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Structural, Vibrational and Electronic Properties of a Crystalline Hydrate from *ab initio* Periodic Hartree–Fock Calculations

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Abstract

The hydrate crystal lithium hydroxide monohydrate LiOH.H₂O has been studied by *ab initio* periodic Hartree–Fock calculations. The influence of the crystalline environment on the local molecular properties (molecular geometry, atomic charges, electron density, molecular vibrations and deuterium quadrupole coupling constants) of the water molecule, the lithium and hydroxide ions has been calculated. A number of crystalline bulk properties are also presented; optimized crystalline structure, lattice energy and electronic band structure. The optimized cell parameters from calculations with a large basis set of triple-zeta quality differ by only 1–3% from the experimental neutron-determined cell, whereas the STO-3g basis set performs poorly (differences of 5–10%). With the triple-zeta basis also the atomic positions and intermolecular distances agree very well with the experiment. The lattice energy differs by ~8% from the experimental value, and by at most 3% when a density-functional electron correlation correction is applied. Large electron-density rearrangements occur in the water molecule and in the hydrogen bond and are in qualitative and quanti-

tative agreement with experimental X-ray diffraction results. The quadrupole-coupling constants of the water and hydroxide deuterium atoms are found to be very sensitive to the O–H bond length and are in good agreement with experimental values when the calculation is based on the experimental structure. The anharmonic O–H stretching vibrations in the crystal are presented and found to be very close to results from calculations on molecular clusters. The electronic band and density-of-states spectra are discussed. Model calculations on a hydrogen fluoride chain were used to rationalize the results.

Introduction

The water molecule and its unique binding properties are of interest to both experimentalists and theoreticians. Crystalline hydrates have consequently been extensively characterized experimentally. The effect of the crystalline environment on the structure, vibrations, electron density, quadrupolar coupling constants *etc.* of the water molecule have been investigated in many hundreds of diffraction and spectroscopic studies (*e.g.* Falk & Knop, 1973;

Olovsson & Jönsson, 1976; Berglund, Lindgren & Tegenfeldt, 1978*a,b*; Chiari & Ferraris, 1982; Hermansson, 1984; Mikenda, 1986; Lutz, 1988). Among the crystalline hydrates one finds examples of a wide variety of water environments, from very weakly to very strongly bound molecules. This is reflected in the broad ranges of measured H...O hydrogen-bond distances (from, say, 3.2 down to 1.65 Å), OH vibrational frequency downshifts (from -150 to ~ -1000 cm⁻¹) and deuteron quadrupole coupling constants (from 240 down to ~ 170 kHz for the most strongly bound water molecules).

The theoretical approach to the study of hydrates has commonly been to use quantum-mechanical calculations on a cluster, often immersed in a set of point charges to represent the more distant part of the crystalline environment. Different variants of the charge-embedded cluster approach have been highly successful in many cases (*e.g.* Almlöf, Lindgren & Tegenfeldt, 1972; Almlöf, Kvik & Thomas, 1973; Lindgren & Tegenfeldt, 1974; Hermansson & Lunell, 1982; Lunell, 1984; Krijn & Feil, 1988; Ojamäe & Hermansson, 1992; Ojamäe, 1993), but there are inherent difficulties and limitations within this approach. First, it assumes that it is possible to identify a molecule or a cluster within the crystal. This will be rather straightforward for many inorganic crystals, but boundary effects, more or less serious for different properties and different crystals, will invariably occur. Second, the correct provision for the long-range electrostatic interactions, beyond the supermolecular cluster, is vital because of the slow convergence of the electric field generated by the external charges. This can be handled, however; one method is to calculate the Madelung potential in a grid over the supermolecule and adjust the magnitude of a small number of point charges to reproduce this potential (Almlöf *et al.*, 1972). The atomic charges in the crystal first need to be chosen, preferably in a self-consistent manner. The major limitation with the supermolecular or cluster method is, however, that only local properties can be studied. Properties such as lattice energies, equilibrium structures and electronic spectra are out of reach.

The periodic Hartree-Fock method, as implemented in the *CRYSTAL92* program (Pisani, Dovesi & Roetti, 1988; Dovesi, Saunders & Roetti, 1992), makes it possible to investigate such 'new' crystalline properties. In the periodic Hartree-Fock approach (André, Gouverneur & Leroy, 1967; Del Re, Ladik & Biczo, 1967; Pisani *et al.*, 1988), the Schrödinger equation is solved with respect to the crystal orbital rather than the molecular orbital. The crystal orbitals are expressed as linear combinations of atomic orbitals (CO-LCAO) of the same type as those used in molecular Hartree-Fock calculations. During many decades a vast body of knowledge has

been built up concerning Hartree-Fock type calculations for molecules (not least with respect to the choice of basis sets). This experience is directly transferable to the periodic Hartree-Fock method.

This is a study of the molecular and bulk properties in a complex molecular crystal using quantum-mechanical *ab initio* methods. Molecular crystals have not been much studied by periodic calculations; the electron density of urea by Dovesi, Causà, Orlando, Roetti & Saunders (1990) was a pilot study. The crystal under study here is LiOH.H₂O, an ionic hydrate where the water molecule is strongly bound, as is manifested by the short H...O distance [1.684 (1) Å] (Hermansson & Thomas, 1982), the large OH frequency downshift (-930 cm⁻¹) (Berglund *et al.*, 1978) and the low ²H quadrupole coupling constant (173 kHz) (Clifford, Smith & Temme, 1975). There are several reasons behind our choice of this compound for a periodic Hartree-Fock study. In LiOH.H₂O many types of interaction play a role: covalent bonds, ionic and dipolar forces and strong water...OH⁻ hydrogen bonds. Another interesting structural feature is the occurrence of infinite linear OH⁻ chains in the crystal. The present study investigates how well the periodic *ab initio* Hartree-Fock calculations can perform for water-containing mixed molecular-ionic crystals.

Another important reason for choosing this compound is the fact that cluster-type calculations have already been made for some molecular properties in this crystal: electron density by Hermansson & Lunell (1982) and OH vibrational frequencies of water by Ojamäe & Hermansson (1992) and of the hydroxide ion by Hermansson (1992). These earlier cluster results enable a straightforward comparison between the two approaches.

In this study we present periodic *ab initio* results for the LiOH.H₂O crystal using both an extensive and a small basis set, and comparisons are made with experimental results and, where feasible, with results from the calculations on charge-embedded molecular clusters. Electron-difference densities, lattice energies, optimized structures, quadrupole-coupling constants, vibrational frequencies and electronic band and density-of-states spectra are reported.

Method

1. Crystal structure

The crystal structure and deformation electron density of LiOH.H₂O have been studied experimentally by a combination of X-ray and neutron diffraction measurements at 295 K (Hermansson & Thomas, 1982); see Table 1. The crystallographic unit cell is fairly small, with four asymmetric units

Table 1. Crystallographic data for the $\text{LiOH}\cdot\text{H}_2\text{O}$ crystal (from Hermansson & Thomas, 1982)

The experimental neutron-diffraction determined atomic positions are given for the five atoms in the asymmetric unit and are expressed as fractional cell coordinates. Here and in the following tables experimental structural parameters always refer to the Neutron 1 results in Hermansson & Thomas (1982).

Space group	Monoclinic $C2/m$		
a (Å)	7.4153 (2)		
b (Å)	8.3054 (2)		
c (Å)	3.1950 (1)		
β (°)	110.107 (4)		
V (Å ³)	184.78		
Z	4		
Li	x, y, z	0	0.34790 (26) 0.5
O1	x, y, z	0.28600 (10)	0 0.39592 (32)
OW	x, y, z	0	0.20668 (8) 0
H1	x, y, z	0.26534 (27)	0 0.67367 (64)
HW	x, y, z	0.11126 (16)	0.13264 (13) 0.13891 (48)

each consisting of one Li^+ atom, one OH^- ion, the water O atom and one water H atom. The primitive cell contains two asymmetric units (see Fig. 1). The water molecule coordinates to two lithium ions and forms two hydrogen bonds to two hydroxide ions; these hydrogen bonds are unusually short [$R(\text{HW}\cdots\text{O1}) = 1.68$ Å] for hydrogen bonds involving a water molecule. The hydroxide ions form almost linear hydrogen-bonded chains, two per primitive unit cell, running in opposite directions essentially parallel to the crystallographic c axis. The space group is $C2/m$.

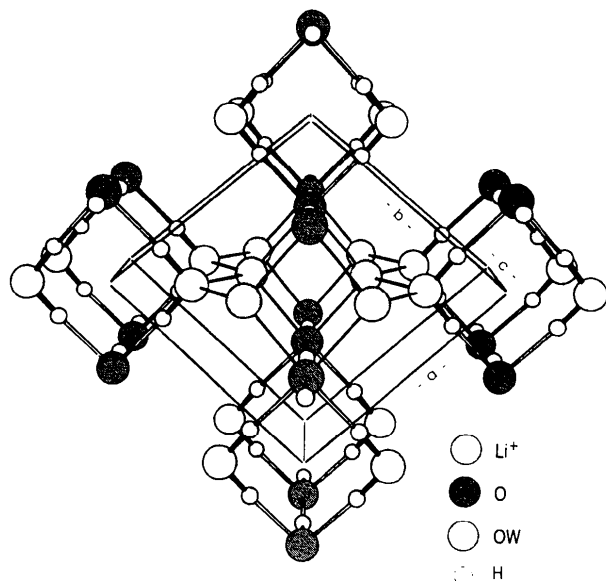


Fig. 1. The $\text{LiOH}\cdot\text{H}_2\text{O}$ crystal structure as viewed down the c axis of the primitive unit cell [a stereographic picture of the crystallographic $C2/m$ cell can be found in the article by Hermansson & Thomas (1982)].

2. Periodic Hartree-Fock method

The periodic Hartree-Fock CO-LCAO method, as implemented in the *CRYSTAL92 ab initio* program (Dovesi *et al.*, 1992), was used for the present calculations. The method is explained by, for example, Pisani *et al.* (1988) or Dovesi *et al.* (1990), and shows many similarities with the usual Hartree-Fock method for molecules. The same strengths (accurate self-consistent exchange as well as Coulomb terms) and weaknesses (lack of correlation energy) are valid for the Hartree-Fock solutions. The same caution concerning the choice of basis sets applies. There are, however, some additional features, due to the crystal periodicity, that need to be recognized. The basis functions used are actually infinite Bloch functions, formed from the local Gaussian basis functions. Since the crystal wave function extends throughout the whole periodical lattice, the matrix form of the Schrödinger equation needs to be solved for each reciprocal lattice vector (in the present calculation, a grid of $4 \times 4 \times 4$ points in the first Brillouin zone was found to give well converged results). Another difference from a conventional Hartree-Fock calculation is the treatment of the influence from molecules at long range. In the *CRYSTAL92* program, Coulomb integrals with atomic orbital overlaps larger than a given threshold are evaluated exactly, whereas the charge distribution of more distant atoms are expressed as multipolar expansions, with the electron-multipolar series evaluated by the Ewald method (Saunders, Freyria-Fava, Dovesi, Salasco & Roetti, 1992).

3. Basis sets and electron correlation

The basis set consisted of Gaussian-type functions, as commonly used in molecular calculations. Two different basis sets were used: the first one consisted of the minimal STO-3g basis sets for O and H (Hehre, Radom, Schleyer & Pople, 1986) and the Huzinaga (1984) 1s basis set for Li^+ . The larger basis set was of triple-zeta quality for oxygen and double-zeta for the lithium ion and H atoms, with polarization functions on all atoms; this basis is hereafter collectively referred to as the '8-411g**' basis set, following the nomenclature of Hehre *et al.* (1986).

More precisely, in the 8-411g** basis set, the H-atom basis was the Pople 3-1g** basis (which is incorporated in the '6-31g**' package), whereas the precursors of our Li^+ and O bases were basis sets that have been used in calculations on Li_2O by Dovesi, Roetti, Freyria-Fava, Prencipe & Saunders (1991). A second sp shell was added to the Li^+ 6-1g basis, and the exponent of the split-valence outer uncontracted Gaussian was optimized for the $\text{LiOH}\cdot\text{H}_2\text{O}$ crystal by minimizing the crystal energy with respect to the exponent to better represent its

less ionic character compared with the Li_2O crystal. This was also performed for the two outer *sp* shells of the O 8-411g** basis. The optimized exponent of the new *sp* shell of Li^+ was 0.216 and the re-optimized exponents of the two outer O *sp* shells were 0.478 and 0.174. The coefficients and the other exponents were the same as in the work by Dovesi *et al.* (1991).

In a series of preliminary calculations we employed the 6-21g** basis set (Hehre *et al.*, 1986) for O. This led to a very non-ionic (and unphysical: in the experimental electron-density map Li appears to be 'ionic' rather than 'atomic') crystal. When the Li^+ basis set was subsequently optimized, a very diffuse, and in fact non-converging, Li^+ outer-valence shell resulted. Only when the O basis was increased did the Li^+ basis, and the resulting water and hydroxide Mulliken charges as well, behave in a more physical manner. The O 6-21g** basis set may thus be deficient for studies of mixed ionic-covalent crystals (*cf.* Nada, Catlow, Dovesi & Saunders, 1992).

A problem connected to the basis-set size is that of the basis-set superposition error, *i.e.* for limited basis sets the calculated interaction energy becomes too attractive because the basis set of the total system is larger than the sets of the isolated monomers. One way to correct the interaction energies for this effect is to use the counterpoise correction scheme (abbreviated as 'CP' in our tables), where the energies of the monomers are calculated on the basis of the total system (Boys & Bernardi, 1970). The two kinds of computed interaction energies – with or without the CP correction – are generally believed to at least bracket the true interaction energy, and most people seem to regard the counterpoise-corrected energies to be closest to the truth. Here, we report the resulting energies both with and without the counterpoise-correction scheme.

The major deficiency of the Hartree-Fock method is its neglect of the electron correlation, *i.e.* each electron experiences an average field from the other electrons instead of the actual field. Presently, no true *ab initio* correlation-energy calculation method is implemented in the *CRYSTAL92* program; therefore, a different route was followed. The correlation energy was estimated *a posteriori* from correlation-energy-only density functionals (Harrison, Saunders, Aprà, Causà & Dovesi, 1992; Causà, Dovesi & Roetti, 1991). The correlation energy is assumed to be a function of the electron density, and the form of this function usually stems from free-electron gas theory (Parr & Yang, 1989). The function may be of local or non-local character, where non-locality implies that the correlation-energy function is also a function of electron-density derivatives. Some different forms of the function were tried (Colle &

Table 2. *Lattice energies (kJ per mole of formula units) calculated for the experimental geometry*

The experimental value is derived from Weast (1983), extrapolated to 0 K, and the zero-point vibrational contribution was subtracted using the vibrational spectrum from, *e.g.* Berglund *et al.* (1978a), assuming harmonic oscillators. The calculated lattice energy is relative to the monomers with experimental gas-phase geometries. The counterpoise (CP) correction is discussed in the text. HF: Hartree-Fock; CA-LDA: Ceperley & Alder (1980) local density approximation; CS: Colle & Salveti (1975); P86: Perdew (1986); P91: Perdew *et al.* (1992).

	Calculated				Experimental	
	STO-3g		8-411g**		298 K	0 K
	No CP	CP	No CP	CP		
HF	1255	1051	1105	1075		
CA-LDA			1140	1116	1130	
CS			1210	1183	ZPE removed	1160
P86			1194	1170		
P91			1177	1154		

Salveti, 1975; Ceperley & Alder, 1980; Perdew, 1986a,b; Perdew *et al.*, 1992).

Results

1. Lattice energies

The lattice energy of the crystal with respect to its building blocks of isolated H_2O molecules and isolated OH^- and Li^+ ions was calculated for the experimental neutron-diffraction determined crystal structure. The results using the small and large basis sets, with and without the CP correction, are given in Table 2. The basis-set superposition error is seen to be non-negligible: the total energy of the isolated water molecule decreases by 5 kJ mol^{-1} and that of the hydroxide ion by 26 kJ mol^{-1} when their 8-411g** basis sets are augmented by the basis sets on their 'ghost neighbours'. The free lithium ion energy is not affected by the penetration of the basis sets belonging to the neighbours. All in all, the large CP correction found here (especially for the smaller basis set) is a consequence of the close-packed atomic arrangement in the crystal. The different density functional schemes are seen to give rather disparate results; the correlation-energy correction works in the opposite direction to the CP correction and adds $30\text{--}110 \text{ kJ mol}^{-1}$ to the interaction energy at the 8-411g** level. The resulting theoretical lattice energy is in excellent agreement with the experiment, only $\sim 3\%$ away from the experimental (zero-K, zero-point vibrational energy-corrected) value. Especially the most recent density functional (Perdew *et al.*, 1992) is seen to give a counterpoise-corrected lattice energy, which is very close to the experimental value.

2. Geometry optimization

Minimization of the total energy with respect to the cell dimensions and atomic positions was per-

formed at the Hartree–Fock level of theory. It was achieved by performing a linear search for each parameter in turn. In each cycle this was performed for all parameters. The iteration was ended when the change in energy between each cycle was less than 0.1 kJ per mole of formula units. For the 8-411g** basis set this required five cycles; for the STO-3g basis 24 cycles, starting from the experimental structure. The *CRYSTAL92* program utilizes the symmetry properties of the space group. This greatly reduces the computational cost, and, therefore, we maintained the same space group throughout the minimization process. For the STO-3g basis set we checked that the minimum obtained was indeed a true one (within the given space group) using a normal-coordinate analysis: no imaginary frequencies were obtained. The gradients were calculated numerically since at present there are no analytical gradients in *CRYSTAL92*. For the 8-411g** basis set, we deemed a normal coordinate analysis too costly. The heavy computational demand is also the reason why a more refined optimization procedure, like the Newton–Raphson method, was not used. Each energy-point calculation took about 8 CPU-min on an IBM RS/6000-320H workstation and requires about 10 Mb of storage at the STO-3g level; the corresponding numbers for the 8-411g** basis are 218 min and 1.4 Gb.

The optimized energies, lattice parameters and atomic positions (expressed as fractional coordinates) are given in Table 3. The cell size from the STO-3g model is seen to be too small and the energy difference between the optimized and the experimental structures is consequently large. The basis-set superposition error, which is large for small basis sets, generally has the effect of decreasing intermolecular distances. The situation is very different for the 8-411g** basis: compared with the experimental structure the optimized structure shows a slight cell expansion, possibly due to the neglect of cohesive van der Waals forces in the Hartree–Fock approximation. The relaxation energy is low.

The experimental structure was determined at 295 K and atmospheric pressure, whereas the theoretically optimized value is really for 0 K and zero pressure. The difference in pressure is negligible, whereas it is possible that close to 0 K the experimental lattice parameters could be smaller. However, the decrease is likely to be less than 0.1 Å.

Some inter- and intramolecular distances in the optimized structures are shown in Table 4. The STO-3g basis gives poor agreement with experiment. The intermolecular distances are well reproduced with the 8-411g** basis and generally lie within 0.1 Å from experiment. The calculated water O—H distance is shorter than the experimental value. It is a well known failure of the Hartree–Fock method that

Table 3. *Optimized geometries and the corresponding lattice energies, calculated with respect to the relaxed geometry of the monomers at the Hartree–Fock level*

In the last cycle of the optimization the shifts of the cell parameters were less than 0.01 Å and 0.1°, and for the atomic fractional coordinates less than 0.0003. The standard deviations of the experimental data are given in Table 1. Δx_i denotes the difference in fractional coordinates between the experimental and optimized structures. The uncertainty in the calculated optimized lattice energies is less than 0.1 kJ mol⁻¹, based on the shifts in the last optimization cycle. δE is the relaxation energy, that is, the difference in calculated lattice energy between optimized structure and the experimental structure.

Parameter	Calculated		Experimental	
	STO-3g	8-411g**		
<i>a</i> (Å)	6.70	7.64	7.42	
<i>b</i> (Å)	7.49	8.44	8.31	
<i>c</i> (Å)	3.03	3.24	3.20	
β (°)	114.0	110.9	110.1	
Li x_i, y_i, z_i	0	0.3534 0.5	0	0.3479 0.5
O1 x_i, y_i, z_i	0.2928 0	0.4073	0.2860 0	0.3959
OW x_i, y_i, z_i	0	0.2077 0	0	0.2067 0
H1 x_i, y_i, z_i	0.2753 0	0.6828	0.2653 0	0.6737
HW x_i, y_i, z_i	0.1067	0.1388 0.1300	0.1113	0.1326 0.1389
R.m.s. Δx_i	0.0144	0.0077	-	
δE (kJ mol ⁻¹)	98	7	-	
E_{lattice} (kJ mol ⁻¹)	1325*	1111†	1160	

* Relative to the optimized STO-3g monomer. H₂O: $r_{\text{eq}} = 0.989$ Å, $\theta = 103.8^\circ$; OH: $r_{\text{eq}} = 1.068$ Å.

† Relative to the optimized 8-411g** monomer. H₂O: $r_{\text{eq}} = 0.944$ Å, $\theta = 106.7^\circ$; OH: $r_{\text{eq}} = 0.949$ Å.

Table 4. *Distances (Å) and angles (°) for the optimized crystal structures and for the experimental structure*

	Calculated		Experimental
	STO-3g	8-411g**	
OW—HW	1.018	0.967	1002 (1)
O1—H1	0.987	0.947	0.951 (2)
HW...O1	1.451	1.813	1.684 (1)
H1...O1	2.052	2.300	2.259 (2)
Li ⁺ —OW	1.757	2.032	1.982 (1)
Li ⁺ —O1	1.768	1.946	1.965 (1)
HW—OW—HW	100.7	106.0	104.3 (1)
OW—HW—O1	174.0	173.9	174.8 (1)
O1—H1...O1	173.7	169.3	167.6 (2)
Li ⁺ —OW—Li ⁺	119.4	105.5	107.4 (1)
O1...OW...O1	96.0	101.7	100.5 (1)
Li ⁺ —O1—Li ⁺	86.5	79.0	80.0 (1)
(HW—OW—HW): (Li ⁺ —OW—Li ⁺) planes	98.6	99.7	101.7 (1)

it predicts intramolecular bonds to be too short. The O—H bond length in OH⁻, on the other hand, is very close to the experimental result. This is likely to be accidental and due to experimental error; a realistic estimate of the error in the experimental OH bond length is probably 0.01–0.02 Å, arising from non-rectilinear motion and anharmonicity, neither of which is properly handled in a regular crystallographic least-squares refinement (Eriksson, Berglund, Tegenfeldt & Lindgren, 1979). Further support for our conclusion that the experimental value is in error (too short) is given by charge-embedded cluster calculations performed for OH⁻ in this crystal

(Hermansson, 1992), where only the O—H bond was allowed to relax: the electron-correlation corrected OH distance for the charge-embedded OH^- cluster with a nearly saturated basis set was 0.968 Å. The corresponding Hartree–Fock value was 0.021 Å shorter, in close agreement with the present periodic Hartree–Fock results.

3. Electron densities

3.1. Effect of the environment on the electron density. One advantage with the periodic Hartree–Fock approach is the straightforward manner in which electron-density and deformation-density maps can be calculated, since no boundary effects are present and the crystal and isolated molecules are described at the same level of theory. Fig. 2 shows the difference in electron density between the crystal and the superposition of the isolated spherical atoms. In all the cases here, the calculations were based on the experimental neutron-diffraction determined structure. These maps can be directly compared with the corresponding experimental maps by Hermansson & Thomas (1982) (note, however, that in our calculation, Li instead of Li^+ is subtracted in the maps). The experimental density was corrected for thermal motion, so that effectively zero-K density maps were obtained. The agreement is very satisfactory, except in the oxygen lone-pair region where the limited experimental $\sin\theta/\lambda$ range renders the experiment

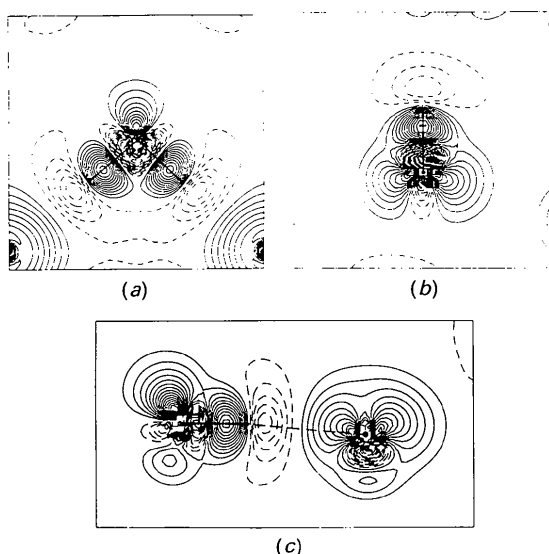


Fig. 2. The deformation electron density, $\rho^{\text{crystal}}(\mathbf{r}) - \sum \rho(\mathbf{r})_{\text{atoms}}$, in $\text{LiOH}\cdot\text{H}_2\text{O}$ calculated from the periodic Hartree–Fock 8-411g** calculations. The contour levels are $\pm 0.05 \text{ e } \text{\AA}^{-3}$. Electron excess is drawn as solid contours, electron deficiency as dashed contours and the zero level is omitted. The same contour levels are used in all figures. (a) In the water molecular plane; (b) in the mirror plane containing OH; (c) in the OW...HW...O plane.

incapable of reproducing very sharp electron-density features. The short hydrogen bond is very well reproduced by the calculation, and is in quantitative agreement with experimental values.

The intermolecular bonding effects are more easily distinguished in molecular difference maps, *i.e.* where the difference is mapped relative to the free molecules/ions. These maps are displayed in Fig. 3. For the water molecule in Figs. 3(a) and (b), the polarization of the molecule in the bulk is manifested in the depletion of the charge density at the H nuclei and a build up of electron density between the OH bonds towards the O atom. Fig. 3(b) also shows that the lone-pair electron density in the direction of the incoming bond is significantly decreased by the intermolecular bond. This was observed for the bound water molecule by Hermansson & Lunell (1982) and later on explained by Krijn & Feil (1987) as a result of occupied–unoccupied orbital mixing due to the perturbation from the electric field; the polarization occurs in fact in the intuitively expected direction if one takes into account the diffuse regions at the periphery of the molecule. The deformation in OH^- (Fig. 3c) shows the same general features as for H_2O . The hydrogen bond is shown in more detail in Fig. 3(d).

3.2. Comparison with cluster calculation results.

The electron density in the $\text{LiOH}\cdot\text{H}_2\text{O}$ crystal has previously been studied by cluster-type calculations at the double-zeta plus polarization (DZP) level (Hermansson & Lunell, 1982). Here we have recalculated those maps using the same basis set as that used in the periodic calculations and virtually the same crystal field, *i.e.* the CRYSTAL92 Mulliken charges were used to generate the Madelung field for the cluster calculations. The purpose of the comparison between the two methods was to be able to better assess the ability of the cluster approach to produce accurate crystal electron densities. Three examples, the molecular difference density in the water plane, in the OH^- plane and in the hydrogen-bond plane, are given in Fig. 4. These maps can be compared directly with the maps in Fig. 3. The two approaches are seen to render maps that are practically identical. For the hydrogen-bond section a special procedure was adopted: the left part of the map in Fig. 4(c) is from the calculations on the charge-embedded $(\text{Li}^+)_2(\text{OH}^-)_2\cdot\text{H}_2\text{O}$ water cluster while the right part is from the charge-embedded $(\text{Li}^+)_2(\text{H}_2\text{O})_2\cdot\text{OH}^-$ hydroxide cluster (the central molecule is denoted by bold letters). Unless this ‘mixed procedure’ is adopted for the map through the hydrogen-bond region, the cluster approach shows signs of boundary effects in the ‘outer parts’ of the map.

3.3. Mulliken charges. The calculated Mulliken charges are given in Table 5. The magnitude of the

charges calculated with the 8-411g** basis set is indicative of an ionic compound. The Mulliken charges in the 8-411g** cluster calculations (see previous paragraph) are listed for comparison and show that although the electron-density distribution at the $\pm 0.05 e \text{ \AA}^{-3}$ contour interval resolution looks very similar for the periodic and the cluster Hartree-Fock calculations, the differences are large enough to show up in the Mulliken charges. It is important to select the right cluster for the comparison, so, for example, the water cluster charges should be taken from the cluster calculations with the water molecule at the centre of the cluster. The 'edge molecules' have Mulliken charges that differ more from the periodic calculations. Angyán & Silvi (1990) compared STO-3g Mulliken charges for the LiOH.H₂O structure from a cluster, from a self-consistent Madelung potential (SCMP) and from a periodic Hartree-Fock

calculation, and the three methods gave rather disparate lithium as well as oxygen charges.

4. Quadrupole coupling constants

The deuterium nucleus has a quadrupole moment and will consequently interact with the electric field gradient at the position of the nucleus. This will manifest itself in a splitting in the NMR or NQR spectrum. The magnitude of the splitting is given by the quadrupole coupling constant, e^2qQ/h , where eQ is the quadrupole moment of the nucleus and $eq = -V_{zz}$ (V_{zz} being the magnitude of the electric field gradient along the main principal axis). The quadrupole coupling constant has experimentally been found to be very sensitive to the hydrogen-bond strength, and has, therefore, been used to characterize a wide range of deuterated crystalline hydrates (Berglund *et al.*, 1978*b*, and references therein). The calculated deuteron quadrupole coupling constants in LiOH.H₂O are shown in Table 6. The constants for the water and hydroxide deuterium have been measured experimentally by Clifford *et al.* (1975). We find that when the calculation is based on the experimental structure, the agreement between calculated and experimental constants is very good for water but not for the hydroxide ion. As will be explained in the next paragraph, this is consistent with the fact that the experimental O—H distance in the hydroxide ion is probably too short.

Experimentally, the quadrupole coupling constant for D in water is downshifted 140 kHz compared

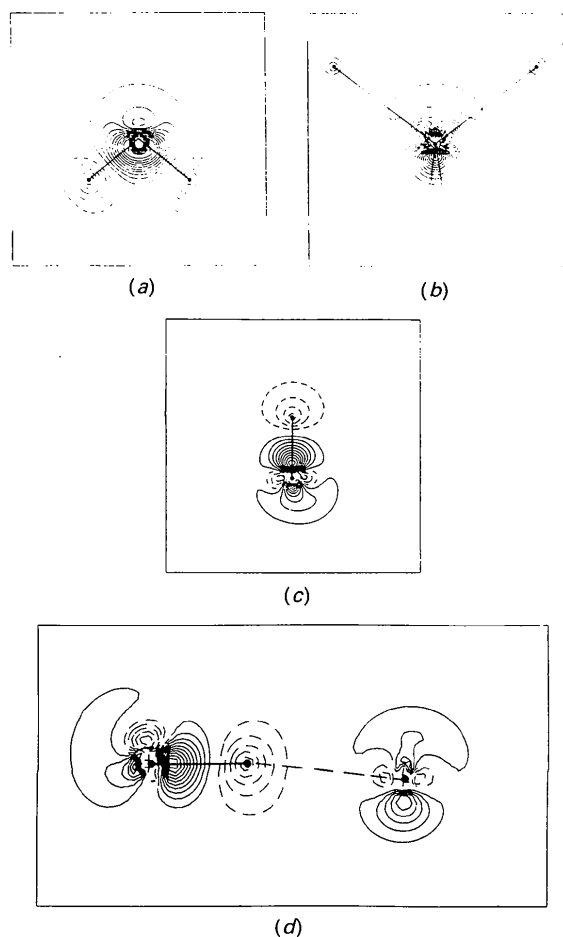


Fig. 3. $\rho^{\text{crystal}}(\mathbf{r}) - [\sum\rho(\text{H}_2\text{O}) + \sum\rho(\text{OH}^-) + \sum\rho(\text{Li}^+)]$ in LiOH.H₂O calculated from the periodic Hartree-Fock 8-411g** calculations. (a) In the water molecular plane; (b) in the Li⁺—OW—Li⁺ plane; (c) in the mirror plane containing OH⁻; (d) in the OW—HW...Ol plane.

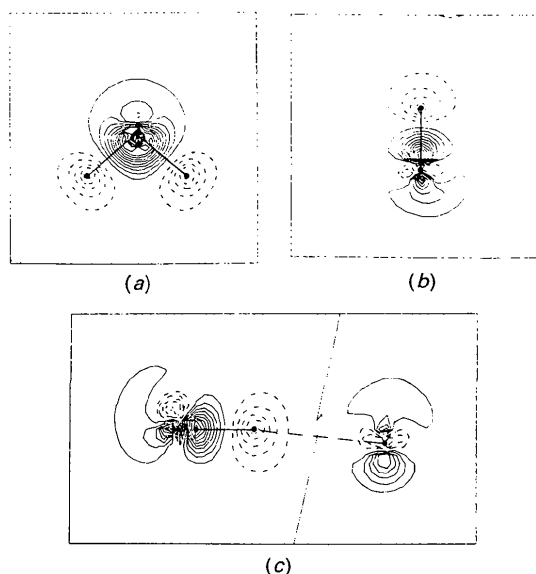


Fig. 4. $\rho^{\text{crystal}}(\mathbf{r}) - [\sum\rho(\text{H}_2\text{O}) + \sum\rho(\text{OH}^-) + \sum\rho(\text{Li}^+)]$ in LiOH.H₂O calculated from the charge-embedded cluster calculations at the 8-411g** level. (a) In the water molecular plane; (b) in the mirror plane containing OH⁻; (c) in the OW—HW...Ol plane.

Table 5. *Mulliken charges for the experimental crystal structure*

The values from the charge-embedded cluster approach (with the same field as in the periodic Hartree-Fock 8-411g** calculations) are given for comparison. The 'H₂O cluster' consists of an H₂O molecule plus its nearest neighbours, and correspondingly for the 'OH⁻ cluster'. For the OH⁻ cluster there are two entries for three of the atoms. The first O1 and H1 charges belong to the 'central ion' and the second ones to the ion closest to its H atom. The first HW atom in the list is the one hydrogen bonding to the central OH⁻ ion, and the second HW is pointing out towards the set of crystal-field point charges.

Atom	Periodic Hartree-Fock		H ₂ O cluster 8-411g**	OH ⁻ cluster 8-411-g**
	STO-3g	8-411g**		
Li	+1.000	+0.980	+1.000	+1.000
O1	-0.780	-1.331	-1.418	-1.344, -1.407
OW	-0.612	-1.013	-1.045	-1.061
H1	+0.005	+0.416	+0.418	+0.441, +0.400
HW	+0.194	+0.474	+0.535	+0.523, +0.496

Table 6. *Calculated quadrupole coupling constants for the deuterium atoms in LiOH.H₂O for two different unit cells, the experimental and the geometry-optimized, using the 8-411g** basis set*

Values in kHz. Experimental values from Clifford *et al.* (1975).

	Experimental	Calculated	
		Expt. structure	Opt. structure
D in D ₂ O	173	180	256
D in OD	272	347	358

with the free D₂O value of 307 kHz (Verhouven, Dymanus & Bluysen, 1969). Also the experimental downshift is well reproduced by our calculations, because the free-water quadrupole coupling constant is ~325 kHz at the 8-411g** level, *i.e.* fairly close to the experimental value. Fig. 5 shows the variation of the quadrupole coupling constant for an isolated D₂O molecule as a function of the O—D distance. We find this plot to be quite insensitive to the basis-set quality, *i.e.* for a fixed molecular geometry, the electric field gradient is not very sensitive to the basis-set quality. The points corresponding to the LiOH.H₂O quadrupole coupling constant calculated for the experimental and for the optimized geometries are included in the plot. We see that a large part of the total electric field gradient at the D site originates from the electron distribution within the molecule/ion itself. We furthermore note that a lengthening of the O—D bond results in a lower quadrupole coupling constant and that approximately 60% of the downshift in LiOH.H₂O originates from the intramolecular geometry change. The remaining 40%, or ~50 kHz, is due to the 'direct' field from the external molecules/ions as well as from the electron rearrangement they give rise to within the 'central' water molecule. Almlöf *et al.* (1972) performed *ab initio* calculations on a water molecule embedded in different point-charge fields

that mimicked the crystal field in NaHC₂O₂.D₂O and LiHC₂O₂.D₂O, and concluded that for these two compounds, where the water molecules are much less strongly bound than in LiOH.H₂O, about 90% of the reduction of the quadrupole coupling constant because of the water environment was a result of the O—D bond lengthening.

5. Vibrational frequencies

The shift in the water OH stretching frequency because of the environment is an often used experimental tool to elucidate intermolecular bond strengths and local structure (Falk & Knop, 1973; Berglund *et al.*, 1978*a,b*). We have calculated here the anharmonic OH frequencies of the water molecule and the hydroxide ion from the potential-energy curves of these protons in their crystalline environments (Wójcik & Lindgren, 1983). Accurate measurements by the isotope-isolation technique exist for the uncoupled stretching vibrations of both the water molecule and the hydroxide ion. For H₂O, the C₂ axis was removed in the calculation: otherwise, the symmetric stretching rather than the uncoupled OH vibration would be modelled. The calculated vibrational frequencies as well as the frequency shifts with respect to the free molecule/ion are given in Table 7. OH frequencies calculated by the Hartree-Fock method are generally too high and it may therefore be better to study the shift relative to the free-monomer frequency. However, the

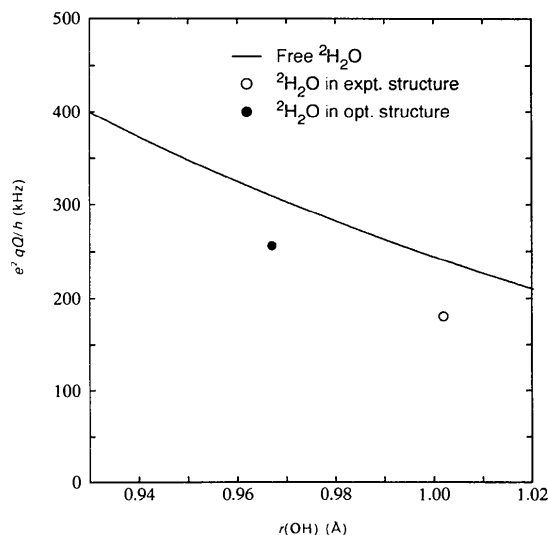


Fig. 5. The quadrupole coupling constant of a free water molecule as a function of O—H distance, calculated at the Hartree-Fock level with the 8-411g** basis set. The water angle was set to 104.52° and the non-flexible OH bond was 0.9572 Å. The experimental and calculated (periodic Hartree-Fock 8-411g**; at the optimized geometry and at the experimental geometry) values for LiOH.H₂O are included in the plot.

Table 7. OH vibrational frequency shifts (cm^{-1}) from the periodic and cluster calculations with the 8-411g** basis set

Shifts are given relative to the frequencies of the free water molecule [calculated 4005, experimental 3707 cm^{-1} (Benedict, Gailar & Plyler, 1956)] and hydroxide ion [calculated 3801, experimental 3556 cm^{-1} (Owrutsky, Rosenbaum, Tack & Saykally, 1986)].

Molecule	Periodic		Cluster		Experimental	
	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
H ₂ O	3329	-676	3316	-689	2775	-932
OH ⁻	3929	+128	3897	+96	3575	+19

Table 8. Calculated OH⁻ vibrational frequencies for infinite OH⁻ chains

O...O distances are 3.20 Å. The monomer frequency is 3801 cm^{-1} .

System	Frequency (cm^{-1})
Each O—H vibrating	3869
Every second O—H vibrating	3871
Every third O—H vibrating	3872

systematic error is only partly circumvented in this way and the major part of the discrepancy between the calculated and experimental shifts can be attributed to the omission of electronic correlation energy and the limited basis set used in the calculation (Ojamäe & Hermansson, 1992). We note that the calculated frequency shifts in Table 7 are at least in qualitative agreement with experimental values.

5.1. Comparison with frequencies from cluster calculations. The vibrational OH frequencies in the LiOH.H₂O crystal have previously been studied by charge-embedded cluster calculations. These calculations were made at the double-zeta plus polarization (DZP) level for water using a $(\text{Li}^+)_2(\text{OH}^-)_2\cdot\text{H}_2\text{O}$ cluster (Ojamäe & Hermansson, 1992) and at the DZP and near the Hartree-Fock limit levels for OH⁻ with an $(\text{Li}^+)_2\text{H}_2\text{O})_2\cdot\text{OH}^- \cdot \text{OH}^-$ cluster (Hermansson, 1992). Here we have repeated these calculations using the 8-411g** basis set and the same crystal fields as in the periodic calculations (Table 7). The frequencies are seen to be very similar to the periodic results: the water frequency differs by only +13 cm^{-1} and the OH⁻ frequency by +32 cm^{-1} . In the cluster case, the vibrations are truly uncoupled. In the periodic case we actually calculate the phonon modes rather than the uncoupled vibrations. Such couplings may influence the results. One might expect that the hydroxide ion which hydrogen bonds to other symmetry-related neighbouring hydroxide ions will be more affected than the water molecule which does not have any replicas as bonded neighbours. On the other hand, the OH⁻...OH⁻ distance is rather long. We have performed model calculations for an infinite chain of OH⁻ ions and investigated the effect of allowing each molecule to vibrate in phase, allowing every

second molecule to vibrate in phase while keeping the others still *etc.* Table 8 shows that the coupling with the neighbours creates only a small downshift for OH⁻. This is thus not the origin of the (small) difference found between periodic and non-periodic frequency results for OH⁻.

6. Electronic energy structure

We have seen that for LiOH.H₂O the Hartree-Fock cluster calculations can compete with the more accurate periodic calculations as far as local molecular properties such as electron densities and intramolecular vibrational frequencies are concerned. One property which is impossible to obtain by the former method is the electronic band structure. The electronic orbital energies will be functions of the periodicity or wave vector of the crystal orbital. For those molecular crystals where there is little covalent contribution to the intermolecular bonding, the energy levels in the band spectrum are usually expected to be flat and horizontal. Inspection of the band spectrum for LiOH.H₂O in Fig. 6 shows that although many band energies vary only a little with the wave vector, there are also several high-dispersion bands. This is particularly apparent along the [001] direction for the band that has an energy ~ -0.56 eV for $k = 0$ (band C). This band was identified to correspond

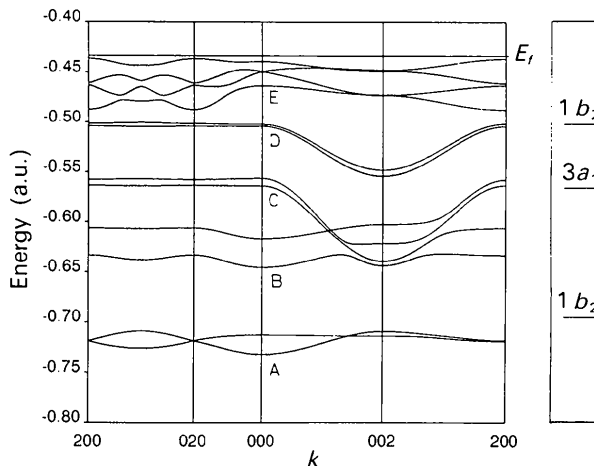


Fig. 6. The electronic band spectrum for LiOH.H₂O. E_f is the Fermi level. The wavevector (k_x, k_y, k_z) on the x axis is given in units of the reciprocal (primitive) cell lengths times 1/4. Main features of the bands A: OW(*p*)—HW(*s*) bonding; B: OW *sp* lone-pair orbital along the water bisector; C: O1—H1 weakly bonding; D: OW *p* lone-pair orbital perpendicular to the water molecule plane. The energy levels of the free water molecule have been indicated on the right-hand side of the figure. Since in the free water molecule b_2 is the *p*_z(OW)—1*s*(HW) bonding orbital, a_1 the *sp*_z(OW) non-bonding orbital along the water bisector and b_1 the *p*_x perpendicular lone-pair orbital, the water molecular orbital energy levels can be thought of as being transformed upon solvation in the crystal as: $b_2 \rightarrow A$, $a_1 \rightarrow B$ and $b_1 \rightarrow D$.

to the weakly bonding σ orbital in OH^- . The OH^- chain runs along the [001] direction. The dispersion can thus be suspected to come from the change in interaction energy between the case where the sign of the orbital on each OH^- ion is the same and the case where the sign is altering between each neighbouring pair. This implies that there is a non-negligible covalent contribution to the bonding in the OH^- chain, as alleged for example in the textbook by Porterfield (1984). Model calculations were made for an infinite hydrogen fluoride chain, which is isoelec-

tronic with an hydroxide chain (Fig. 7). The bands in the band spectrum are relatively flat except for the band corresponding to linear combinations of the F—H weakly bonding σ orbitals. When the distance is decreased between the molecules, the dispersion increases. The appearance of the spectrum is analogous to that of the hydroxide chain. This is the 'band-spectrum' view of the hydrogen bond.

Also the bands around -0.50 show a large dispersion. This band consists mainly of the water molecule b_1 orbital, *i.e.* the p -orbital orthogonal to the

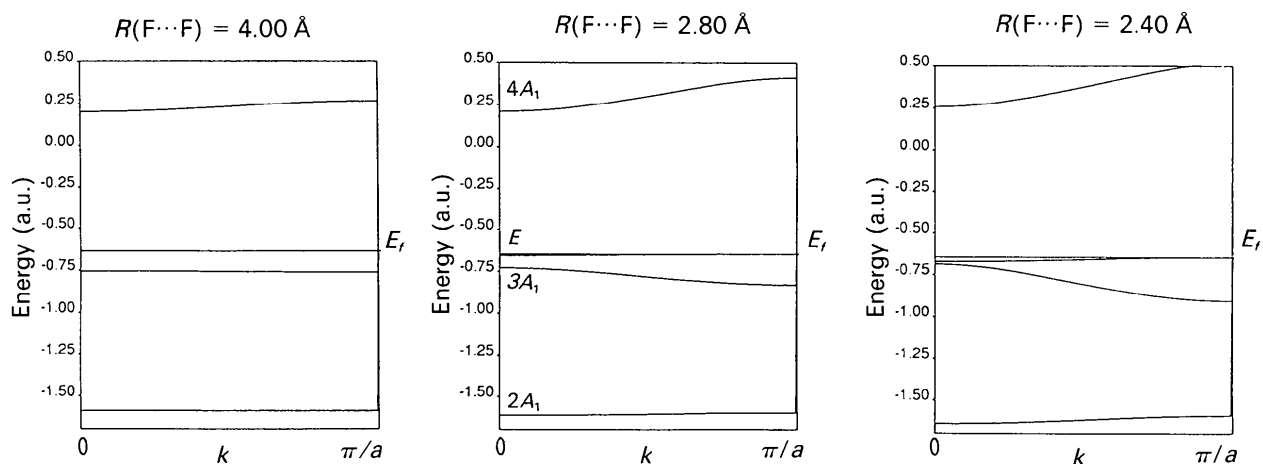


Fig. 7. Electronic band spectra of an infinite linear HF chain for three different F...F distances ($=a$ on the abscissa). The F—H distance was kept fixed at 0.90 Å. The 6-31g** basis set was used.

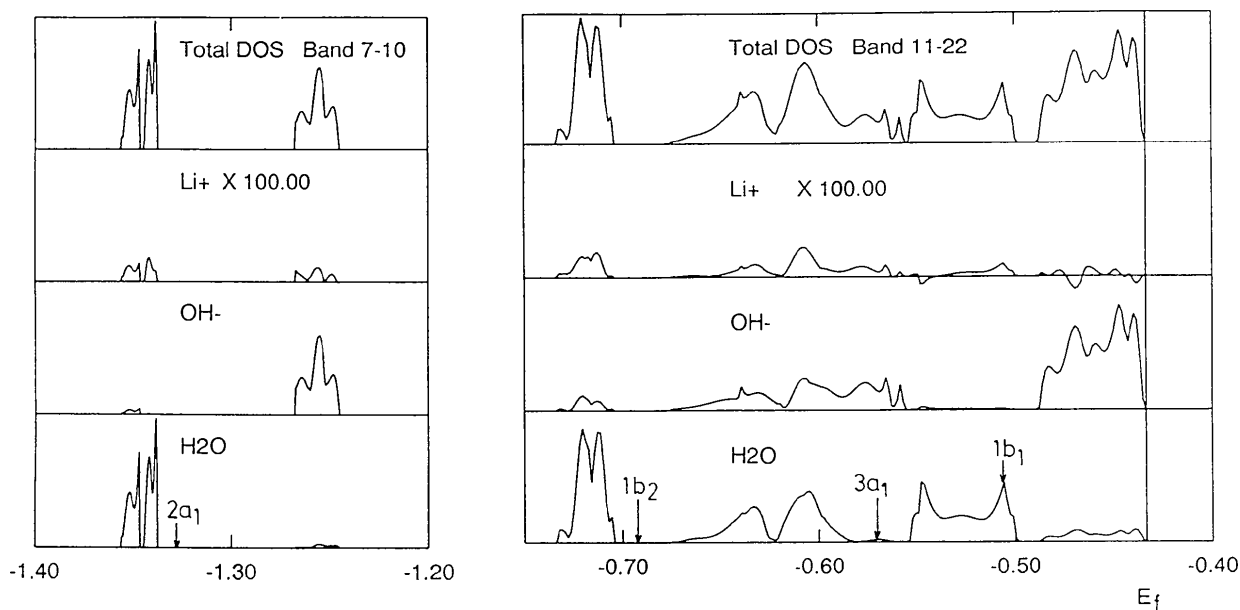


Fig. 8. The electronic density of states for $\text{LiOH}\cdot\text{H}_2\text{O}$. The position of the energy levels for the free water molecule have been indicated by arrows. The DOS projected on the atomic orbitals of the Li^+ ion has been enlarged by a factor of 100. E_f denotes the Fermi energy level. The energy scale on the x axis is in atomic units (1 a.u. = 27.2 eV).

plane of the water molecule. The water molecules which are one *c*-axis length apart (3.2 Å) are thus close enough to have some orbital overlap (although the sum of the van der Waals radii of the O atoms is only 2.8 Å). The density of states spectrum in Fig. 8 shows the broadening of the orbital energy levels in the bulk.

Concluding remarks

The LiOH.H₂O crystal is largely ionic in nature, as shown by the electron-density maps and the Mulliken charges, but there is a contribution of extended covalent bonding particularly in the hydroxide ion chains, as evidenced by the band spectrum.

Periodic Hartree-Fock calculations at the 8-411g** level can accurately model the LiOH.H₂O crystal both with respect to local properties, such as the quadrupole coupling constants and electron densities, and non-local properties such as lattice energies and crystal structure. Cluster calculations also give good results for properties such as the electron densities and vibrational frequencies, but cannot be used to derive, for example, lattice energies, optimized structure and electronic structure. It may also be that the cluster calculations underestimate the covalent bonding in the crystal.

Considering that LiOH.H₂O is a mixed ion/molecule system and thus exhibits a variety of bond types, the present results are promising for the future use of the crystal-orbital method. The major disadvantage is the high computational cost when large basis sets are used, which is necessary if structural optimizations are to be made. The major advantage is the abundance of crystal information that can be obtained from the calculations. For example, the accurate electron-density calculations are an attractive feature for structural chemists and crystallographers, and the accurate lattice energies make interesting structural-stability studies possible.

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***Ab initio* Hartree–Fock Study of Lithium and Sodium Sulfides: Electronic and Scattering Properties**

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Abstract

The electronic structure of lithium sulfide and sodium sulfide in the solid state is established at the Hartree–Fock level, as implemented in the *CRYSTAL* program. Two all-electron basis sets are adopted for each compound. Mulliken analysis, band structure, density of states and electron charge density are studied: these exhibit the highly ionic character of both compounds; this seems rather surprising because of the weak electronegativity and large polarizability of the sulfur. Form factors of the sulfur are deduced from the structure factors and analysed in order to show the deformations of this anion in the crystal environment. Finally, electron momentum density and Compton profiles confirm the almost fully ionic character of the compounds and prove the quality of the calculated wavefunctions.

1. Introduction

Lithium sulfide (Li_2S) and sodium sulfide (Na_2S) are the first two compounds of a series of two and five polysulfides, respectively, in the equilibrium phase diagram of the metal–sulfur system (Oei, 1973); their study presents particular interest in the development of new solid-state batteries, since the metal polysulfides are well known for their outstanding electrical properties, including fast ionic conduction (Janz & Rogers, 1981; Kizilyalli, Bilgin & Kizilyalli, 1990).

These two compounds belong to the family of the alkaline sulfides: they have the same antifluorite-type structure, with the F_{m3m} space group. In spite of their simple and symmetric structure, there is a relative lack of physical data, particularly in the elastic and inelastic scattering field. Among the principal and most recent results, those obtained by Bühner, Altorfer, Mesot, Bill, Carron & Smith (1991) and Bühner & Bill (1977, 1980), from inelastic neutron scattering, can be cited: the phonon-dispersion curves established at low temperatures allowed these authors to compute lattice dynamic properties, such as elastic constants and mean-square ionic displacements.

To explain the scarcity of experimental X-ray data, Kizilyalli *et al.* (1990) highlight numerous difficulties in the preparation and handling of Na_2S and in the rapid deterioration of the samples exposed to X-rays, and also the peculiarities of sulfide crystal structures.

In a few theoretical studies (Agnihotri, Singh & Sanyal, 1984; Jain & Shanker, 1982; Thakur & Pandey, 1975; Agarwal, Sharma, Sharma, Sharma & Shanker, 1977; Holbrook, Sabry-Grant, Smith & Tandel, 1990), interionic potentials are discussed and used to calculate binding energy, elastic constants, bulk modulus, Debye temperature and electron affinities of chalcogenide ions. It can be noted, therefore, that, among this data, there is nothing concerning the electronic structure of the two sulfide