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Charge Distributions on Polyatomic Ions, and Their Relationships with Cohesive Energies of Ionic Crystals

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Some current approaches to the determination of the charge distributions on polyatomic ions are considered. The methods involving cohesive energies of ionic solids on the one hand and those using molecular-orbital calculations on the other hand are compared and discussed. New charge distributions are presented for a series of polyatomic ions.

Key words: Polyatomic ions – Ionic crystals – Lattice energy – Charge distributions – Cohesive energy

1. Introductory Discussion

Recent years have seen an interest in determining the charge distributions on polyatomic ions through studies on the energetics of ionic crystals. Different workers have used differing techniques. Ladd [1], in studying some of the alkali-metal cyanides, equated the cohesive energies of the cubic (NaCl structure type) and orthorhombic polymorphs at their transition temperatures. Jenkins and Pratt [2] determined the cohesive energies of alkali-metal and ammonium perchlorates, as a function of the charge on the oxygen atom, by a minimization technique, carried out with respect to the unit-cells' lengths. Yuen, Lister and Nyburg [3] analysed calcite and aragonite by a minimization procedure, first suggested by Busing [4], but with respect to Coulombic force rather than Coulombic energy. In addition to these studies, calculations have been carried out on several polyatomic ions by CNDO/2, INDO, NDDO, extended Hückel and *ab initio* MO methods [5–13]. Dean and Richards [14] have discussed the meaning of the term "charge on an atom", and have given results for several compounds of nitrogen.

In some cases, the results given by the different methods agree strikingly, and agree with MO calculations. In other examples, it can be seen that there are some

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Table 1. Results of charge assignments in polyatomic ions

Reference	Technique	$[CO_3]^{2-}$ ion	
		z_O/e	r/Å
Batsanov [37]	Use of electronegatives	−0.66	—
Connor *et al.* [5]	*Ab initio* MO calculations	−1.00	1.27
Jenkins *et al.* [31]	Cohesive energy calculations	−0.26	—
Jenkins *et al.* [32]	Cohesive energy calculations	−0.54	1.283
Ladd [38]	Cohesive energy calculations	−0.76	1.26
Ladd [39]	CNDO/2 and INDO MO calculations	−0.77	1.26
		−0.80	1.26
Ladd (this work)	*Ab initio* MO calculations	−0.95	1.310
		−0.93	1.283
Yuen *et al.* [3]	Zero-force minimization calculations	−0.94	1.283
		−0.98	1.283
Yuen *et al.* [3]	*Ab initio* MO calculations	−0.97	1.283

Reference	Technique	CN^- ion	
		z_N/e	r/Å
Demnynck *et al.* [7]	*Ab initio* MO calculations	−0.57	1.15
Hillier *et al.* [8]	*Ab initio* MO calculations	−0.59	1.18
Jenkins *et al.* [30]	Cohesive energy calculations	−0.58	—
Ladd [1]	Cohesive energy calculations	−0.60	1.05 1.08
Ladd [1]	CNDO/2 and INDO MO calculations	−0.39	1.05
		−0.38	1.08
Ladd [1]	*Ab initio* MO calculations	−0.70	1.05
		−0.61	1.08
Ladd (this work)	*Ab initio* MO calculations	−0.50	1.05
		−0.54	1.08
		−0.62	1.15
		−0.64	1.17

Reference	Technique	ClO_4^- ion	
		z_O/e	r/Å
Connor *et al.* [5]	*Ab initio* MO calculations	−0.21	—
Cox *et al.* [9]	Extended Hückel MO calculations	−0.39	1.43
Höjer *et al.* [10]	CNDO/2 MO calculations	−0.51	—
Jenkins *et al.* [2]	Cohesive energy minimization	−0.34	—
Ladd (this work)	*Ab initio* MO calculations	−0.58	1.68
		−0.73	1.50
		−0.74	1.463
Mehrotra *et al.* [11]	CNDO/2 MO calculations	−0.33	1.463
		−0.64	1.463
	NDDO MO calculations	−0.67	1.463
		−0.79	1.463
	Ab initio MO calculations	−0.44	1.463

Reference	Technique	SO_4^{2-} ion	
		z_O/e	r/Å
Gianturco *et al.* [13]	K_α fluorescence measurements	−0.93	—
Hillier *et al.* [12]	*Ab initio* MO calculations (small basis)	−0.86	1.44

Table 1—*Continued*

		SO$_4^{2-}$ ion	
Reference	Technique	z_0/e	r/Å
Jenkins [40]	Cohesive energy calculations	-0.80	1.46 1.51
Ladd (this work)	*Ab initio* MO calculations	-1.01	1.61
		-1.07	1.44
Mehrotra *et al.* [11]	*Ab initio* MO calculations	-0.74	1.488
Murfitt [6]	*Ab initio* MO calculations	-0.75	—

		PO$_4^{3-}$ ion	
Reference	Technique	z_0/e	r/Å
Ladd (this work)	*Ab initio* MO calculations	-1.29	1.63
		-1.35	1.555
Mehrotra *et al.* [11]	*Ab initio* MO calculations	-1.05	1.555
Murfitt [6]	*Ab initio* MO calculations	-1.30	—

disturbing variations in the charge distribution in one and the same ion; Table 1 indicates some of these situations. One has to consider why this should occur, and what the most reliable procedure is for evaluating these charge distributions and, hence, cohesive energies and dependent parameters.

The effect of a charge distribution in a polyatomic ion on the cohesive energy of an ionic solid has been discussed earlier [15–18]. However, Ladd [19] first showed that charge distributions could be obtained by calculations in which the cohesive energies of polymorphs were equated at their transition temperatures. Subsequently, other workers adopted this approach, some with modifications (Table 1). There are certain weaknesses in the approach through cohesive energies which cannot be overcome in a completely satisfactory manner.

In the calculation of cohesive energy from an electrostatic model, the largest contribution comes from the Coulombic energy, and this quantity is clearly defined through a Madelung constant. The repulsion energy is the second largest term. With crystals which are isotropic, and where compressibility data are available, the repulsion energy can be calculated reliably [1] (Eq. (3)). If the term-by-term calculation is used [2] (Eq. (1)) the repulsion exponent ρ has to be assigned, and the so-called basic radii have also to be chosen. Since ρ cannot be a constant for different solids, if it is forced to be, then, for a correct cohesive energy, the error in ρ must be compensated by a corresponding adjustment in a parameter which correlates with ρ, such as a basic radius. Among a series of interconnected compounds, like the alkali-metal halides or the alkaline-earth-metal chalcides, a self-consistent set of basic radii can be deduced [20]. For a few isolated compounds, the corresponding procedure is not well defined [21] and, thus, of unknown precision.

Another technique that has been used involves a least-squares minimization of the cohesive energy with respect to physical and structural parameters. This method was introduced by Busing [4]: it has certain questionable features. For example, in cubic $SrCl_2$, the cohesive energy was found to be -2166 kJ mol^{-1}. The repulsion energy was quoted as 568 kJ mol^{-1} (0.25 of the total electrostatic energy) and the van der Waals energy as -425 kJ mol^{-1} (0.20 of the cohesive energy). Among ionic compounds such as the alkali-metal halides and the alkaline-earth-metal chalcides, for which adequate data are available for calculating ρ, it is found that the repulsion energies usually lie between 0.09 and 0.13 of the corresponding electrostatic energies [1, 22] with the van der Waals energies between 0.01 and 0.05 of the cohesive energy. Other recent results [23] support these conclusions. Thus, the values quoted above for $SrCl_2$ lie well outside these ranges, and one may need, therefore, to consider possible correlation effects between the parameters which are refined. Well-known correlation effects arise, for example, between atom temperature factors, intensity scale factors and atom occupancy factors in the least-squares refinement of a crystal-structure determination.

Calculation of the cohesive energy of $SrCl_2$ by the method of Ladd [1, 24], gives -2100 kJ mol^{-1}, insignificantly different from Busing's value, but in which the repulsion energy is 300 kJ mol^{-1} and the van der Waals energy about -100 kJ mol^{-1}. It is interesting that the value of ρ/r_e, where r_e is the equilibrium interionic distance, implied by Busing's results would be about 0.25. Hence, the van der Waals energies would then seem to be repulsive rather than attractive [1]. Although a reasonable value for the cohesive energy may be obtained, the multi-dimensional surface which is being explored by least squares contains many minima, and unless minimization begins near the correct solution, the desired parameter may be moved, inadvertently, into a secondary minimum.

Similar reservations may attach to more recent implementations of the minimization technique [2, 3]. One would expect that, from good crystallographic studies, unit-cell dimensions and atomic coordinates are known with sufficiently high precision to represent constants of the structure. It is possible that relaxing the structural parameters is equivalent to obtaining a best fit for the energy parameters, but that correlation prevents these two effects from being disentangled. However, Yuen, Lister and Nyburg [3] obtained very satisfactory results for the $[CO_3]^{2-}$ ion, as judged against MO calculations, but further applications of their technique will be needed before it can be appraised fully.

It is noteworthy that, where good structural and energy data are available, the charge distributions obtained through cohesive energy calculations are in good agreement with those given by *ab initio* MO calculations. One important reason for determining charge distributions is that one is then able to proceed, through cohesive energies, to the evaluation of thermodynamic parameters which cannot be realized experimentally. In view of this application and of the paucity of energy data for crystals containing polyatomic ions, it may be best first to calculate charge distributions directly by MO methods and then to use the results in the evaluations of cohesive energies. This paper presents the results of some of the first of these calculations.

2. Experimental and Concluding Discussion

Charge distributions on a series of polyatomic ions have been evaluated by an *ab initio* method [25, 26], using a 6-31G basis for first-row elements, but a 4-31G basis for second-row elements and for boron. For each species, calculation of the total electronic energy was carried out over a range of geometry which both included the energy minimum and spanned the published values of the geometry of the species. In this work, results are reported mainly for single-parameter ions, that is, those species in each of which the geometry is, through symmetry, governed by a single parameter, a bond length.

The results for each ion have been treated in two ways. Firstly, the charge z_x on the more electronegative atom z_x, in the species at equilibrium geometry, has been fitted to a quadratic curve, in terms of the distance parameter r between the two dissimilar atoms in the complex ion. The results are presented in Table 2. Secondly, the energy minimum has been obtained by fitting a quadratic curve, by a similar technique, to five energy/distance data nearest to the energy minimum: the geometry and charge parameters at this minimum are listed in Table 3. In all cases the r.m.s. errors in fitting the polynomials were less than 10^{-3}. In using Table 3 to draw comparisons with other results, it is clearly essential to consider the same value of r. Regrettably, several results for charge distributions on polyatomic ions considered herein, have been published without a clear statement of the corresponding values of r. Again, it is not sufficient to quote a reference to a structure determination. For example, in the precise analysis of the structure of aragonite [27], the significantly different C—O distances of 1.48 and 1.50 Å obtain.

Table 2. Constants of the polynomial $z_x = ar^2 + br + c$

Ion	Literature range of r/Å	X	a/e Å^{-2}	b/e Å^{-1}	c/e
$[NH_4]^+$	0.94–1.06	N	2.9762	−6.9738	3.0929
$[NO_2]^+$	1.12–1.24	O	1.9940	−4.3970	2.5448
$[PH_4]^+$	1.36–1.44	H	−0.41071	1.3125	−0.83805
$[BF_4]^-$	1.36–1.46	F	1.5179	−4.5291	2.7816
$[BH_4]^-$	1.22–1.30	H	0.07143	−0.26100	−0.06692
$[ClO_4]^-$	1.46–1.56	O	1.3447	−3.4711	1.4553
$[CN]^-$	1.08–1.19	N	2.3181	−6.3428	3.6063
$[HF_2]^-$	1.10–1.18	F	0.80357	−1.7746	0.19373
$[N_3]^-$	1.10–1.20	N	−1.0268	3.1416	−2.7814
$[NO_3]^-$	1.22–1.30	O	1.0714	−2.5970	1.0294
$[OH]^-$	0.94–1.02	O	1.0714	−1.5000	−0.71466
$[CN_2]^{2-}$	1.14–1.28	N	3.7500	−10.4167	6.1799
$[CO_3]^{2-}$	1.24–1.34	O	2.6786	−7.4493	4.2145
$[SO_4]^{2-}$	1.44–1.54	O	1.6445	−4.6580	2.2298
$[PO_4]^{3-}$	1.54–1.66	O	−1.6368	5.6002	−6.0687

N′ is an outer nitrogen atom

Table 3. Ion parameters at equilibrium geometry

Ion	Symmetry	Distance/Å		Charges/e			
$[NH_4]^+$	$\bar{4}3m$	r_{N-H}	1.012	z_N	−0.916	z_H	0.479
$[NO_2]^+$	∞m	r_{N-O}	1.207	z_N	0.714	z_O	0.143
$[PH_4]^+$	$\bar{4}3m$	r_{P-H}	1.401	z_P	0.220	z_H	0.195
$[BF_4]^-$	$\bar{4}3m$	r_{B-F}	1.417	z_B	1.352	z_F	−0.588
$[BH_4]^-$	$\bar{4}3m$	r_{B-H}	1.239	z_B	0.124	z_H	−0.281
$[ClO_4]^-$	$\bar{4}3m$	r_{Cl-O}	1.678	z_{Cl}	1.332	z_O	−0.583
$[CN]^-$	∞	r_{C-N}	1.174	z_C	−0.355	z_N	−0.645[b]
$[HF_2]^-$	∞m	r_{H-F}	1.145	z_H	0.570	z_F	−0.785
$[N_3]^-$	∞m	$r_{N'-N''}$	1.176[a]	$z_{N'}$	−0.507	$z_{N''}$	0.014
$[NO_3]^-$	$\bar{6}m2$	r_{N-O}	1.260	z_N	0.626	z_O	−0.542
$[OH]^-$	∞	r_{O-H}	0.983	z_O	−1.154	z_H	0.154
$[CN_2]^{2-}$	∞m	r_{C-N}	1.247	z_C	−0.044	z_N	−0.978
$[CO_3]^{2-}$	$\bar{6}m2$	r_{C-O}	1.310	z_C	0.841	z_O	−0.947
$[SO_4]^{2-}$	$\bar{4}3m$	r_{S-O}	1.613	z_S	2.020	z_O	−1.005
$[PO_4]^{3-}$	$\bar{4}3m$	r_{P-O}	1.632	z_P	2.156	z_O	−1.289

[a] N′ and N″ are outer and central nitrogen atoms respectively.

[b] r_{C-N} different from that in Table 1 (Ladd [1]).

The charge distributions are considered to represent a reliable self-consistent set which can be applied to various structural and energetic calculations. In a number of the ions, the change in charge with the distance r is not large. Since inclusion in a structure would, in general, be expected to produce small perturbations on the free-ion geometry, then insofar as these perturbations would manifest themselves as changes in r, so the differences between the charge distributions tabulated and those existing in corresponding solids can reasonably be expected to be negligible to a good approximation. Thus, the data may be used in crystals, subject to an adjustment in terms of the value of r found from crystallographic studies. There appears to be no simple relationship between z_x and r for species of a given symmetry type.

One should remark on the rather large differences between the calculated equilibrium interatomic distances (r) in some species and the values already reported for the same parameters. For example, in $[SO_4]^{2-}$, the calculated value of r is 1.61 Å, whereas reported values range from 1.44 to 1.54 Å. Again, in $[ClO_4]^-$, r is 1.70 Å, and reported values range from 1.46 to 1.56 Å. In view of the fact that a number of the experimentally-derived r values pertain to X-ray analysis, some quite early, on metal salts wherein no corrections were made for absorption effects, the validity of such values may be questioned. The precise analyses of calcite [28, 29] give C—O values of 1.294(4) and 1.283(2) Å, their difference being insufficiently significant to suggest an obvious preference. It is worth remembering also that X-ray bond lengths are distances between the electron density maxima, and will not, in general, be the same as equilibrium internuclear distances. The differences will depend upon the polarizabilities of the species, and may be expected to vary from one polyatomic ion to another.

Values have been reported for the dipole moments and quadrupole moments of some of the ions studied herein [3, 30–32]. It seems to the author that they are simply other ways of expressing the charge distributions, for given values of r. In the absence of corresponding experimental measurements, they would appear to add very little of substance. The calculated dipole moment for CN^- has been reported at values between 1.3×10^{-30} C m and 6.1×10^{-30} C m [30]. The quadrupole moment θ_{zz} for CO_3^{2-} has been reported at -1.0×10^{-39} C m^2 [31] and $+3.9 \times 10^{-39}$ C m^2: it has been compared with that for CO_2 [31], -1.0×10^{-39} C m^2. A valid comparison would be with the isoelectronic BF_3, for which θ_{zz} is $+4.0 \times 10^{-39}$ C m^2, a result that supports a value for z_0 in the CO_3^{2-} ion of about -0.95.

The main difficulties with all classical models for cohesive energy calculations may be summarized in the following two points:

a) Except for the halides and chalcides of both the alkali metals and the alkaline-earth metals, and perhaps a very few other simple ionic crystals, there is no way of obtaining an independent check on the reliability of a cohesive energy model.

b) Among ionic compounds, in which 85–90% of the cohesive energy is electrostatic, any repulsion energy function which is equivalent to a high inverse power of the interionic distance will lead to satisfactory cohesive energies which will compare well with the thermodynamic (Born–Haber cycle) values, having regard to the precision of such data as compressibilities on the one hand, and of enthalpies of sublimation of metals and enthalpies of formation of the ionic solids on the other.

It does not follow necessarily that a model tested and found satisfactory on the simple cubic halides will be valid for structures of greater complexity and lower symmetry.

The van der Waals energy terms can be evaluated adequately in a manner [33, 34, 24] which avoids the uncertainties in estimating the so-called characteristic energies [4, 23, 35, 36]. If the cohesive energy is required at temperatures other than 0 K, as is usual, then it must be borne in mind that the omission of the equation-of-state function [1, 36] will produce a discrepancy which is between 2% and 3% of the cohesive energy. In the particular case of sodium chloride, the best measure of the cohesive energy is probably -774 kJ mol^{-1}. If the equation-of-state function is omitted, the result is -757 kJ mol^{-1}. It may be noted that while this function is explicit in derivatives of the Born–Mayer type of equation [17], it is implicitly present in the Huggins–Mayer term-by-term calculation [2], for it must be included in the assigned value of ρ. It is suggested that these points are not insignificant where cohesive energies are used to obtain thermodynamic parameters, as the uncertainties in the energies must be transmitted to the derived quantities.

It seems likely, however, that where cohesive energies lead to charge distributions which are in good agreement with the currently best MO calculations (Table 1), such energies may be taken to be reliable.

Further work will be directed towards two-parameter species. Preliminary results along these lines have shown that in ClO_3^-, for example, equilibrium geometry occurs for Cl–O = 1.65 Å, O–Cl–O = 111° and $z_0 = -0.70$ e. Cohesive energy results for $NaClO_3$ [41] lead to a value of -0.8 e for z_0: these authors take note of earlier *ab initio* and other theoretical estimates of z_0, the most recent of which [5] gives the numerically smaller value of -0.24 for z_0.

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