

Calculation of bond distances, one-electron energies and electron density distributions in first-row tetrahedral hydroxy and oxyanions

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Abstract

The tetrahedral hydroxyanions $T(OH)_4^-$ and oxyanions of the first row elements from Li to N are studied using the *ab initio* SCF MO method. Equilibrium T-O distances calculated using small orbital basis sets are within 0.05Å of their average values in solids so long as the charge on the anion is small. One electron orbital energies from larger basis set calculations on the oxyanions are used to interpret the valence region photoemission spectrum of BeO and to predict the spectral characteristics of tetrahedral B, C and N. Contour maps of the difference in electron density between molecular cluster and superimposed spherical neutral atoms show features which can be qualitatively interpreted in terms of ionic or covalent bonding.

Introduction

Since its invention more than fifty years ago, molecular orbital (MO) theory has steadily progressed in its ability to predict the properties of both simple and complex molecules. One of the major achievements of the version of MO theory known as the self-consistent field (SCF) MO *ab initio* method has been the reproduction of bond lengths and angles of small molecules (Collins *et al.*, 1976; Schmiedekamp *et al.*, 1979; Wallmeier and Kutzelnigg, 1979). Another has been the generation of accurate vertical ionization potentials and one electron energy diagrams for many molecules (Schwartz, 1977). In particular, *ab initio* SCF MO calculations for model systems in the

realm of silicate mineralogy has been quite successful in the calculation of (1) X-ray emission and photoelectron spectra for quartz and vitreous silica (Collins *et al.*, 1972; Tossell *et al.*, 1973; Gilbert *et al.*, 1973; Griscom, 1977; Newton and Gibbs, 1979), (2) tetrahedral bond length and bridging angle variations for the framework silicates (Newton and Gibbs, 1980; Swanson *et al.*, 1980; Meagher *et al.*, 1980; Gibbs *et al.*, 1980), (3) the bulk modulus of low quartz (O'Keeffe *et al.*, in press) and (4) the room temperature distribution of the bridging angle of molecular crystal siloxanes (Meagher *et al.*, 1980). The method has been equally successful in the calculation of triangular bond lengths for borates, carbonates and nitrates (Gupta and Tossell, manuscript; Radom, 1976;

Julg and Letoquart, 1978) and the reproduction of qualitative features of experimental electron density difference maps for the carbonate ion of calcite (Peterson *et al.*, 1979; Tossell, 1979). Clearly, each of these results suggests that reliable estimates of geometric and spectral properties of certain solids can be obtained from *ab initio* calculations on model systems containing the same coordination polyhedra as the solids (Gibbs *et al.*, 1972; Tossell, 1973; Tossell and Gibbs, 1977, 1978; Sauer and Zurawski, 1979; Tossell, 1979).

One of the reasons for undertaking the present study was to determine how well *ab initio* calculated bond lengths and spectral properties for first row tetrahedral $T(\text{OH})_4^n$ ($T = \text{Li}$ through N) hydroxyanions compare with experimental values obtained for solids. From simple radius ratio arguments, only the elements Li through B are indicated to occur in three-fold coordination. An examination of the literature shows that although Li occurs in five- and six-coordination, it has been reported in four-fold coordination in numerous minerals and synthetic compounds. On the other hand, the geochemistry of Be is dominated exclusively by the BeO_4^{-6} ion although triangular Be has been reported for a few synthetic solids. Borate minerals contain B in either three- or four-coordination with oxygen or in both types of coordination as expected from radius ratio considerations. Although carbon and nitrogen geochemistry is dominated by the triangular ion, their adoption of tetrahedral coordination in tetramethoxymethane (Mijlhoff *et al.*, 1973) and Na_3NO_4 (Jansen, 1979), recently synthesized at ambient pressure, is at variance with radius ratio considerations. Hence, we see that all of the first row elements Li through N may occur in tetrahedral coordination with oxygen despite radius ratio arguments to the contrary.

Several semi-empirical MO studies have previously been performed for first row tetrahedral oxyanions. For example, extended Hückel calculations for LiO_4^{-7} , BeO_4^{-6} and BO_4^{-5} tetrahedral oxyanions extracted from solids have established correlations between bond overlap populations and bond length and angle variations (Hill and Gibbs, 1978; Schlenker *et al.*, 1978; Tossell and Gibbs, 1977). In addition, approximate SCF MO theory has been used to generate one electron energy levels for BeO_4^{-6} and BO_4^{-5} ions that are in reasonable agreement with the limited available experimental data (Vaughan and Tossell, 1973; Armstrong *et al.*, 1977). Recently, a theoretical study on the borate tetrahedral oxyanion was reported by Gupta and Tossell (manuscript)

using the *ab initio* SCF MO method. However, to our knowledge, no other calculations have been completed for first row tetrahedral oxyanions using *ab initio* theory.

In this paper the results of *ab initio* SCF MO calculations on first row tetrahedral hydroxyanions and oxyanions are presented to explore how bond lengths, force constants, vibration frequencies, one-electron energy levels, and difference electron density distributions change as the central tetrahedral atom is changed from Li through N . The minimum energy bond distances, force constants, and vibrational frequencies were first calculated for tetrahedral hydroxyanions using small numbers of orbital functions to expand the molecular orbitals and results were compared with experimental data. Calculations on tetrahedral oxyanions with bond lengths fixed at experimental values were then performed using larger sets of orbital expansion functions to systematically analyze one electron orbital energies. Similar calculations were used to generate difference electron density distributions for $\text{Be}(\text{OH})_4^{-2}$, $\text{B}(\text{OH})_4^{-1}$ and $\text{N}(\text{OH})_4^+$. This procedure was necessary since the computational expense increases greatly as the size of the orbital basis increases. Fortunately, the smallest basis set yields good distances although larger bases are needed to accurately calculate many other properties.

Computational method

The SCF MO theory on which the paper is based was developed by Roothaan (1951). In this theory the total wavefunction of a system is represented as a product of one electron molecular spin orbitals which are antisymmetrized to account for the indistinguishability of the electrons. The molecular Hamiltonian within the Born–Oppenheimer approximation and neglecting spin-orbital coupling consists of kinetic energy, electron–nuclear attraction, electron–electron repulsion and nuclear–nuclear repulsion terms. The molecular orbitals, ψ_i , are chosen in a manner so as to minimize the total energy of the system. The individual molecular orbitals are, in practice, expanded in terms of a linear combination of atomic orbitals (or nuclear centered basis functions to be more appropriate) (LCAO) χ_k ,

$$\psi_i = \sum_k C_{ki} \chi_k \quad (1)$$

The coefficients C_{ki} and one electron energy ϵ_i associated with molecular orbital ψ_i are determined using the Roothaan equations (Roothaan, 1951). The

total molecular wavefunction is of value in determining various properties of the system. For the purpose of this paper, one electron energies, ϵ_i , which according to Koopmans (1934) theorem represent the ionization potential of the electron in the molecular orbital ψ_i , and the expectation value of the electron charge density operator, $\rho(\mathbf{R})$, are further explored. For a closed shell molecule within the LCAO approximation,

$$\rho(\mathbf{R}) = 2 \sum_i \psi_i^2(\mathbf{R}) \quad (2)$$

where the summation is over all the occupied orbitals. Using equation (1)

$$\rho(\mathbf{R}) = \sum_{kl} 2 \sum_i C_{ki} C_{li} \chi_k(\mathbf{R}) \chi_l(\mathbf{R}) \quad (3)$$

In the *ab initio* method all the molecular integrals over the basis functions are determined accurately using standard computer algorithms. The accuracy of the molecular orbital depends on the number of basis functions used for the LCAO expansion. A large number of basis functions is required to achieve the best wavefunction possible within this independent electron model. However, in this work the minimum basis set (MBS) designated STO-3G (Hehre *et al.*, 1969; Ditchfield *et al.*, 1970), and containing one expansion function for each atomic orbital was used for the purpose of geometry optimization. This choice has proved to be very successful for the calculation of equilibrium geometries in small organic molecules (Hehre, 1976). A basis set employing two functions for each atomic orbital (the double zeta (DZ) basis of Dunning (1970) in which a (9S, 5P) primitive Gaussian basis is contracted to [4S, 2P] basis) was employed to obtain the molecular wavefunctions for $\text{Be}(\text{OH})_4^{2-}$, $\text{B}(\text{OH})_4^-$, $\text{N}(\text{OH})_4^+$, BeO_4^{6-} , BO_3^{3-} and NO_3^- at the experimental geometry. A STO 4-31G basis function (Ditchfield *et al.*, 1971), of slightly less flexibility as compared to the Dunning (1970) double zeta basis was used to compute the molecular wavefunction of $\text{C}(\text{OH})_4$ and CO_4^{4-} at the experimental distance.

The *ab initio* SCF MO calculations were carried out using the HONDO (Dupuis *et al.*, 1977) or Gaussian 76 (Binkley *et al.*, 1978) programs. A density map program written by Dr. R. M. Stevens (Department of Chemistry, Harvard University) was used to prepare density contour maps. The separated neutral atom densities were calculated using near Hartree-Fock atomic wavefunctions (Clementi and Roetti, 1974).

Calculation of equilibrium geometries

The tetrahedral oxyanions of first row elements carry a large negative charge. This, as has been pointed out by Gupta and Tossell (manuscript), generates extraneous electron-electron repulsion producing an erroneously high value of the equilibrium bond distance. Therefore, the negative charge has been partially or fully neutralized by adding terminal hydrogen atoms in all the clusters. Thus, the equilibrium geometry calculations were carried out on the clusters $\text{Li}(\text{OH})_4^{3-}$, $\text{Be}(\text{OH})_4^{2-}$, $\text{B}(\text{OH})_4^-$, $\text{C}(\text{OH})_4$ and $\text{N}(\text{OH})_4^+$. STO-3G calculations were carried out at different T-O distances for clusters of point symmetry D_{2d} and minimum energy T-O distances were obtained by a parabola fit to three points near the minimum in the total energy curve. The results were found to be insensitive to choices of O-H distance between 0.96 and 1.03 Å and T-O-H angle between 105° and 114°. For the Li and Be hydroxyanions the inclusion of T2p functions (technically not included in a minimum basis set) was found to significantly lower the equilibrium T-O distance, improving agreement with experiment. Calculated equilibrium distances are compared with experimental values in Table 1. For Li, Be and B average experimental values are taken from Griffen and Ribbe (1979) while the value for C is from gas phase $\text{C}(\text{OCH}_3)_4$ (Mijlhoff *et al.*, 1973) and that for N from Na_3NO_4 (Jansen, 1979). The largest differences of calculated and experimental distances occur for $\text{Li}(\text{OH})_4^{3-}$, with a high negative charge, and for $\text{N}(\text{OH})_4^+$, for which the distance may depend significantly on details of the O-O interaction. However, even in these cases the errors are only 0.06 Å and overall agreement with experiment must be considered very good.

A set of model calculations with STO-3G basis sets on the Be tetrahedral oxyanion with all the negative

Table 1. Experimental and calculated equilibrium T-O distances for $\text{T}(\text{OH})_4^z$

T	n	Experimental ^a (Å)	Calculated (Å)
Li	-3	2.01	2.06
Be	-2	1.64	1.63
B	-1	1.48	1.48
C	0	1.40 ^b	1.42
N	+1	1.39 ^c	1.44

^a From Griffen and Ribbe (1979).

^b Mijlhoff *et al.* (1973).

^c Jansen (1979).

charge (-6) neutralized by protonation in the form $\text{Be}(\text{OH})_2(\text{OH}_2)_2$ predicted B-O bond length of 1.59 Å when all the Be-O bonds were simultaneously optimized. The Be-O bond lengths turned out to be 1.51 Å and 1.68 Å for Be-OH and Be-OH₂ respectively when separately optimized. These two values although reasonably far apart give an average of ~1.59 Å, and are comparable with the experimental range of 1.58-1.67 Å. The overall effect of neutralizing the residual -2 charge in $\text{Be}(\text{OH})_4^{2-}$ has been to lower the equilibrium Be-O bond length; thus it is conceivable that such a model will also provide a better assessment of bond length in Li tetrahedral oxyanion.

Calculation of force constants and vibrational frequencies

The T-O stretching force constants calculated by taking the second derivative of energy with respect to T-O distance near the minimum in the potential energy curves and the frequency of the A' fundamental vibration mode evaluated for T_d symmetry are presented in Table 2 along with the available experimental data. Although no experimental frequency is reported for tetrahedral oxyanions of carbon, the fundamental modes are expected to be close to those of CF₄ due to near mass equality of the F and OH group. Nakamoto (1970) has reported the A' vibration of CF₄ to be at 908 cm⁻¹, which compares well with the calculated value of 916 cm⁻¹. LiO₄ tetrahedra in Li₂CO₃ exhibit their fundamental vibration modes in the frequency range 530-410 cm⁻¹ (Tarte, 1964). Therefore, the predicted Li-O A' vibration is probably nearly 35 percent in error. With the exception of Li-O symmetric stretching mode, the agreement between experiment and theory is good. It

Table 2. Calculated and experimental force constants and frequencies for hydroxyanions of Li through N (experimental values in parentheses).

	Force constant (m dyne/A)	Frequency (cm ⁻¹)
$\text{Li}(\text{OH})_4^{3-}$	0.76	75
$\text{Be}(\text{OH})_4^{2-}$	3.71 (2.4) ^a	608
$\text{B}(\text{OH})_4^-$	7.69	903 (946) ^b
$\text{C}(\text{OH})_4$	7.92	916
$\text{N}(\text{OH})_4^+$	7.97	919 (843) ^c

^a Huckaby *et al.* (1975).

^b Devarajen *et al.* (1974).

^c Jansen (1977).

should be noted at this point that the largest error in equilibrium distance prediction was also found for the lithium oxyanion (Table 1). The underestimation of the stretching frequency evidenced in Table 2 is consistent with a calculated bond which is longer and weaker than that observed experimentally.

Electronic structure and spectral properties

The electronic structures of tetrahedral oxyanions of non-transition elements has been studied in some detail (Connor *et al.*, 1972; Nefedev *et al.*, 1975). The valence region follows the orbital ordering: $1a_1$, $1t_2$, $2a_1$, $2t_2$, $1e$ $3t_2$, $1t_1$ in order of increasing orbital energy with $1t_1$ being the highest occupied orbital. These orbitals divide into three sets on the basis of their orbital characteristics, mainly O2p nonbonding ($1e$, $3t_2$, $1t_1$), σ bonding ($2t_2$ and $2a_1$) and O2s nonbonding ($1a_1$, $1t_2$). The electronic structure and orbital energies of the valence region of oxyanions BeO_4^{4-} , BO_4^{5-} , CO_4^{3-} are presented in Table 3. For the sake of comparison, the highest occupied level ($1t_1$) is set as a reference (energy = 0 eV) and only relative energies are tabulated.

The general features of the OK α X-ray emission spectra (XES) of these oxyanions predicted by the *ab initio* calculations are similar to those in other tetrahedral oxyanions of non-transition elements. The spectra consist of one intense transition from the $1e$, $3t_2$, $1t_1$ orbital set and a relatively weak transition from the $2a_1$, $2t_2$ orbital set to the oxygen core. Similarly the valence region photoemission spectra (PES) of such materials are observed to show a O2p nonbonding orbital peak, one or two bonding orbital peaks and an O2s peak (Connor *et al.*, 1972; Nefedev *et al.*, 1975). The calculated separations between the orbital energies in the clusters studied show a consistent behavior, with the upper valence region width (from $1t_1$ to $2a_1$) increasing significantly as the atomic number of the central atom increases. Since the C and N oxyanions have almost the same T-O distance, the valence region width depends on cation identity as well as bond length. Similar trends in binding energies were also noted in the three coordinated oxyanions of these atoms, where a comparison was made with experimental data (Gupta and Tossell, manuscript). In the experimental and theoretical F K α spectra of the isoelectronic fluorides, BeF_4^{2-} , BF_4^- and CF₄, trends in orbital energy separations are of similar nature (Nefedev *et al.*, 1975). The above authors have also provided some explanation for these trends based on bond ionicity and energy separation in the valence orbitals (2s and 2p) of the cen-

Table 3. Relative orbital energies (eV) for BeO_4^{6-} , BO_4^{5-} and NO_4^{3-}

Orbitals	BeO_4^{6-}	BO_4^{5-}	CO_4^{4-}	NO_4^{3-}
$1t_1$	0	0	0	0
$3t_2$	-0.64	-1.29	-1.01	-0.83
$1e$	-1.47	-2.18	-2.49	-2.39
$2t_2$	-2.51	-4.45	-6.10	-6.92
$2a_1$	-3.78	-6.64	-9.36	-11.97
$1t_1$	-20.41	-21.61	-22.45	-22.81
$1a_1$	-21.39	-24.01	-26.84	-30.06

tral atom. It is noteworthy that the energy gap in the σ levels ($2t_2 - 2a_1$) decreases in going from the oxyanions to isoelectronic fluorides with the same central atom (2.19 eV and 1.9 eV for BO_4^{5-} and BF_4^- respectively; 3.26 eV and 3.1 eV for CO_4^{4-} and CF_4 respectively), indicative of reduced covalent bonding.

Although our results reproduce the expected qualitative spectral features for tetrahedral oxyanions, little experiential data are available on the particular clusters we have studied. For BeO, containing BeO_4^{6-} molecular clusters, X-ray PES shows on O2p non-bonding orbital peak, a bonding orbital peak 2.8 eV below it and an O2s peak about 16.3 eV below the O2p (Hamrin *et al.*, 1970). Calculated average separations of the $2a_1$, $2t_2$ bonding orbital set and the $1a_1$, $1t_2$ O2s orbital set from the $1e$, $3t_2$, $1t_1$ O2p non-bonding orbital set are 2.2 and 20.0 eV, respectively. The observed exaggeration of the O2p–O2s separation has been observed in other *ab initio* SCF MO calculations (Connor *et al.*, 1972).

Neither OK α XES nor valence region PES have yet been obtained for Na_3NO_4 . A measurement of such properties would provide a valuable test of the calculated orbital energies. Comparing the orbital energies we have calculated for NO_4^{3-} with those calculated for NO_3^{2-} (Considine *et al.*, 1977) leads to a prediction that the upper valence region width ($1t_1 - 2a_1$) in NO_4^{3-} salts will be greater than that observed in nitrates (about 9.6 eV; Considine *et al.*, 1977) by about 1 eV. A similar comparison suggests that when solids containing CO_4^{4-} groups are prepared (perhaps by procedures similar to those used to make Na_3NO_4) their valence region spectral widths will be greater than those in carbonates.

Calculation of electron densities

The difference density, $\Delta\rho$, contour maps prepared by subtracting spherical neutral atom electron den-

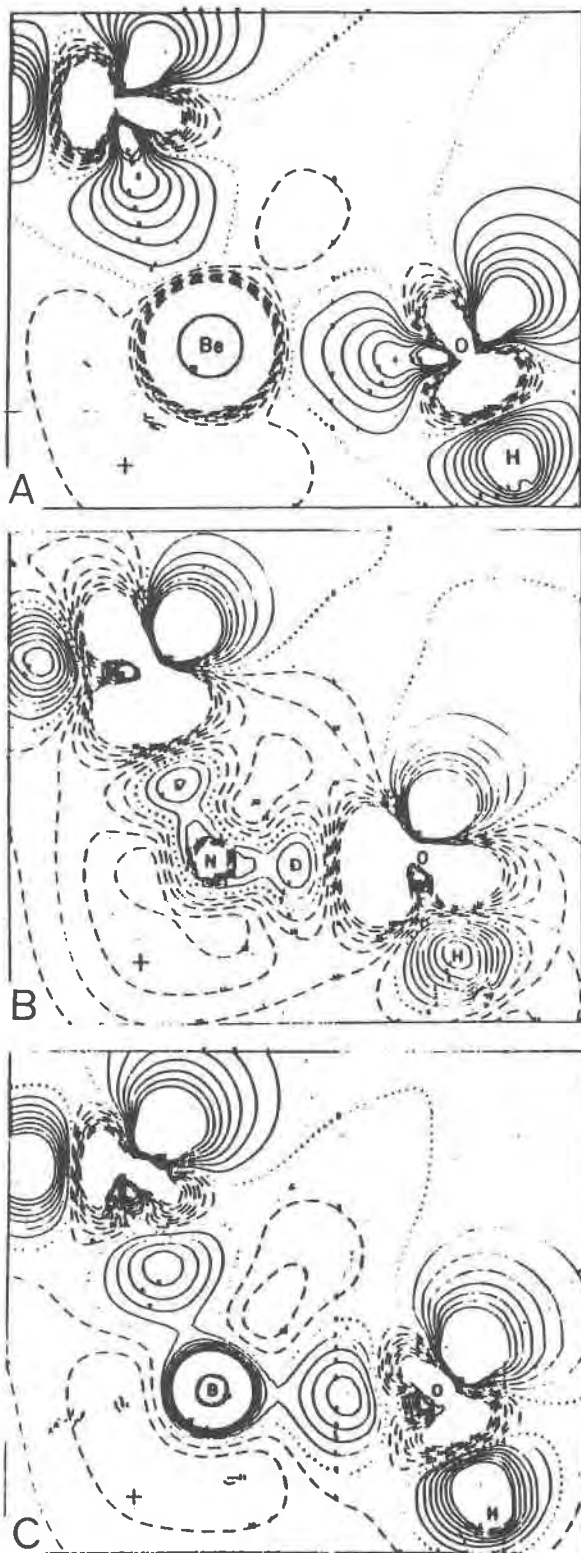


Fig. 1. Electron density differences, $\Delta\rho$, between molecule and superimposed neutral spherical atoms. Negative contours are dashed, zero contour dotted and positive contours solid. Contours change by intervals of ± 0.05 electrons (A^{-3}). (a) $\text{Be}(\text{OH})_4^{2-}$, (b) $\text{B}(\text{OH})_4^-$, (c) $\text{N}(\text{OH})_4^+$.

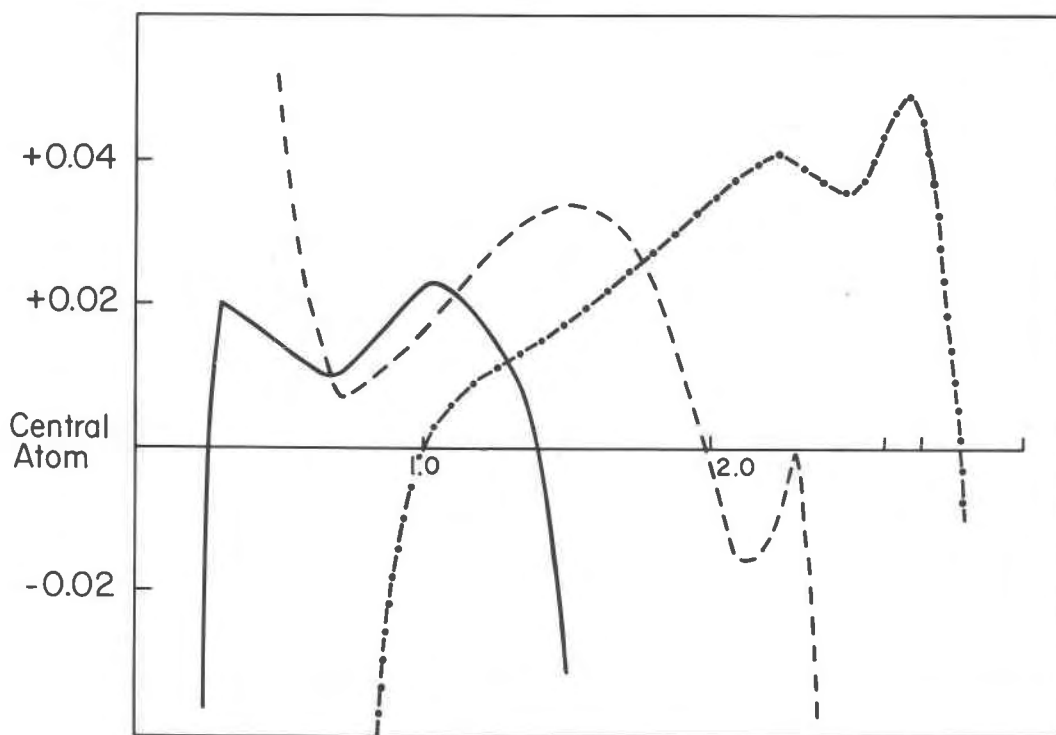


Fig. 2. Electron density difference ($\Delta\rho$) profiles in units of electrons (\AA)⁻³. Horizontal axis represents distance from T and vertical axis represents the corresponding $\Delta\rho$ value. Solid curve, $\text{N}(\text{OH})_4^+$; dashed curve, $\text{B}(\text{OH})_4^-$ and dash-dot curve, $\text{Be}(\text{OH})_4^{2-}$. Vertical lines on distance scale represent positions of oxygen nucleus in order of increasing distance from central atom in N, B and Be hydroxyanions.

sities from the molecular density are presented in Figure 1. Contours are presented in a plane containing the central atom and two oxygens with contour intervals of 0.05 electrons (e)/ \AA^3 . These maps represent a composite effect of charge shift and net number of electrons (*i.e.*, $\Delta\rho \neq 0$). A comparison of BO_3^{3-} and $\text{B}(\text{OH})_3$ difference density maps show that the later effect in bonding region is small (slightly more charge build up in the B–O bond in BO_3^{3-}) (Gupta and Tossell, manuscript). The three examples considered here show the expected qualitative features. These are a depletion of charge from the central atom, charge transfer to oxygen, concentration of charge density in the oxygen lone pair region and an increase in charge in the T–O and O–H bond regions. The charge gain in the T–O bond region is associated with oxygen in the case of $\text{Be}(\text{OH})_4^{2-}$, whereas, for $\text{B}(\text{OH})_4^-$ and $\text{N}(\text{OH})_4^+$ it protrudes towards the central atom. Another distinct difference is the change in oxygen lone pair direction in these density maps. These differences are related to the bond character of the T–O bond which is more ionic for $\text{Be}(\text{OH})_4$ and more covalent for $\text{B}(\text{OH})_4^-$ and $\text{N}(\text{OH})_4^+$. The O lone pair

electron density also becomes larger and more diffuse as T changes from N to B, consistent with an increasing degree of underbonding and a greater receptivity to approach by additional cations.

According to qualitative theory a covalent bond charge is transferred into the interatomic region and the internuclear separation of the two atoms forming a covalent bond is approximately given by the sum of their atomic radii. Therefore, it is reasonable to expect the position of the maximum in the difference density profile (Fig. 2) to be related to the atomic radii. Based on a similar argument, in an ionic bond where the charge is transferred from one atom to the other the node in difference density profile should provide a measure of the ionic radii of the atoms. Alternatively the point of contact of the ionic radii could be defined as that point along the bond where the molecular density is a minimum. Atomic radii from Slater (1964) and the positions of maxima in our calculated difference density profile are compared in Table 4. The disparities between Slater's estimates and the calculated values obtained in this way are fairly small. In fact, some of the discrepancy

could be an artifact of our choice of atomic and molecular wavefunctions of somewhat different accuracy.

The crystal radii given by Shannon and Prewitt (1969) are based upon the empirical radii of Fumi and Tosi (1964) which in turn agree fairly well with ionic radii determined from the observed position of minimum electron density along the bonds in ionic materials (Witte and Wölfel, 1958). Thus, we expect that the Shannon and Prewitt crystal radii will be roughly comparable with our calculated ionic radii defined in terms of nodes in $\Delta\rho$ maps. The values given in Table 4 indicate that such is approximately true for $\text{Be}(\text{OH})_4^{2-}$. However, for the more covalent clusters no node in $\Delta\rho$ is observed so that ionic radii cannot be defined on this criterion. Therefore, only $\text{Be}(\text{OH})_4^{2-}$ (and presumably $\text{Li}(\text{OH})_4^{3-}$) can be effectively analyzed in terms of qualitative ionic bonding concepts while the Be, B, C and N hydroxyanions can be interpreted using covalent bonding concepts.

Although such a qualitative analysis of the $\Delta\rho$ maps yields insight it is important to understand that the electron density is a quantum mechanical observable and susceptible to direct experimental measurement while radii are simply conceptual tools and have no unambiguous definition. We therefore look forward to direct measurements of electron density for these clusters using X-ray diffraction methods.

Conclusions

Ab initio SCF MO calculations show a very consistent change in calculated T-O bond distances, one electron energies and difference densities as the central atom of the anion TO_4^n is changed from lithium to nitrogen. The calculated properties also compare well with the limited experimental data available. A close correspondence between the trends in spectral properties predicted by these calculations and those observed in trigonal oxyanions of these elements, which have been extensively studied, gives us confidence in predicting that measurement of the $\text{OK}\alpha$ XES or the valence region photoemission spectra of Na_3NO_4 should give an upper valence region width about 1 eV greater than that in nitrates. Finally the $\Delta\rho$ maps substantiate the idea of relatively "ionic" bonding in Li and Be tetrahedra and relatively "covalent" bonding in B, C and N oxyanions.

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Table 4. Standard atomic and ionic radii and those inferred from calculated $\Delta\rho$ maps.

Atom	Atomic radii (Å)		Ion	Crystal radii (Å)	
	Slater ^a	Calculated		SP ^b	Calculated
Li	1.45	-	Li^+	0.73	
Be	1.05	1.17	Be^{2+}	0.41	0.66
B	0.85	0.79	B^{3+}	0.26	
C	0.70	0.66 ^c	C^{4+}	0.18 ^d	
N	0.65	0.54	N^{5+}	0.17 ^d	
O	0.60	0.69-0.85 ^e	O^{2-}	1.22	1.00 ^e

^a Slater (1964).

^b Shannon and Prewitt (1969).

^c L.C. Allen (private communication).

^d C-O distance in $\text{C}(\text{OCH}_3)_4$ (Mijlhoff *et al.*, 1973) minus SP crystal radius of 1.22 for O.

^e This range is evaluated by subtracting the calculated atomic radius of the central atom from the inter-nuclear distance in the cluster.

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