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Application of Semi-Empirical Molecular Orbital Methods to the Calculation of Properties of Ionic Crystals

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Investigations are continued into the usefulness of semi-empirical molecular orbital techniques to the calculation of the electronic properties of ionic crystals. The cluster model is used, on which the molecular orbital calculations are made, with the remaining material approximated by the inclusion of a Madelung potential derived from those atoms not in the cluster.

Applications have been made to the bulk properties of LiF and MgO, with very good results. Surface properties of MgO have been investigated using a surface Madelung potential to represent the remaining crystal; the results in this case show a closure in the band gap on approaching the surface, which is consistent with experimental observations.

The long term aim of the work is to provide a simple, computationally viable method for the investigation of complex defects in ionic crystals. To this end we have performed a calculation on the *U* centre in LiF. Consistently good results have been obtained for all these properties showing that this is a viable method for these systems and that complex defects may be approached with some optimism that the method provides a useful tool.

Key words: LiF — MgO — Ionic crystals

1. Introduction

Semi-empirical molecular orbital methods have been developed for the study of large molecules where the use of *ab-initio* techniques, even in the one electron approximation, is precluded on computational cost grounds. Consequently methods have been devised which circumvent the direct calculation of two electron integrals by empirical parameters and numerical approximations. Obviously, such a procedure requires great care so that essential physical effects are not ignored.

There are many variants of the semi-empirical methods, but the most widely used are Extended Hückel Theory (E.H.T.) [1] and Complete Neglect of Differential Overlap (CNDO) [2]. The essential difference between them is that the CNDO calculations are taken to self consistency. The use of these methods in quantum chemistry is widespread and their behaviour is well documented [3].

Several attempts have been made to apply such techniques to problems concerning solids. In particular, Messmer and Watkins [4] have used E.H.T.

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extensively for calculations on covalent systems, notably diamond and its deep defect level and carbon interstitial [5]. These authors used a cluster approach, increasing the number of atoms treated to investigate convergence of cluster size. The results of this work were very encouraging, although the reservations pointed out by Larkins [6] must be taken into account. Later work [7] has included periodic boundary conditions, again with useful results. CNDO has been applied to several different problems concerning solids; Bennett *et al.* [7] have considered chemisorption on graphite surfaces and Baetzold [8] has looked at aggregates of transition metals. All of this work has shown semi-empirical molecular orbital methods to be a useful tool for bulk problems.

With the cluster model in mind, we have attempted to use a semi-empirical approach to the bulk and surface properties of ionic crystals. Since large charge shifts must be accounted for in this case, we have used the CNDO method and adapted it as necessary for application to ionic crystals. The model lends itself best to the study of defects in a crystal since, in many cases a good representation of their electronic properties may be obtained by considering relatively few of the neighbouring atoms. Consequently, in the development and adaptation of the method we have concentrated on providing a model of ionic crystals which can subsequently be used for defect centres. It is simple to use, economical in computing demands and has uncomplicated chemical and physical interpretations.

The method has not been developed for calculations of band properties; we have no periodic boundary conditions and hence obtain no wave-vector dependent quantities. It is, therefore, not intended for use on metallic or covalently bonded systems, although in the latter case, the technique of saturating floating bonds can provide a useful model. Since the method is based on the one electron approximation no second order quantities, e.g. dispersion or polarizability, can be accounted for.

The method is useful for band energies, obtained from the molecular orbital eigenvalue spectrum and the energies of localized defect levels. Only relative quantities will be emphasised since absolute values of the binding energy are known to be not well reproduced [7].

The present work continues an investigation into the applicability of the method for calculations on bulk systems from an early preliminary study on LiF [9] and LiF : H^- [10]. Results for the band gap and widths have been obtained for LiF and MgO with the effects of the bulk of the crystal outside the cluster represented by a classical Madelung potential. A study has also been made of the surface of MgO, for which some experimental results are available. These calculations allow us to draw conclusions on the usefulness of this method and on the behaviour of the CNDO/2 parameterization when used for bulk calculations.

The simplest defect centre, that of the substitutional hydrogen atom in LiF (the *U* centre), has also been investigated. Results are obtained which indicate that a range of crystal properties may be consistently described and that viable calculations on complex defect centres may be undertaken.

The results obtained for the band properties, e.g. band gap and *F* 2*p* valence band width are not markedly affected by the inclusion of the Madelung term since these quantities rely upon differences between one electron energy levels. The inclusion of these terms is more important when considering the properties of electron excess and electron deficient defect centres. This is indicated here by calculations on the U centre in LiF and will be followed later by applications to the F centre.

2. Method

The CNDO method has been described in detail by Pople and Beveridge [3] and here we shall list only the approximations, parameters and adaptations needed to perform calculations on solids.

The basic CNDO method requires detailed information of the following quantities: ionization energies and electron affinities of the constituent atoms, parameterization of the resonance integrals, orbital exponents, and, of course, the particular geometry. For calculations on bulk, perfect systems we have retained the CNDO/2 parameterization completely. Further, only one lattice parameter has been considered.

2.1. Residual Madelung Potential

All our CNDO calculations implicitly include terms equivalent to the electrostatic interaction of an electron belonging to a cluster ion (i), with all the other ions in the cluster. Since our model is to describe an ionic crystal, whose basic nature is that of a lattice of point ions, we include a term equal to the electrostatic interaction of an electron at lattice site i, with the remainder of the crystal outside the cluster. This region of crystal is considered to be made up of point ions.

The additional term involves the use of an extra parameter, q, the charge assigned to the point ion lattice and is obtained by the following method.

The electrostatic energy of an electron at a particular lattice site i within the cluster, is written

$$E(r_i) = -\sum_{s \neq c, i}^{\infty} \frac{q_s}{|r_s - r_i|} - \sum_{c \neq i}^{c} \frac{q_c}{|r_c - r_i|} \tag{1}$$

where s runs over all point charge lattice points outside the cluster and c over the cluster only. The charge on ions outside the cluster is $|q_s|$ and on ions within the cluster $|q_c|$. The second term on the right hand side of Eq. (1) is that implicitly included in the calculation, the first is the extra term. We define the residual Madelung constant α_R^i

$$\alpha_R^i = \sum_{s \neq c, i}^{\infty} \frac{a \operatorname{sgn}(q_s)}{|r_s - r_i|} \tag{2}$$

in a similar way to the classical Madelung constant α

$$\alpha = \sum_{s \neq i}^{\infty} \frac{a \operatorname{sgn}(q_s)}{|r_s - r_i|} \tag{3}$$

s here running over all lattice sites except i.

The residual Madelung constant can thus be obtained from α using

$$\alpha_R^i = \alpha - \sum_{c \neq i}^{c} \frac{a\,\mathrm{sgn}(q_c)}{|r_c - r_i|} \tag{4}$$

and is a measure of the potential of an electron at site i due to the bulk, after removing from the Madelung sums those terms which appear explicitly in the molecular orbital calculation. α_R^i is introduced into the calculation by adding this term to the diagonal elements of the Fock matrix, so that in Pople's nomenclature these become;

$$\begin{aligned} F_{\mu\mu} = & -\tfrac{1}{2}(I_\mu + A_\mu) + [(P_{\mathrm{AA}} - Z_{\mathrm{A}}) - \tfrac{1}{2}(P_{\mu\mu} - 1)]\,\gamma_{\mathrm{AA}} \\ & + \sum_{\mathrm{B} \neq \mathrm{A}} (P_{\mathrm{BB}} - Z_{\mathrm{B}})\,\gamma_{\mathrm{AB}} - \alpha_R^{\mathrm{A}} |q_s|/a \,. \end{aligned} \tag{5}$$

It should be noted that the added term is equal to expanding the sum over atoms B in (5) to include all atoms outside the cluster, assuming the approximation that for these atoms γ_{AB} is equal to the inverse of the interatomic separation of A from B. The factor $-(P_{\mathrm{BB}} - Z_{\mathrm{B}})$ is just the net ionic charge.

At this stage we have not attempted to adjust the off diagonal terms $F_{\mu\nu}$ since these represent the change in electronic energy caused by the effects of the overlap charge distribution and the representation of the residual Madelung potential requires information on its variation away from a lattice site. An examination of $F_{\mu\nu}$ shows that these terms derive from 3-molecule interactions in the same approximation of γ_{AB} as above, since these interactions are neglected throughout CNDO we neglect them here. However this simple method for the Madelung potential should be seen as a first approximation and further detailed work is required to take into account higher order effects. A further difficulty lies in the choice of the charge on the lattice ($|q_s|$). This can be made in several ways. The first and most obvious is to put $|q_s| = 1$ which then agrees with the value used in classical theory for the alkali halides, and is known to give a good representation of the cohesive energy. In the case of MgO values of 1.5 or 2 could be rationalized on similar grounds. However, a much lower charge is found from a Mulliken population analysis of the valence charges obtained from the CNDO calculations. There are difficulties in interpreting these populations as charges on ions since exchange is only included approximately in the method and only valence electrons are explicitly calculated. However if the extra term is to be regarded as an extension of the interionic interactions sum in $F_{\mu\mu}$ to include ions outside the cluster, the value of $|q_s|$ should be the same as the mean ionic charge within the cluster, otherwise the cluster cannot be thought of as a representative crystal segment. A second scheme is to vary the magnitudes $|q_s|$ of the charges outside the cluster until the same value is found for the charges on the ions in the cluster derived from the Mulliken populations. This has been done and the results are presented for a range of q values.

In order to perform calculations it is necessary to evaluate α_R^i for each site in the array of atoms. This is a one-off task for each crystal geometry and cluster size. Obviously for NaCl structure the symmetry reduces the number of unique positions. Figure 1 shows these positions for a cluster containing 27 atoms. Table 1 gives the values of α_R^i for this arrangement and also for the 5×5 planar system

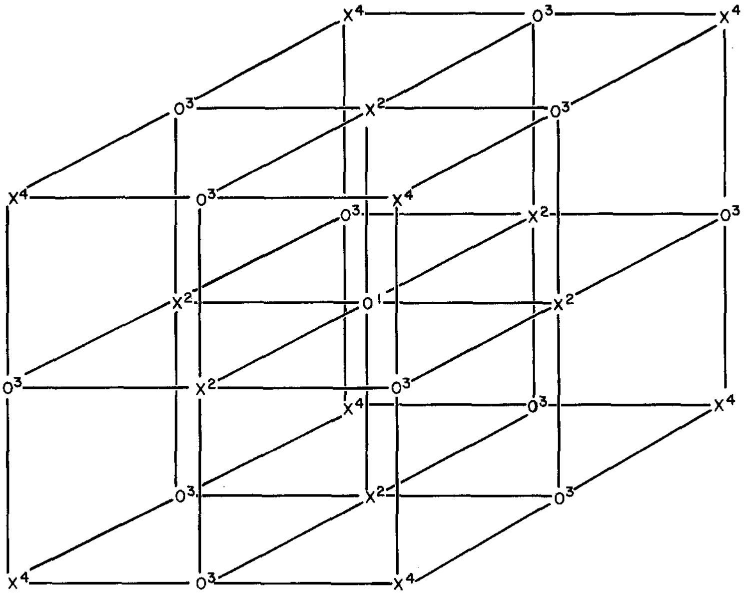

Fig. 1. 27 atom cluster. Sites are labelled for the residual Madelung constants α_R^i which appear in Table 1

Table 1. Values of reduced Madelung potential for bulk and surface systems. Atomic positions refer to those shown in Fig. 1 for bulk and Fig. 3 for surface systems

Atomic position	α_R^i Bulk material ($\alpha_M = 1.74756$)	α_R^i Surface ($\alpha_B = 1.6810^a$)
1	−0.3860	0.3459
2	−0.4392	0.3505
3	−0.2353	0.4701
4	−0.6836	0.7329
5	—	0.1413
6	—	0.2224

[a] see Ref. [20].

used for the surface of MgO, in this case with the appropriate surface Madelung constant.

2.2. Computing Requirements

Further modifications to the original CNDO program include the facility of increasing or decreasing the size of the basis and for performing calculations with a maximum of 50 atoms or 200 basis functions. Computing requirements for the largest program on an IBM 370/175 are approximately 1 M byte of core and 3 minutes per iteration in the SCF cycle. Calculations on LiF for the 27 atom cube (108 basis functions), require approximately 3 minutes to achieve self consistency (approximately 15 iterations, with an accuracy of 10^{-7} a.u.). The core requirements for this version of the program are < 500 kbytes.

3. Results and Discussion

3.1. Bulk and Surface Calculations with No Residual Madelung Potential

As a preliminary to the calculation of defect properties we have investigated the bulk properties of LiF and MgO and the surface of MgO to ascertain the behaviour of the method for widely differing ionic crystals. LiF consists of only first row elements and has a classical charge transfer of 1, whilst MgO involves a second row element, magnesium and is associated with a charge transfer of 2. Further, the use of a second row atom allows an investigation of the effects of *d*-orbitals and their parameterization.

For LiF preliminary calculations with various cluster sizes have already been reported [9]. This work showed that the eigenvalue spectrum of the clusters was of the correct nature for an ionic crystal, i.e. that of a narrow band insulating solid. The results were obtained using a 27 atom cluster for both LiF and MgO. In each case the interionic separation was maintained at the experimental values of 2.01 Å and 2.10 Å respectively.

Since the calculations on a 27 atom cluster necessarily involve an extra atom (of either species) we add or subtract charge to render the whole system closed shell for computational convenience. We have performed calculations with open shell systems for both LiF and MgO, with essentially identical results. In both cases there is a non-degenerate level close to the bottom of the conduction band. In the earlier work this level was assumed to be part of the conduction band. An examination of its eigenvector shows that it is of *s*-type (A_1) symmetry with its electron density distributed mainly over the 6 nearest neighbours arranged octahedrally about the central ion. This is, in fact, the model adopted by Overhauser [11] for the exciton in MgO, which is intermediate in character between Frenkel and Wannier excitons. Exciton absorption in MgO is known to lie at the conduction bands edge with an energy of 7.76 eV [12]. However, the experimental energy corresponds to a delocalized exciton, whereas our model forces localization within the cluster. We would suggest, therefore, that our calculated values should correspond to those for a trapped exciton. Absorption levels in a distorted MgO crystal have been studied [13] and interpreted [14] as being those of an exciton trapped at an *F* centre. Since the *F* centre is a powerful trapping site, and it is not obvious that the localization due to the cluster approximation is as strong, the observed level might be expected to lie below the value obtained here. This is so, with the observed level lying at 5.73 eV and our calculated 5.85 eV above the valence band. Allowing the interpretation of this level as a localized exciton, the band gap in MgO is found to be 7.34 eV which agrees reasonably well with the experimental value of 7.77 eV [12].

For LiF a band gap of 12.25 eV was obtained with the non-degenerate lying at 10.5 eV, 1.75 eV below the conduction band. The experimental band gap is 13.6 eV [15]. No experimental results exist for the trapped exciton in LiF, although Bassini and Inchauspe [16] estimate that for alkali halides these states lie approximately 0.6 eV below the free exciton energy. For LiF this places the level some 1.6 eV below the conduction band, which then agrees with our interpretation of this level.

Since there are experimental results available for the surface states of MgO [17, 18] we have performed calculations for this system in order to extend our

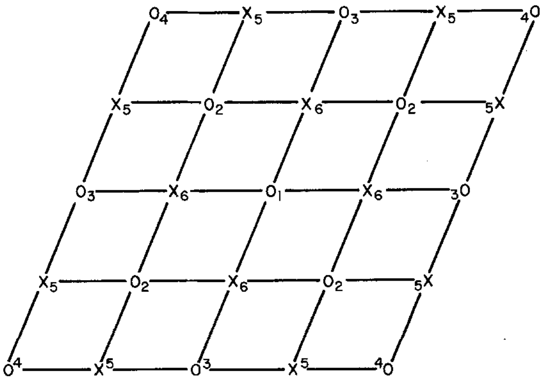

Fig. 2. 5 × 5 planar arrangement used for surface calculations sites are labelled for the residual Madelung constants which appear in Table 1

investigation of the range of applicability of the method. Surface states of crystals may be considered to have exponential damping along an axis normal to the surface plane, thus localizing them in the region of the surface [19]. A one-dimensional treatment of ionic crystals shows that two surface levels appear in the band gap [20]. For a 3-dimensional system these levels would broaden to form surface bands, the number of surface ion-pairs determine the number of levels in these bands. Here we studied three systems, one layer, two layers and three layers (corresponding to the bulk).

Preliminary work varying the number of atoms in the planar cluster from 9 to 25, showed that the planar band gap decreased with increasing number of atoms and was close to a limiting value for 25 atoms. The two layer band gap was identical in the two cases considered and gave confidence in its interpretation as a two layer result. The calculated band gap using the 5 × 5 planar cluster show in Fig. 2 was 5.63 eV, for the two layer case both twenty four and eighteen atom clusters gave 6.9 eV and the bulk twenty seven atom arrangement 7.34 eV. The model calculations show a decrease in band gap with crystal thickness, a result which is confirmed qualitatively by the experimental measurements. Evidence for a surface band gap at approximately 5 eV has been found by Nelson *et al.* [17] when investigating chemisorption on MgO surfaces. The diffuse reflectance of MgO powers has been measured [17, 18] showing an absorption due to the surface band gap peaking at approximately 5.7 eV with an onset in the region of 5.0 eV.

It should be noted that edge effects for the cubic case and the one layer plane are quite different since, of the 26 atoms on the cube faces, only six lie in positions equivalent to surface atoms, even then with their nearest neighbours in positions of symmetry far removed from those of the surface. The importance of edge effects has already been stressed [9], but it should be reemphasised that we are only concerned with relative quantities and that edge effects in these areas will cancel as long as the two systems have similar geometries.

No non-degenerate level was found for the surface calculations using the planar system. This follows from our arguments concerning the localization of level in the cubic calculation. In that case there was but one unique site for the level, whilst for the plane there are six and these are shown in Fig. 2. Consequently, if there is an exciton level, it will be delocalized, and should lie in the heavily bunched states at the bottom of the conduction band. A further test of this contension is given by a calculation on a $4 \times 3 \times 3$ cluster of MgO. This gives much more structure and a band gap which is very difficult to discern, the reason being that the exciton can be trapped not only on the octahedrally co-ordinated site, but also on the four equivalent positions having five neighbours. Detailed results are not available since a full valence orbital calculation on this system is beyond the capabilities of the current version of the program. The results obtained were for a restricted *s*-*p* basis on the magnesium atoms.

3.2. Results with the Residual Madelung Term

The variation of the band gap with charge assigned to the lattice outside the cluster is shown in Fig. 3 for MgO. A value of q of 0.375 gives the experimental band gap. However, it is more in keeping with the spirit of the calculation to choose a value equal to the mean charge on the atoms in the cluster. This is obtained from the charge densities by removing the core charges and the net charge on the system, then averaging the ionic charges. The result is similar to an iterative treatment of the charges leading to a self-consistent value for q, as carried out by Deutsche [21] for linear chains. The value obtained in this way for q is 0.45, which leads to a band gap of 7.57 eV. The results are summarized in Table 2. The trapped exciton level is at 6.46 eV. This increase from the previous value of 5.85 eV is due to the Madelung potential allowing the exciton to interact with the remaining crystal and to give some delocalization. Naturally, complete delocalization is not possible, and the energy of the free exciton, 7.76 eV is not obtained. The width of the conduction band has also been found. It varies slowly with q and at $q = 0.45$ has the value 13.77 eV. The experimental value lies between 13 and 17 eV [22].

The results for LiF, shown in Fig. 4, exhibit similar features to those for MgO. A balanced charge was obtained in the same way as for MgO and is 0.23. The band gap and exciton energies are 12.51 eV and 10.83 eV respectively. At $q = 1$, the value which would be chosen from considerations of the point-ion calculations, the band gap and exciton energies are 13.4 eV and 11.4 eV. The experimental value for the band gap is 13.6 eV and for the trapped exciton, using the arguments of Bassini and Inchauspe [16], 12.0 eV. Previous band gap calculations have given results of 15.0 eV from the tight binding calculations of Lafon *et al.* [23] and 12.8 eV from the mixed basis calculations of Kunz *et al.* [24].

For LiF the band gap and exciton energy vary approximately linearly with q, in contrast to MgO, where there is maxima in both curves. This change in shape may be attributed to the unoccupied Mg *d*-orbitals acting as an electron sink at high q values. We have performed calculations with these orbitals arbitrarily excluded and this then gives a curve similar to that for LiF. For small q values the inclusion of *d*-orbitals has no significant effect and, if a q of 0.45 is used considerable savings may be had by discarding the *d*-orbital part of the valence basis. A similar effect has been found with preliminary calculations on NaF.

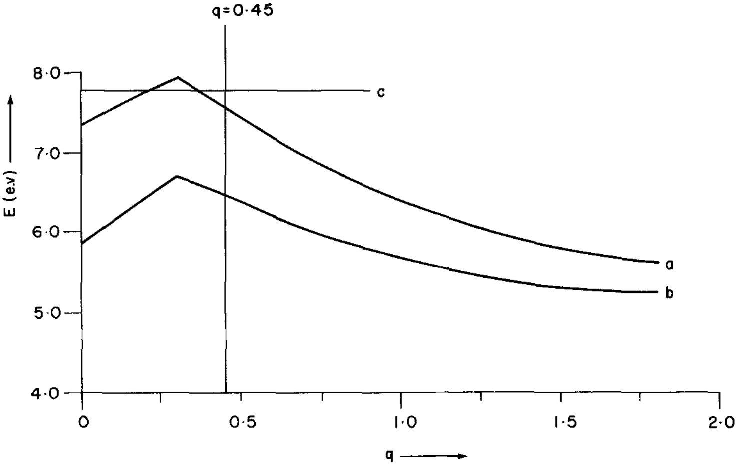

Fig. 3. Variation of band gap and trapped exciton level with q for MgO a = band gap, b = trapped exciton level (eV above valence band edge), c = experimental band gap

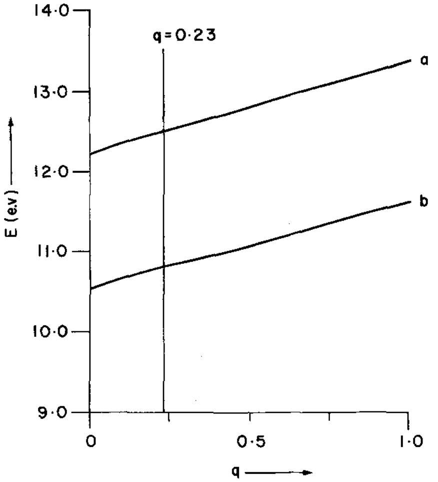

Fig. 4. Variation of band gap and trapped exciton level with q for LiF a = band gap, b = trapped exciton level (eV above valence band edge)

Table 2. Summary of results for MgO. Effective ionic charges are quoted as fractions of an electron. Band gaps, exciton energies and conduction band (C.B.) widths in electron volts

q	Bulk crystal				Crystal surface	
	Effective ionic charge	Band gap (eV)	C.B. width (eV)	Exciton level (eV)	Effective ionic charge	Band gap (eV)
0.00	0.36	7.34	13.41	5.85	0.28	5.63
0.30	0.42	7.91	13.72	6.7	0.34	5.60
0.35	0.43	7.83	13.76	6.63	0.35	5.63
0.45	0.45	7.57	13.85	6.46	0.37	5.70
0.9	0.52	6.57	14.22	5.78	0.45	6.35

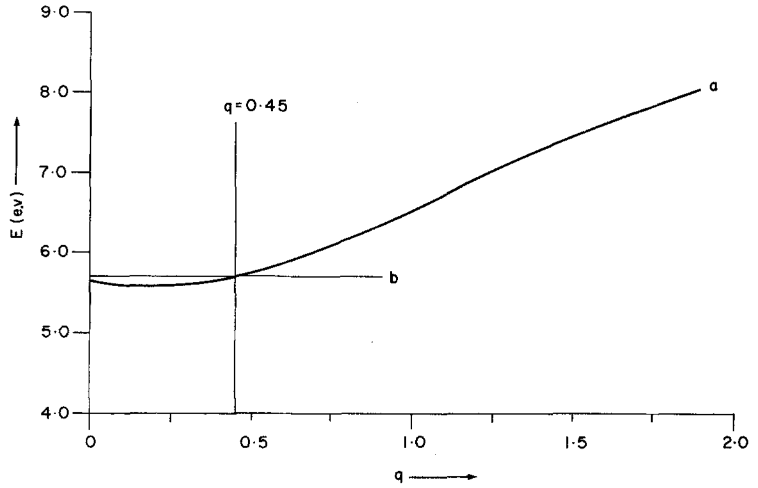

Fig. 5. Variation of band gap with q for the MgO surface a = band gap, b = experimental band gap

Table 3. Summary of results for bulk LiF. Effective ionic charges are given as fractions of an electron

q	Effective ionic charge	Band gap (eV)	Valence band width (eV)	Exciton level (eV)
0.00	0.22	12.23	2.5	20.54
0.15	0.22^5	12.43	2.4^7	10.73
0.23	0.23	12.52	2.4^7	10.83
0.25	0.23^1	12.53	2.4^6	10.84
0.30	0.23^6	12.6	2.4^5	10.9

The width of the valence band in LiF has been obtained. At $q = 0.23$ it is 2.4 eV which is in good agreement with the value of 2.3 eV found by Kunz *et al.* [24]. There is a group of four levels split away some 1.2 eV from the bottom of the valence band. If the valence band width is measured to the bottom of these levels the value obtained is 3.9 eV, which agrees with the value of 3.9 eV obtained by Ewing and Satz [25]. It would seem that which value is taken depends upon whether these levels are included or not. However, the gap between them and the rest of the valence band is large enough to indicate that they should be excluded. A summary of the results for LiF is given in Table 3.

Surface calculations were again performed for MgO and the variation of the band gap with q is shown in Fig. 5. A shallow dip occurs in the region q: -0 -0.45, the curve thereafter rising sharply. The mean ionic charges for the surface are slightly lower than for the bulk ions. The residual Madelung potential is however contributed to mostly by the bulk ions, thus we have taken the bulk value of 0.45 as the balanced charge. At this value of q the mean surface charge is 0.37 and the band gap 5.7 eV. Thus, the prediction of the model of a lowering of the band gap for the surface is maintained and is in reasonable agreement with the experimental values. The results for the surface of MgO are included with those for the bulk in Table 2.

3.3. The U Centre in LiF

Probably the simplest defect in the alkali-halides is the *U* centre. This consists of a halide replaced by a hydrogen ion (H^- for F^- in LiF). Calculations for this defect are straightforward, requiring no modifications to the method. Experimental results for LiF have only very recently become available (Private Communication Dr. J. Beaumont), an excitation energy of approximately 9.75 eV having been found. This may be compared with the value of 9.45 eV given by Ivey's law [26] and the point calculations of Spector *et al.* [27] which gave 8.11 eV. Calculations without the Madelung correction terms gave 9.15 eV, whilst for $q = 0.23$ we obtained 9.35 eV and at $q = 1$, 9.50 eV. Thus indicating, along with the results for the band gap, that for $q = 1$, good agreement with experiment is obtained.

4. Conclusions

In this work we have demonstrated that the semi-empirical macro-molecular orbital technique provides a convenient tool for studying a wide range of the electronic properties of ionic crystals. Band widths and gap have been calculated for LiF and MgO and give consistently good results. The surface of MgO has been studied and the results indicate that the method is capable of giving reasonable, consistent results in this case too. The inclusion of a Madelung potential has proved successful for both LiF and MgO and for the *U* centre in LiF.

Since it is the intention to use this method specifically for the calculation of the electronic properties of complex defects in ionic crystals (the *F* centre and *F* aggregate centres, for example), this work should be viewed as an initial step only. However, in order to proceed with more complex defects one must demonstrate that the simplest systems are well represented. This we have done with this work.

There are several aspects of this study which call for further investigation and the method itself could be improved in various ways. For example our interpretation of the non-degenerate level in the band gap for bulk calculations on both LiF and MgO requires further clarification, and the whole field of crystal surfaces demands a much more intensive study than was undertaken here.

The computing methods could be improved in the matrix handling routines and by the specific inclusion of the symmetry properties of the lattice; very much larger clusters could be accommodated in this way with little increase in computing demands. However, such modifications are time-consuming and we felt that some information as to the applicability of the method to the systems was desirable before making such an investment.

The techniques used in this work must suffer from the same restrictions as found previously in applications to molecules. In particular the calculated total energies are in error due to the use of empirical parameters to represent the core orbital energies. Consequently we have not investigated the total energies of the systems, nor have we considered the changes in these quantities brought about by the inclusion of the Madelung terms. As we have pointed out, these are preliminary results, reported here to allow an assessment of the possible usefulness of the CNDO method and to indicate some of the difficulties. Further work is now being undertaken to consider a reparameterization of the CNDO scheme for use in calculations on solids. When sufficient experience has been gathered we shall then be able to consider the usefulness of the method for predicting a wider range of observable parameters.

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