brown and Shannon (1973) emphasized the difference between the ionic model and the bond-valence formalism. In the latter, a structure consists of a series of atom cores held together by valence electrons that may be associated with chemical bonds. The valence electrons may occupy a symmetric (covalent) or asymmetric (ionic) position in the bond, but a priori knowledge of this character is not a requirement for the application of the above equation. Indeed, the correlation between bond valence and the covalent character of a bond shown by Brown and Shannon (1973) indicates that the asymmetry of charge in the chemical bond may be qualitatively derived from this model.

In the last 15 yr, Gibbs and his coworkers (see summary in Gibbs, 1982) have approached the structure of minerals from a molecular orbital viewpoint and have made significant progress in both rationalizing and predicting geometrical and spectroscopic properties of minerals. Early in this work (Gibbs et al., 1972), it was shown that bond-overlap populations derived from Mulliken population analysis were strongly correlated with p_0 , a measure of the deviation of an anion from exact agreement with Pauling's second rule (Baur, 1970, 1971). This parallel aspect of the molecular-orbital and bond-valence approaches was stressed by Brown and Shannon (1973), who represented bond valence as the measure of the covalence of a bond. Approaching this question from the other direction, Gibbs and Finger (1985) presented bond-length bond-valence curves derived from molecular orbital theory that are very similar to those given by Brown and Shannon (1973) for the isoelectronic series Li, Be, B and Na, Mg, Al, Si, P, S.

This progressive convergence of the bond-valence and molecular-orbital models of chemical bonding is very striking. If the two methods are more or less equivalent, then one can use whichever one is of most use to the problem at hand, without being overly concerned about inconsistency of approach. To date, the parallels between the schemes have been demonstrated by numerical correlations. Here we attempt to establish an algebraic connection between the two models.

PRELIMINARY CONSIDERATIONS

The geometry of a molecule or solid may be expressed as a function of a distortion coordinate, q , which takes the system from a reference geometry ($q = 0$) to a distorted version of this geometry ($q \neq 0$). The energy of the system may be written as a simple expansion

$$E = E^0 + \left(\frac{\partial E}{\partial q}\right)_0 q + \frac{1}{2} \left(\frac{\partial^2 E}{\partial q^2}\right)_0 q^2 + \dots \quad (2)$$

Within the harmonic oscillator model, the second derivative of the energy is equal to the vibrational force constant. In principle, we can evaluate these terms from the electronic wave functions of the ground (i) and excited (j) electronic states of the system at the reference geometry. It may be readily shown that, for the ground state i , we

may write the energy E as

$$E_i = \langle i | \mathcal{H}^0 | i \rangle + \langle i | \left(\frac{\partial \mathcal{H}}{\partial q} \right)_0 | i \rangle q + \frac{1}{2} q^2 \left[\langle i | \left(\frac{\partial^2 \mathcal{H}}{\partial q^2} \right)_0 | i \rangle - 2 \sum_{i \neq j} \frac{|\langle i | \left(\frac{\partial \mathcal{H}}{\partial q} \right)_0 | j \rangle|^2}{E_i^{(0)} - E_j^{(0)}} \right] + \dots \quad (3)$$

Let us see how we can simplify this expression for the typical minerals with which we are concerned. The first term is simply an energy zero; for our purposes, it may be discarded. The second term is only nonzero for degenerate electronic states, i , and describes the energetics of the first-order Jahn-Teller distortion; for the systems we treat, it is zero. The term in brackets describes the vibrational force constant associated with motion along q and consists of two components: the classical force constant $\langle i | \partial^2 \mathcal{H} / \partial q^2 | i \rangle$ controls the energetics of the movement of the nuclei within the electronic charge distribution of the reference geometry; the second summation term allows this charge distribution to relax. If there is a low-lying electronic state (j) of the correct symmetry, such that the denominator of the relaxation force constant is small, then this term may be large enough to overwhelm the classical contribution and lead to a negative force constant. This implies an instability, and the configuration will distort along the coordinate q . An example might be that of an NH_3 molecule artificially held in a planar geometry. There is a low-lying state of the correct symmetry to ensure a large relaxation contribution to the out-of-plane bending force constant, and so the molecule becomes pyramidal. However, in most oxide and oxysalt minerals, there is a large energy gap between the filled oxide levels and the empty cation levels, so that such distortions of the second-order Jahn-Teller type (as they are labeled) are usually not important. Some exceptions to this generalization are the perovskites and minerals with ReO_3 arrangements (e.g., wickmanite $[\text{MnSn}(\text{OH})_6]$ is a derivative structure) in which O-M-O bond alternation probably arises through this mechanism (Wheeler et al., 1986).

In the absence of first- and second-order Jahn-Teller effects, we may concentrate on the behavior of the classical part of the force constant, the geometrical dependence of the energy E . In this paper, we use molecular orbital ideas to provide links between apparently different ways of looking at these particular solids. Specifically, we show how the workings of the bond-valence rule may be derived analytically from an orbital picture.

MOLECULAR-ORBITAL STABILIZATION ENERGY

Within the framework of the simplest type of molecular orbital theory, the one-electron model, the details of the interaction between two orbitals located on two cen-

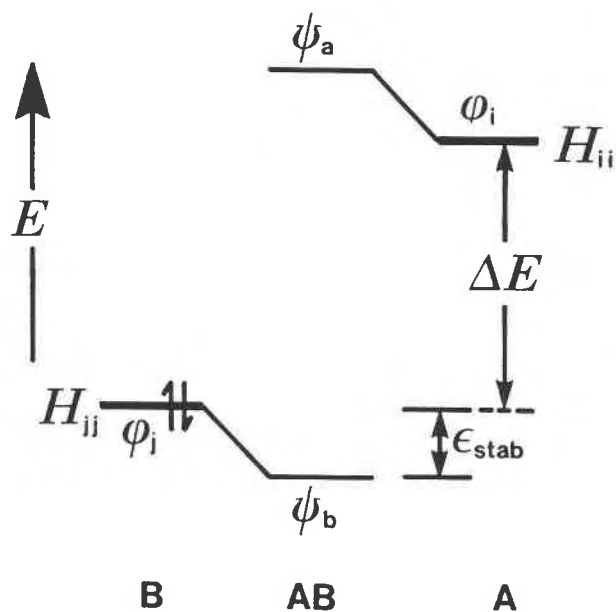


Fig. 1. Interaction of two atomic orbitals ϕ_i and ϕ_j on A and B to give two molecular orbitals ψ_a and ψ_b ; the stabilization energy of the lower (filled) orbital is ϵ_{stab} .

ters are handled by a secular determinant (e.g., Burdett, 1980). This is a useful way of extracting the eigenvalues (molecular orbital energies) and eigenvectors (description in terms of a simple approach using a linear combination of orbitals) of the molecular Hamiltonian. It should be stated that Madelung terms (i.e., on-site terms) are explicitly ignored in one-electron orbital models, such as are used here, and in tight-binding theory. We emphasize that the idea is to focus on the orbital part of the electronic problem.

The simple two-orbital problem shown in Figure 1 is characterized by two atomic orbitals, ϕ_i and ϕ_j , located on different centers. We have shown ϕ_j with lower energy than ϕ_i , and lying on the atoms of higher electronegativity than ϕ_i . Below we identify ϕ_j with an orbital of an O atom and ϕ_i with an orbital of a cation. The energy of an electron in orbital j is given the label \mathcal{H}_{jj} ; numerically, it may be identified with the ionization potential from that orbital. The secular determinant for the problem is simply

$$\begin{vmatrix} \mathcal{H}_{jj}-E & \mathcal{H}_{ij} \\ \mathcal{H}_{ij} & \mathcal{H}_{ii}-E \end{vmatrix} = 0 \quad (4)$$

where \mathcal{H}_{ij} represents the interaction between the orbitals i and j . Mulliken suggested that it was proportional to the overlap integral, S_{ij} , between the orbitals i and j , and we shall use his relationship here. Slightly more sophisticated treatments of the problem include overlap in the off-diagonal elements of this determinant. The results generated by such schemes are of the same form as we derive here, but for clarity we use the simplest model in our treatment.

In general, the secular determinant is constructed by

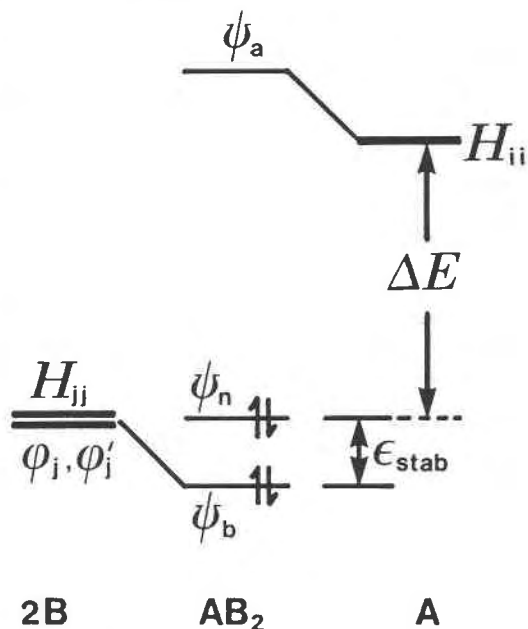


Fig. 2. Interaction of three atomic orbitals for the AB_2 case to give three molecular orbitals; ψ_b , ψ_a , and ψ_n are bonding, antibonding, and nonbonding orbitals, respectively.

placing along the diagonal entries of the form $\mathcal{H}_{kk}-E$ for each orbital k of the problem and an interaction integral \mathcal{H}_{kl} in each off-diagonal position to represent the interaction of each orbital pair k and l . The most basic model suffices for our treatment here and includes nonzero \mathcal{H}_{kl} elements only between orbitals located on adjacent atoms; thus interactions between nonbonded atoms are explicitly excluded.

For a simple two-orbital AB problem (Fig. 1), the new molecular orbital energies are given by the two values of E obtained through expansion of the determinant of Equation 4. Of course, this is an approximation, but one well established in theories based on one electron. The lower value of E represents a bonding orbital (labeled Ψ_b), and the higher value of E represents an antibonding orbital (labeled Ψ_a). We are interested in the stabilization energy of the system with two electrons in Ψ_b , namely $2\epsilon_{\text{stab}}$. In general, the cation-centered orbitals will be empty and the anion-centered orbitals will be full. Expansion of Equation 4 and identification of the lower energy root of E simply lead to an expression for ϵ_{stab} of the form

$$\epsilon_{\text{stab}} = \frac{\mathcal{H}_{ij}^2}{\Delta E} + \frac{\mathcal{H}_{ij}^4}{(\Delta E)^3} + \dots \quad (5)$$

This expansion clearly fails in the case where $\Delta E = 0$, but we are generally concerned with oxide and oxysalt minerals, in which there is a large nonzero gap between the interacting orbitals on anion and cation. Equation 5 forms the basis for our estimation of the overlap forces that provide the attractive force holding atoms together in molecules and solids.

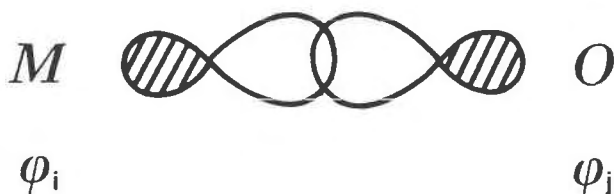


Fig. 3. The bond of Fig. 1, in which we have specifically identified A and B with a cation M and an O atom, respectively.

The orbital picture that describes a metal atom coordinated by two oxide ions (AB_2) is shown schematically in Figure 2. In this case, the secular determinant is simply

$$\begin{vmatrix} \mathcal{H}_{ii}-E & \mathcal{H}_{ij} & \mathcal{H}_{ij} \\ \mathcal{H}_{ij} & \mathcal{H}_{jj}-E & 0 \\ \mathcal{H}_{ij} & 0 & \mathcal{H}_{jj}-E \end{vmatrix} = 0. \quad (6)$$

One of the roots occurs at $E = \mathcal{H}_{jj}$, and so one orbital (a linear combination of ϕ_j and ϕ_j') remains unchanged in energy; this nonbonding orbital we label Ψ_n . The lowest energy root is readily extracted and gives the following expression for ϵ_{stab} :

$$\epsilon_{\text{stab}} = \frac{2\mathcal{H}_{ij}^2}{\Delta E} - \frac{4\mathcal{H}_{ij}^4}{(\Delta E)^3} + \dots \quad (7)$$

Notice that although the term in \mathcal{H}_{ij}^2 is linear with coordination number in Equations 5 and 7, the quartic term is not. Thus the molecular orbital stabilization energy per linkage in the twofold-coordinated case (obtained by multiplying the stabilization energy of Eq. 7 by 2, the number of electrons in the filled orbital) is different (smaller) than that of Equation 5. As a general result, the reader may find that for an α -coordinated metal atom, the total interaction energy summed over all occupied anion orbitals is

$$\sum \epsilon_{\text{stab}} = \frac{\sum \mathcal{H}_{ij}^2}{\Delta E} - \frac{(\sum \mathcal{H}_{ij}^2)^2}{(\Delta E)^3} + \dots \quad (8)$$

which, if all the interactions are equal, gives a stabilization energy per linkage (Δ) of

$$\Delta = \frac{2\mathcal{H}_{ij}^2}{\Delta E} - \frac{2\alpha\mathcal{H}_{ij}^4}{(\Delta E)^3} + \dots \quad (9)$$

For the more complex system in which the metal atom is coordinated either by different atoms or by atoms with different bond lengths, suitably different \mathcal{H}_{ij} and ΔE parameters are needed for Equation 9.

What do the bonds look like in the two cases depicted in Figures 1 and 2? It is easy to see that, in Figure 1, it is no more than a conventional two-center, two-electron bond formed from the overlap of ϕ_i and ϕ_j , as shown in Figure 3, in which we have used two sp^3 hybrid orbitals for illustration. The bonding picture for Figure 2 requires an intermediate step, as our picture shows one bonding orbital and one nonbonding orbital. The usual trick here is to localize the delocalized orbitals that molecular orbital theory gives us by taking linear combinations of the

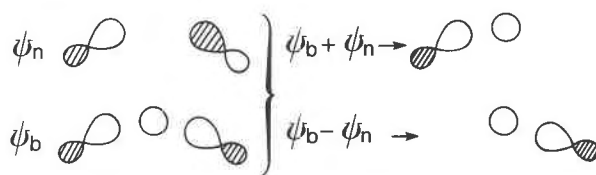


Fig. 4. Localization of the occupied molecular orbitals of Fig. 2 (ψ_b, ψ_n) to give two localized bonds.

occupied orbitals, as shown in Figure 4. The actual forms of Ψ_b and Ψ_n are obtained in the standard manner from the secular determinant. As can be seen, the result is to generate two bonds between the atoms A and B .

These basic results may be amplified and applied to the more realistic situation of a solid containing anions (e.g., O) and cations (e.g., Si, Al). Each oxide ion has four valence orbitals (three 2p and one 2s orbitals), and so the stabilization energies of equations 5, 7, and 8 need to be expanded by summing over all pairs of interactions between the orbitals on the anion and cation. We shall continue to describe solids in terms of these local coordination environments. To be more exact, we ought to use the ideas of band theory that take into account the translational periodicity of the solid (see for example Burdett, 1984). However, we will always be able to extract a set of localized bonds from such a picture in an exactly analogous route to that shown for the AB_2 system above (this is done, for example, in Burdett, 1992). Thus the molecular orbital ideas described here for small units have their exact analogies in the tight-binding theory for solids.

Let us assume initially that each ion is fourfold coordinated. Following the technique of Figure 4, the result will be a set of four bonding interactions of the type shown in Figure 3, which link anions and cations together. Of course, this is no different from the traditional way of describing the bonding in typical tetrahedrally coordinated solids. However, whereas such a picture is usually only used for covalent materials, we extend these ideas into the realm of materials often considered as ionic (of course, the work of G. V. Gibbs explicitly pursues the same idea).

For sixfold-coordinated ions, the bonding picture of four directed hybrid orbitals is clearly not appropriate. In the valence-bond scheme, one needs to involve d orbitals to produce six directed hybrids. In molecular orbital terms, this is not necessary; the sixfold coordinated system is handled in exactly the same way as the fourfold-coordinated one, except that as there are now only four filled bonding orbitals at each O atom and six ligands, the bond order is $4/6$, i.e., $2/3$ per bond. Obviously, what we cannot do is localize our four pairs of bonding electrons as in Figure 4, but the mathematical description by means of Equation 7 is still applicable. In summary, the delocalized description of the orbital problem is always applicable, irrespective of coordination number or geometry; the localized description in terms of two-center, two-electron bonds is only a valid description for fourfold coordination or less (in the latter, unused pairs of elec-

trons occur as lone pairs). Similar ideas are applicable to molecules (e.g., Albright et al., 1985).

As the O 2s orbital lies deep in energy, the expressions for the stabilization energy suggest that it will probably be less important in influencing the total bond strength than interactions with the p orbitals. Indeed, in the Rundle-Pimentel model for viewing aspects of molecular structure (Burdett, 1980), it is ignored altogether except as a storage location for a pair of electrons. As an approximation, we will write for a system of stoichiometry AB

$$\Delta[\alpha] = \frac{2\mathcal{H}_{AB}^2}{\Delta E_{AB}} + \frac{4\alpha\mathcal{H}_{AB}^4}{(\Delta E_{AB})^3} + \dots \quad (10)$$

where \mathcal{H}_{AB} (negative) represents an average interaction integral and ΔE_{AB} (positive) represents an average electronegativity difference.

In this section, we have considered the situation of cation coordination by anions and have evaluated the sum of the interactions between a single cation and α^+ anions, where α^+ is the cation coordination number. The results are just as easily derived if we look at the anion coordination environment, with coordination number α^- . For simplicity, taken an AB_n solid with Z formula units per cell and no close $A-A$ or $B-B$ contacts. Then, by analogy with Figures 1 and 2 and Equation 10, the energy per cell, E_{tot} , is given by

$$E_{\text{tot}} \propto Z_n \left[-\frac{\mathcal{H}_{AB}^2}{\Delta E_{AB}} + \frac{\alpha^- \mathcal{H}_{AB}^4}{(\Delta E_{AB})^3} + \dots \right]. \quad (11)$$

Because α^\pm and n are related by the network connectivity as $n\alpha^- = \alpha^+$, we can very simply rewrite Equation 11 in terms of the cation coordination

$$E_{\text{tot}} \propto Z_n \left[-\frac{\mathcal{H}_{AB}^2}{\Delta E_{AB}} + \frac{\alpha^+ \mathcal{H}_{AB}^4}{n(\Delta E_{AB})^3} + \dots \right]. \quad (12)$$

It is interesting to note that although mineralogists have traditionally focused on the details of cation coordination polyhedra, it is the environment at the anion, where the valence electron density is largely located, that is important in an orbital scheme. The two viewpoints are intimately related, as we have just shown.

ANGULAR GEOMETRY

The orbital stabilization energy derived above provides a useful way to explore the angular preferences for the anion and cation coordination geometries. It is true that the octahedral geometry for sixfold coordination and the tetrahedral geometry for fourfold coordination minimize steric repulsions between the ligands (irrespective of their anionic or cationic nature), but is there an electronic driving force associated with anion-cation interaction that reinforces this? The answer is yes. Let us consider a collection of four cations surrounding an anion. For the reasons described above, we ignore the anion valence s orbital (except that we will store two electrons in it), and we concentrate on the angular dependence of the interaction

energy associated with the overlap of the group of cation orbitals with the anion p orbitals. We use Equation 8 to describe the total interaction energy.

As noted above, the Mulliken relationship emphasizes the dependence of \mathcal{H} on the overlap integral. Figure 5 shows that the angular dependence of S is described by a simple geometric function; as an example, we show the interaction of a hybrid orbital with a p orbital. In general (Burdett, 1980), for two orbitals separated by a distance r ,

$$S_{ij}(r, \theta, \phi) = S_{ij}(r)f(\theta, \phi) \quad (13)$$

where the $f(\theta, \phi)$ are tabulated elsewhere, and θ, ϕ are the polar coordinates that define the location of the two overlapping orbitals. One extremely useful property of the $f(\theta, \phi)$ is that $\Sigma f^2(\theta, \phi)$ over all the pairs of interactions between the ligands and the collection of three p orbitals is simply equal to the coordination number (i.e., the number of ligands). Thus in Equation 8, the first term is independent of angular geometry. The minimum-energy angular geometry is then determined by the minimization of the second term in Equation 8. This is an easy problem; the Schwarz inequality tells us that if three numbers add to a constant, then the minimum in the sum of their squares occurs when the three numbers are equal. In the present case, this implies that each of the three p orbitals experience equal interactions with the ligands. For a fourfold-coordinated atom, this occurs at the ideal tetrahedral geometry, and for a sixfold-coordinated atom, this occurs at the ideal octahedral geometry.

The bond lengths in molecules are determined by the stabilization energy Δ of Equation 9 (*vide infra*), and, in qualitative terms, the bond-length change with angular geometry is simply approached by consideration of the change in Δ . As we show elsewhere (Burdett, 1979) for distortion from regular octahedral geometry, the variation in internuclear separation is well described by considering the variation in the weight of the first term (\mathcal{H}_{ij}^2) in Equation 9, apportioned to a given linkage by the angular dependence of the overlap integrals (Eq. 13).

To conclude this section, we stress that the tetrahedral geometries adopted by most fourfold- and sixfold-coordinated anions and cations are consistent with (1) minimum electrostatic interactions between the cations and anions, respectively; (2) minimum steric repulsions between the ligands; (3) (of importance in our viewpoint here) maximum orbital stabilization between the central atom and the ligand orbitals. Thus the predictions of both covalent and ionic models are coincident for these coordination geometries, a result which is not often recognized.

DETERMINATION OF INTERNUCLEAR SEPARATION (BOND LENGTH)

In general, a one-electron model of this type does not allow for an accurate determination of the equilibrium internuclear separation. However, changes in interatomic distances as structures are distorted, and even the large changes involved in bond breaking have been shown to

be well described within such a model, keeping the second moment of the energy density of states constant (Petifor and Podlucky, 1984; Hoistad and Lee, 1991; Lee, 1991; Burdett and Lee, 1985). This may be rephrased for the present system by requiring that

$$\sum_j \mathcal{H}_{ij}$$

for all of the interactions linking an atom i to its neighbors, j , is kept constant from one system to another. For the geometrical situation described earlier, where one O atom has α neighbors,

$$\sum_j \mathcal{H}_{ij} = \alpha \mathcal{H}_{AB} = k \text{ (constant)}. \quad (14)$$

In general, the overlap integral and thus \mathcal{H}_{AB} varies with distance in the region of chemical interest as Ar^{-m} . Thus

$$\alpha A^2 r_c^{-2m} = k \quad (15)$$

or

$$r_c^{-2m} = \frac{1}{\alpha} \cdot \frac{k}{A^2}. \quad (16)$$

Now Harrison (1983) has shown that the overlap dependence on distance for two main-group elements is roughly described by $m \approx 2$, and between a main-group and a transition element by $m \approx 1/2$. For interactions between a main-group element and O (Al, Si, P, etc.), $2m$ should be equal to 4, and for interactions between a transition metal and O, $2m$ will be somewhere between 4 and 7, depending on the relative importance of O orbital interactions with the metal d and s,p orbitals. Note that a prediction of the model is that the equilibrium bond length increases with coordination number. This is in general true, but this quantitative prediction can be tested; if a typical $^{14}\text{Si-O}$ distance is 1.63 Å, then a typical $^{60}\text{Si-O}$ distance should be 1.80 Å, which indeed it is.

THE CONCEPT OF BOND VALENCE

Following the recent work of Brown (1981), we show how this idea may be phrased within an orbital framework, based upon the ideas of the previous sections.

If the ratio k/A^2 , the product of two constants of the system from Equation 16, is set equal to ν (whose meaning will become clear below), then we may write

$$\left(\frac{r_c}{r_0}\right)^{-2m} = \frac{1}{\alpha} \cdot \nu. \quad (17)$$

Summing over all linkages leads to

$$\sum \left(\frac{r_c}{r_0}\right)^{-2m} = \nu. \quad (18)$$

The bond valence s is defined as

$$s = \left(\frac{r_c}{r_0}\right)^{-N} \quad (19)$$

where r_0 and N are dependent upon the identity of the

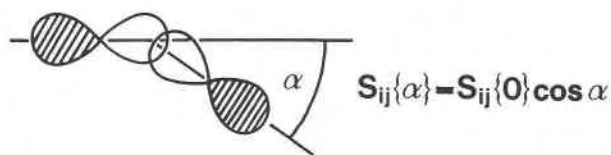


Fig. 5. Angular dependence of the overlap integrals on geometry; here we show the specific case of the overlap between a p_z orbital and an sp hybrid orbital.

atoms of the bond. If ν is the valence of the atom concerned, the sum rule is just

$$\sum S = \nu. \quad (20)$$

The orbital and phenomenological descriptions of the picture are thus identical, if the exponent N of Equation 19 is identified with $2m$ of Equations 15–18.

We remarked above on predictions made for the magnitude of the exponent $2m$ based on the form of the distance dependence of the overlap integral. The values of N in Equation 19 are found experimentally (Brown, 1981) to be between 5 and 7 for bonds between transition metal and O and around 4 for bonds between O and Al, Si, or P, as expected from Equations 18 and 19. [Of course, the exponential form of the bond-valence expression (Brown and Altermatt, 1985) is simply approachable by writing an overlap integral (and hence \mathcal{H}_{AB}) with a similar dependence on distance.] This then is the first orbital explanation for the bond-valence sum rules, which are traditionally phrased in ionic terms.

Brown and Shannon (1973) also gave an alternative expression for bond valence:

$$s = s_0 \left(\frac{r}{r_0}\right)^{-n'} \quad (21)$$

where s_0 is the Pauling bond strength, and r_0 and n' are refined parameters derived from a large number of structures. This is a useful expression, as it allows us to develop some simple intuitive arguments concerning the relationship of the bond-valence formalism to simple ideas of bond length and charge delocalization. In Equation 21, r_0 is formally a refined parameter but is obviously equal to the grand mean bond length for the particular bond pair and cation coordination number under consideration. Thus $(r/r_0) \approx 1$, and s_0 is actually a scaling factor that ensures that the sum of the bond valences around an atom is approximately equal to the magnitude of its valence. Let us suppose that there is a delocalization of charge into the bonds, together with a reduction in the charge of each atom. For an $A-B$ bond, let the residual charges change by zp_A and zp_B , respectively. The Pauling bond strength (\equiv scaling parameter s_0 in Eq. 21) is given by zp_A/a^x , in which a^x is the coordination number of atom A . Inserting these values into Equation 21 and summing over the bonds around B gives

$$\sum_B = p_A \sum s_0 \left(\frac{r}{r_0}\right)^{-n'} = p_B |z_B|. \quad (22)$$

If $p_A \approx p_B$, these terms cancel and the bond-valence equation works, provided the relative delocalization from each formally ionized atom is not radically different. Thus the equation should apply from very ionic to very covalent situations.

Note that Equation 21 works no matter what values of r_0 and r are used, provided that the value of r/r_0 is correct. However, it is only when we use Brown and Shannon's (1973) values of r_0 , derived from a large number of well-refined structures, that the equation is scaled correctly (i.e., to the actual bond lengths observed in solids).

Brown (1977) has shown the analogies between sums of bond valences around circuits in structures and Kirchoff's laws for electrical circuits. A result of such a study is the conclusion that the bond valences around any given center should be as equal as possible. We saw above a result concerning the angular geometry at an anion or cation that was derived from an equality associated with the interactions of the ligands with the central atom p orbitals by the term in \mathcal{H}_{AB}^4 . We can show that the observation of Brown (1977) drops out of our model in a straightforward way by a study of the unsymmetrical AB_2 system.

A little algebra shows that the electronic part of the energy for this system in the symmetrical arrangement is given by

$$\frac{\mathcal{H}_{12}^2 + \mathcal{H}_{13}^2}{\Delta E} - \frac{1}{2} \left[\frac{(\mathcal{H}_{12}^2 + \mathcal{H}_{13}^2)^2}{(\Delta E)^3} + \frac{4\mathcal{H}_{12}^2\mathcal{H}_{13}^2}{(\Delta E)^3} \right] \quad (23)$$

where (in the B_2 - A - B_3 unit) \mathcal{H}_{12} and \mathcal{H}_{13} (equal if $r_1 = r_2$) are the interaction integrals for the two linkages. In terms of Equation 14, which demands that $\mathcal{H}_{12}^2 + \mathcal{H}_{13}^2$ is a constant, the energy on asymmetrization is controlled by the third term in Equation 23. Given the constraint on this sum, the minimum value of the energy will occur when $\mathcal{H}_{12} = \mathcal{H}_{13}$ (i.e., when the two A - B distances are equal). Algebraically and electronically, this result has come about for the same reason described above for the electronic stability of the tetrahedral and octahedral geometries. Brown's rule drops out of this approach, as the energy is minimized when the two distances are equal and hence have equal bond valences.

This fourth-order term is thus an extremely important one, controlling aspects of both the angular geometry around an anion or cation and the relative variation of interatomic distances around that ion. Note that these results are obtained by considering nearest-neighbor interactions only; we shall see how this conclusion needs to be modified a little when more distant interactions are included.

In most systems, the distances around a central atom are not equal; they are constrained to be different by the coordination environment. Equation 24 shows that the dependence of r_{1e} on the value of r_2 is given by

$$r_{1e}^{-m} + r_2^{-m} = \text{constant}. \quad (24)$$

Many plots of r_1 vs. r_2 for a variety of systems (Burgi, 1975) show a hyperbolic relationship between the two;

the curvature of such plots is controlled in our model by the value of $N = 2m$.

BOND-OVERLAP POPULATION

A useful parameter from a molecular orbital calculation, which measures the bond strength or bond order, is the bond-overlap population. Consider the example shown in Figure 1. If the bonding orbital is written as $\Psi = a\phi_j + b\phi_i$, where a and b are the orbital coefficients, then the contributions to the AB bond overlap population is $2N_e ab S_{ij}$, where $N_e (= 2)$ is the number of electrons in the orbital. Expressions like this may be summed over all occupied orbitals to give a total bond-overlap population. If we write an approximation for Ψ_b as

$$\Psi_b \cong \phi_j + \lambda\phi_i \quad (25)$$

then a little bit of algebra gives

$$\lambda = \frac{1}{2} \left[\left(\frac{\mathcal{H}_{ij}}{\Delta E} \right) - \left(\frac{\mathcal{H}_{ij}}{\Delta E} \right)^3 \right] \quad (26)$$

from which the overlap population P_{AB} is

$$P_{AB} \cong 2S_{ij} \left[\left(\frac{\mathcal{H}_{ij}}{\Delta E} \right) - \left(\frac{\mathcal{H}_{ij}}{\Delta E} \right)^3 \right]. \quad (27)$$

Knowing that S_{ij} and \mathcal{H}_{ij} have the same functional dependence on geometry and taking the lead term in Equation 27, we may write

$$P_{AB} \propto r^{-2m} \quad (28)$$

an equation with a very similar appearance to Equation 15. Summing over the nearest-neighbor bonds just leads to a constant with Equations 16–18. Thus the sum of the bond-overlap populations is independent of coordination number. However, it is important to stress that the interatomic separations are different (larger) in the unit with the higher coordination number. There is another expression for the definition of bond valence (Brown and Altermatt, 1985), which has an additional advantage:

$$s = \exp\left(\frac{r - r_0}{B}\right). \quad (29)$$

B may be regarded as a constant (0.37), and there is just one parameter for each atom pair. Comparing the lead terms in a series expansion for the two definitions of s leads to the following relationship between the parameters:

$$N \approx \frac{r_0}{B} \quad (30)$$

or, a little more accurately,

$$N + [N(N + 1)]^{1/2} \approx \frac{2r_0}{B}. \quad (31)$$

Use of Equation 29 in our mathematical discussion above is not as straightforward, but the connection between the two forms is quite easy to see. The overlap-population sum depends only on the difference in energy between the interacting orbitals of adjacent atoms. This is what one

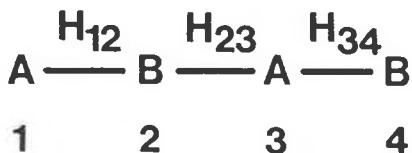


Fig. 6. Orbital parameters of a four-atom *A-B-A-B* chain.

would intuitively expect if bond-valence and bond-overlap population are analogous parameters.

Although we have shown that an orbital model is quite consistent with the operation of the bond-valence rules, one feature we have not discussed is the identification of Σ_s with an actual valency or atomic charge. In many situations, v is just an adjustable constant (as shown in the derivation of Eq. 17), but sometimes it may really be identified with an atomic charge, as in the discussion of McCarley et al. (1985) on the stoichiometry of $Ca_{3.45}Mo_{18}O_{32}$.

THE INDUCTIVE EFFECT

The transmission of electronic effects along a chain of atoms, whether in a molecule or a solid, is not a feature that readily drops out of an ionic model. However, using our orbital approach, we may readily examine the effect on a linkage induced by a change in the nature of an atom two bonds away. Again, the result will be achieved by considering the algebra that describes the energy levels of a suitable orbital picture. The simplest model we could choose would be an *A-B-A-B* chain (Fig. 6), which could have interesting changes in the stabilization energy associated with the linkage between atoms 3 and 4, as a result of a change in the nature of atom 1 by its ϕ_{12} interaction parameter. Figure 7 shows the energy diagram for such a unit. We are interested in the sum of the stabilization energy of the two lowest orbitals: $\epsilon_{stab} + \epsilon'_{stab}$. The secular determinant for this problem is

$$\begin{vmatrix}
 \alpha_A - E & \mathcal{H}_{12} & 0 & 0 \\
 \mathcal{H}_{12} & \alpha_B - E & \mathcal{H}_{23} & 0 \\
 0 & \mathcal{H}_{23} & \alpha_A - E & \mathcal{H}_{34} \\
 0 & 0 & \mathcal{H}_{34} & \alpha_B - E
 \end{vmatrix} = 0. \quad (32)$$

Correct to fourth order in \mathcal{H}_{ij} , the sum of the two stabilization energies is readily evaluated as

$$\begin{aligned}
 & \epsilon_{stab} + \epsilon'_{stab} \\
 &= \left(\frac{\mathcal{H}_{12}^2 + \mathcal{H}_{23}^2 + \mathcal{H}_{34}^2}{\Delta E} \right) \\
 & \quad - \left[\frac{\mathcal{H}_{12}^4 + \mathcal{H}_{23}^4 + \mathcal{H}_{34}^4 + 2\mathcal{H}_{12}^2\mathcal{H}_{23}^2 + 2\mathcal{H}_{23}^2\mathcal{H}_{34}^2}{(\Delta E)^3} \right]. \quad (33)
 \end{aligned}$$

This is an interesting result in that the fourth-order term contains elements that connect adjacent linkages (e.g., $\mathcal{H}_{12}^2\mathcal{H}_{23}^2$) but contains no contribution from $\mathcal{H}_{12}^2\mathcal{H}_{34}^2$, which would connect the two terminal linkages of the unit. This is actually quite an understandable result. As shown else-

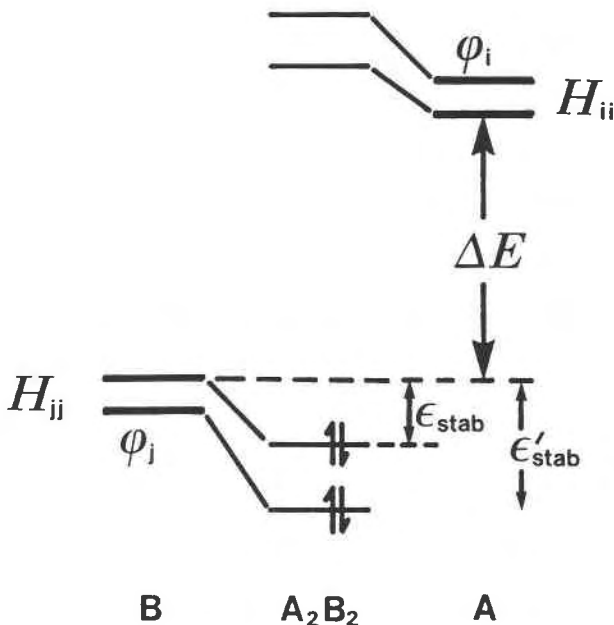


Fig. 7. Energy level diagram for the four-atom chain of Figure 6.

where (Burdett, 1987), for an atom to interact with another atom y linkages away, we need to expand the interaction energy up to order $2y$, the number of steps it takes to go from one atom to the other and back. For our case, these two linkages should be coupled in sixth order in \mathcal{H}_{ij} , and indeed we find that this term contains a contribution proportional to

$$\frac{\mathcal{H}_{12}^2\mathcal{H}_{23}^2\mathcal{H}_{34}^2}{(\Delta E)^5} \quad (34)$$

Energetically, this is a less important term than one appearing in fourth order, and in general, the effects of substitution at a given center drop off as we move away from this site. Perhaps this statement is quite obvious, but it is supported by the mathematical underpinnings of molecular orbital theory, as we have shown here.

CURIE'S RULE

An idea developed in this paper is that bonds around a given center will tend to be as symmetrically distributed as possible. Such a result is reminiscent of Curie's rule (Curie, 1894), which presented a similar idea. In classical terms, it is easy to see the origin of this rule. We assume that the total energy of a system described by a set of displacement coordinates $\{q\}$ can be written as a diagonal quadratic expansion about its equilibrium position:

$$2V = \sum f_{qq} (q_e - \Delta q)^2. \quad (35)$$

In this case, q will be associated with the stretching and contraction of bonds and the opening and closing of bond angles. If we impose the restriction that an increase in q for one coordinate is matched by a decrease in q for an-

other related coordinate and that the displacements are of similar magnitude, then the energy is minimized for $\Delta q = 0$. For the present discussion, we note our angular results, which lead to stabilization of the regular tetrahedral and octahedral coordinations, and the discussion of bond lengths, which leads to an understanding of Brown's valence-sum rule. In our approach, it has been the form of the fourth-order perturbation expression that has led to the mimicking of this state of affairs. This is not proof of the orbital control of structure; a similar result would come from an electrostatic scheme. Under the constraints outlined above, movement about an equilibrium position is always energetically penalizing for a cation surrounded by anions (or the converse) in this model.

SUMMARY

The purpose of this paper has been to show that simple molecular orbital ideas may be used to probe the origin of some of the most powerful rules of crystal chemistry. The simplicity of the approach highlights the major thrust of the electronic picture. In principle, other orbital interactions involving metal d orbitals or O s orbitals may be added by extending the perturbation theory sums. The picture will be more complex, but the general idea is the same. Perhaps one unanswered question is the role of the valency, v , which appears in formulations of the scheme. As we have shown, its inclusion is somewhat arbitrary, but in combination with r_{σ}^{-2m} it leads to a system-dependent parameter. Its dramatic use in the $\text{Ca}_{5.45}\text{Mo}_{18}\text{O}_{32}$ case described above encourages us to think further about its meaning. Overall, however, the result is an algebraic derivation of bond-valence theory from a molecular orbital basis. This complements the earlier findings of Burdett and McLarnan (1984) concerning the molecular orbital underpinnings of Pauling's rules. There, it was shown that the traditional ionic viewpoint often has an orbital analogue. Here we go further, and show that bond-valence theory may be considered as a very simple form of molecular orbital theory, parameterized by means of interatomic distance.

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