

## A study of the variational convergence of the $F$ centre energy levels of LiF

by J. TENNYSON and J. N. MURRELL

School of Molecular Sciences, University of Sussex,  
Brighton BN1 9QJ, England

(Received 30 June 1980; accepted 2 September 1980)

SCFMO calculations have been made on the  $F$  centre states of LiF using a crystal fragment whose potential closely approximates that of the full crystal. The effect of including electrons of up to third neighbours has been studied. The most extensive calculation gives a binding energy for the  $^2S$  state in the unrelaxed lattice of 5.25 eV and a  $^2S \rightarrow ^2P$  transition energy of 4.6 eV. Lattice relaxation has been calculated in a model appropriate to all lithium halides in which only nearest neighbour electrons are considered. For LiF an outward displacement of nearest neighbour ions by 2.5 per cent of the lattice parameter has been calculated. For the other halides the predicted displacements are smaller.

### 1. INTRODUCTION

The optical properties of  $F$  centres in alkali halides have been the subject of much theoretical work. Early model based calculations were made by Inui and Uemura [1], Kojima [2], Gourary and Adrian [3], and Wood and Joy [4]. Variational calculations have since been performed by Martino [5], Bartram *et al.* [6] and Wood and Opik [7, 8]. However, none of these are full *ab initio* as they all employ model or pseudo potentials for the ions surrounding the vacancy. The agreement with experimental data that is reached in these calculations may be due to the excellence of the wavefunctions or to a fortunate choice of potential. In fact by the present standards of molecular calculations the variational wave functions were all quite modest.

A more recent calculation by Chaney and Lin [9] used a LCAO variational scheme with a large basis. However, no basis functions were specifically optimized for the defect. More seriously the Slater exchange approximation was used and only a single iteration in a self-consistent-field cycle was performed. As this single iteration changes the binding energy of the ground state by  $-0.089 E_h$  (2.4 eV) it is impossible to estimate accurately the converged SCF energies.

Most studies of the  $F$  centre have assumed that the ions surrounding the vacancy are at the sites of the perfect lattice. However, it is clear that the optical transition energies are sensitive to the geometrical parameters of the lattice; the large difference between the  $F$ -centre absorption and emission energies is explained by lattice relaxation [10]. Kojima [2] in an early calculation deduced that in the  $F$ -centre ground state of LiF the nearest neighbour cations were displaced inwards by 7.4 per cent of the lattice parameter. Wood and Korringa [11] calculated an outward displacement of 1 per cent for LiCl and Bartram *et al.* [6] calculated an inward displacement for most alkali halides but LiF was an exception with a small outward displacement of approximately 1 per cent.

In this paper we use a standard molecular *ab initio* SCFMO program to calculate the energy levels of the *F* centre of LiF and to determine the ground state nearest-neighbour relaxation. Such programs are generally established with a maximum size to the basis ( $N$ ) and to the number of charge centres ( $C$ ). The program we used, ATMOL3 [12], was originally established with  $N=127$ ,  $C=50$ , but during the course of the present work these were increased to  $N=254$  and  $C=100$ . (A preliminary report on the early calculations was given in [12 a].) Although these numbers might appear large the restriction on  $N$  would prevent the achievement of Hartree-Fock accuracy for clusters of heavy ions. Computational time increases very rapidly with basis size and it would be difficult to justify calculations with more than about 150 functions. For this reason our calculations have been made on LiF in order to explore the variational limit most fully, although some deductions about other lithium halides can be made in a first neighbour approximation. Computational time is relatively insensitive to the number of centres but although the restriction of  $C=100$  allows us to represent up to eighth neighbours in the LiF lattice as point charges this gives a cluster whose radius is only three lattice spacings.

We can justify the validity of a cluster model for the ground state and first excited state of the *F* centre vacancy electron by the fact that these energies are well above the occupied band energies of the perfect crystal and below the conduction band. However, it is clear that these energies will be sensitive to the Coulomb potential of the crystal and hence the cluster must reproduce this accurately. The first section of the paper is concerned with this problem.

## 2. THE CRYSTAL POTENTIAL

Table 1 specifies the structure of the crystal local to the vacancy. The  $i$ th shell has  $n_i$  equivalent ions at distance  $aD_i$  from the centre where  $a$  is the lattice parameter.

Our initial studies were made with the program having  $C=50$  and were therefore restricted to only four shells of ions. Due to the very slow convergence of the Madelung expansion of the potential the Coulomb potential in the vacancy is very poorly represented by net charges of  $\pm 1$  on the lattice sites. We can achieve a correct potential at the vacancy centre by taking an effective charge on the fourth neighbours of  $-0.1286$  (which is independent of lattice parameter). However, this potential, which we call model 1, is too attractive for electrons away from the centre as can be seen from table 2. The potential at  $a/2$  (towards nearest neighbours) is in error by only 0.07 per cent, but at  $3a/2$  the error is 24 per cent.

With the limit  $C=100$  we were able to take up the eighth neighbours and it was now possible to obtain a Coulomb potential, model 2, which was correct at the centre

Table 1. Structure of the crystal lattice local to the defect. There are  $N_i$  equivalent  $i$ th neighbours at distances  $D_i a$  from the centre. The net charges refer to the two models described in the text.

$i$	1	2	3	4	5	6	7	8
$N_i$	6	12	8	6	24	24	12	6
$D_i^2$	1	2	3	4	5	6	8	9
Net charges								
Model 1	+1	-1	+1	-0.1286	0	0	0	0
Model 2	+1	-1	+1	-1	+1	-1	+0.5170	-0.2574

Table 2. Comparison of the exact and model electrostatic potentials  $V(r)$  and  $V(r) + |a-r|^{-1}$  at distance  $r$  from the centre along the line to the nearest neighbours (the [100] direction). All potentials are to be divided by  $a$  the lattice parameter.

$r$	Exact		Model 1		Model 2	
	$V(r)$	$V(r) +  a-r ^{-1}$	$V(r)$	$V(r) +  a-r ^{-1}$	$V(r)$	$V(r) +  a-r ^{-1}$
0	1.7476	0.7476	1.7477	0.7477	1.7476	0.7476
$a/2$	2	0	2.0015	0.0015	2.0001	0.0001
$a$	$\infty$	-0.7476	$\infty$	-0.7099	$\infty$	-0.7476
$3a/2$	0.6667	-1.3333	0.8252	-1.1748	0.6498	-1.3502

and at nearest neighbours by choosing effective charges on the seventh and eighth neighbours equal to 0.5170 and -0.2574 respectively. Table 2 shows that the potential is in error by only 2.5 per cent at  $3a/2$ .

### 3. BASIS SETS

Calculations were made with contracted gaussian functions. For the fluorine atom van Duijneveldt [13] has derived an  $(8s, 4p)$  basis contracted to  $(3s, 2p)$ ; this symbolism stands for three  $s$  and two  $p$  gaussian functions. This double-zeta basis was used for the central anion vacancy. A further contraction to  $(2s, 1p)$  was made with coefficients derived from a calculation on  $F^-$ . For  $Li^+$  we took the van Duijneveldt [13]  $(8s)$  contracted to  $(3s)$  plus a  $(4p)$  contracted to  $(2p)$  given by Williams and Streitwieser [14]. This  $(3s, 2p)$  basis was used in some calculations for the nearest neighbours but for most calculations a further contraction to  $(2s, 1p)$  was employed. This was based upon a  $Li^+$  calculation, the occupied and first two virtual orbitals being selected.

In addition to the  $F(3s, 2p)$  functions at the vacancy centre we added diffuse  $s$  and  $p$  gaussian functions whose exponents were optimized in model 1 calculations in which nearest neighbour electrons were explicitly considered but only in a minimal basis representation. The diffuse  $s$  functions are a set of even tempered [15] gaussians, with exponents  $\alpha$ ,  $\alpha\beta$  and  $\alpha\beta^2$ . We found no significant improvement in using such a set for the  $p$  functions over a single function optimized at each value of the lattice parameter  $a$ . Table 3 defines these bases.

Calculations on diatomic LiF gave the results shown in table 4. These are compared with Hartree-Fock and experimental values in the same table. It can be seen that both the double-zeta and minimal bases give satisfactory results but it should be mentioned that a minimal basis optimized for neutral atoms rather than ions gives very poor results.

### 4. RESULTS FOR THE UNRELAXED LATTICE

Initial calculations were made to investigate the dependence on basis functions most closely localized to the defect, i.e. the defect centre and nearest neighbour ions. Table 5 shows the binding energies of the first two states of the  $F$  centre obtained by separate SCF calculations. These states have different symmetries and can be designated  $^2S$  and  $^2P$ ; a symmetry equivalencing procedure was followed for the  $^2P$  state [18]. The binding energies are relative to the vacancy without an electron (usually called the  $F_x$  centre) and the total SCF energy of this is given. Calculations were made only in model 1 with all sites except nearest neighbours represented by

Table 3. Minimal basis functions and defect centre functions used in this paper. The double zeta functions for F and Li are given in [13, 14].

Symmetry	Exponent	Contraction coefficient	
		Li <sup>+</sup>	F <sup>-</sup>
s	0.6306	0.3388	7.6089
	1.9212	0.4718	22.2218
	6.1767	0.2469	69.4023
	22.0827	0.0775	246.2363
	97.1551	0.0162	1082.6764
	647.0636	0.0213	7213.1380
s	0.0281	0.6206	0.4012
	0.0725	0.4450	1.3570
p	0.0240	0.5089	0.5330
	0.2750	0.1389	1.3512
	0.5002	0.8348	4.9935
	1.5343	0.0228	22.7476
Defect			
s	0.1370	1.0	
s	0.1849	1.0	
s	0.2496	1.0	
p(a=3.80 a <sub>0</sub> )	0.0166	1.0	
p(a=4.86 a <sub>0</sub> )	0.0104	1.0	
p(a=5.20 a <sub>0</sub> )	0.0102	1.0	
p(a=5.67 a <sub>0</sub> )	0.0101	1.0	

Table 4. Calculated equilibrium bond length and dissociation energy (to ions) of diatomic LiF. a<sub>0</sub> = 5.292 × 10<sup>-11</sup> m, E<sub>h</sub> = 27.21 eV is equivalent to 2626 kJ mol<sup>-1</sup>

Basis	r <sub>e</sub> /a <sub>0</sub>	D <sub>e</sub> /E <sub>h</sub>
Minimal	3.05	0.290
Double zeta	2.99	0.321
Hartree-Fock [16]	2.96	0.296
Expt. [17]	2.96	0.290

Table 5. Calculated total energy of the F<sub>x</sub> centre and binding energies of the <sup>2</sup>S and <sup>2</sup>P F centre states. All calculations are for the unrelaxed lattice with lattice parameter a = 3.796a<sub>0</sub>. Min. = minimal basis, DZ = valence double zeta basis, dif. = diffuse functions at defect centre.

Nearest neighbours	Basis Defect centre	Energies/E <sub>h</sub>			ΔE <sub>sp</sub> /eV
		F <sub>x</sub>	<sup>2</sup> S	<sup>2</sup> P	
Min.	F <sup>-</sup> DZ	-48.5862	0.1536	0.0353	3.2
Min.	F <sup>-</sup> DZ + dif.	-48.5862	0.2001	0.0945	2.9
DZ	F <sup>-</sup> DZ	-48.5864	0.1885	0.1022	2.3
DZ	F <sup>-</sup> DZ + dif.	-48.5864	0.2022	0.1007	2.8

the point charges specified in table 1. Both minimal and double zeta bases were used for nearest neighbour electrons as described in the table.

The energy of the  $F_2$  state (six  $\text{Li}^+$  in the Coulomb field of point charges) is largely unaffected by the basis. The energies of both the  ${}^2S$  and  ${}^2P$  states are lowered significantly by using DZ rather than minimal basis for the  $\text{Li}^+$  when no diffuse functions are included at the defect centre. However, with diffuse functions there is little improvement on using the DZ basis. In other words a minimal basis at the first neighbours and DZ plus diffuse functions at the centre appears to be nearly saturated. For this reason, and with reasonable computational economy, we shall adopt this basis for the more extensive calculations which we shall describe.

Table 6 shows calculations of the  ${}^2S$  and  ${}^2P$  binding energies in models 1 and 2 with successive inclusion of the neighbouring ion electrons. The first calculations in the table correspond to the point charge model of Gourary and Adrian [3] as no neighbour ion electrons are explicitly considered in the SCF calculations. However, the first neighbour lithium  $2s$  and  $2p$  basis functions were included to give added flexibility to the wavefunctions. The relatively high binding energy, similar to that obtained by Gourary and Adrian, reflects the lack of orthogonality to the  $\text{Li}^+$   $1s$  orbitals.

Table 6. Calculated binding energy ( $E_b$ ) of the  ${}^2S$  and  ${}^2P$  states and the resulting excitation energy.  $L$  is the number of shells neighbouring the defect whose electrons have been explicitly included in the SCF calculations. The experimental value of  $\Delta E_{sp}$  is 5.08 eV [22].

$L$	${}^2S$	Model 1 ${}^2P$	$\Delta E_{sp}/\text{eV}$	${}^2S$	Model 2 ${}^2P$	$\Delta E_{sp}/\text{eV}$
0	0.299	0.130	4.6	0.299	0.129	4.6
1	0.202	0.101	2.8	0.199	0.068	3.6
2	0.186	0.088	2.7	0.195	0.052	3.9
3	0.180	0.062	3.2	0.193	0.023	4.6

The most extensive calculations included first, second and third neighbour electrons and, to economize, the lithium  $2s$  and  $2p$  functions on third neighbours were omitted from the basis. The binding energy of the  ${}^2S$  state appears to converge quite quickly with  $L$  and there is little difference between the results of the two models. There is a wide variation in previous calculation of this binding energy and in many instances it is considerably overestimated. For example, a recent SCF  $X_\alpha$  calculation gives a binding energy of  $-1.16 E_h$  [19]. Photoelectron ejection studies have not been made on LiF but for RbI [20] they indicate that the  ${}^2S$  state is bound by approximately  $0.11 E_h$  and the  ${}^2P$  state is only just bound. Our results are consistent with this view.

The convergence of the  ${}^2P$  state with  $L$  is slower than that of the  ${}^2S$  state and the difference between the two models is significant when measured against the  ${}^2S \rightarrow {}^2P$  transition energy. The  ${}^2P$  state is much more diffuse than the  ${}^2S$  and the model 1 potential becomes progressively too attractive as the distance from the defect centre increases. For this reason we believe that the results of model 2 are more reliable. A Mulliken population analysis of our best wavefunctions (model 2 with  $L=3$ ) gives  $2 \times 10^{-6}$  in each third neighbour  $\text{Li}^+(1s)$  orbital for the  ${}^2S$  state but  $74 \times 10^{-6}$  in each orbital (symmetry equivalent) for the  ${}^2P$  state.

From this wavefunction of the  $^2S$  state we have calculated the spin densities at the first and third neighbour Li nuclei and find the values  $6.0 \times 10^{-2} a_0^{-3}$  and  $2.6 \times 10^{-4} a_0^{-3}$  respectively. These numbers are both dominated by the  $\text{Li}^+$  ( $1s$ ) contributions to the wavefunction. We have not calculated the second neighbour fluorine spin density because we expect its absolute value to be inaccurate and we can make no comparison of relative values for different shells. From ENDOR studies on LiF, Holton and Blum [21] deduce spin densities of  $2.3 \times 10^{-2} a_0^{-3}$  and  $2.9 \times 10^{-4} a_0^{-3}$  at first and third neighbour  $\text{Li}^+$ , values which are in reasonable agreement with our calculations.

The experimental absorption band associated with the  $^2S \rightarrow ^2P$  transition is broad and structureless and for LiF has its maximum at 5.08 eV at 5 K [22]. By the Franck-Condon principle this maximum should correspond to the vertical excitation energy at the equilibrium geometry of the  $^2S$  state. None of our calculations gives a value as high as experiment but our best calculation only differs by 0.5 eV, an amount which might be expected in a molecular calculation at this level of treatment. However, we have not yet examined the relaxation of the lattice.

Examination of the virtual levels of the  $F_a$  state suggests that other excited states of the  $F$  centre might be bound. When second neighbour electrons are included in the calculation a second  $s$  virtual level is found to be close in energy to the first  $p$  level. Third neighbour electrons raise the energy of this orbital slightly.

For model 2 with  $L = 3$  the first three virtual levels of the  $F_a$  state are at  $-0.185(s)$ ,  $-0.023(p)$  and  $+0.012(s)$ . As is seen from table 6 the first two are very close to the binding energies of the  $^2S$  and  $^2P$  states. Hence we deduce that an excited  $^2S$  state lies close to the ionization continuum.

Because  $^2S \rightarrow ^2S$  transitions are symmetry forbidden, any absorption band associated with the second excited state is difficult to see. A second  $^2S$  state has, however, been observed in potassium halides by use of an electric field to lower the symmetry (the Stark effect) [23] and is found to be just above the  $^2P$  state.

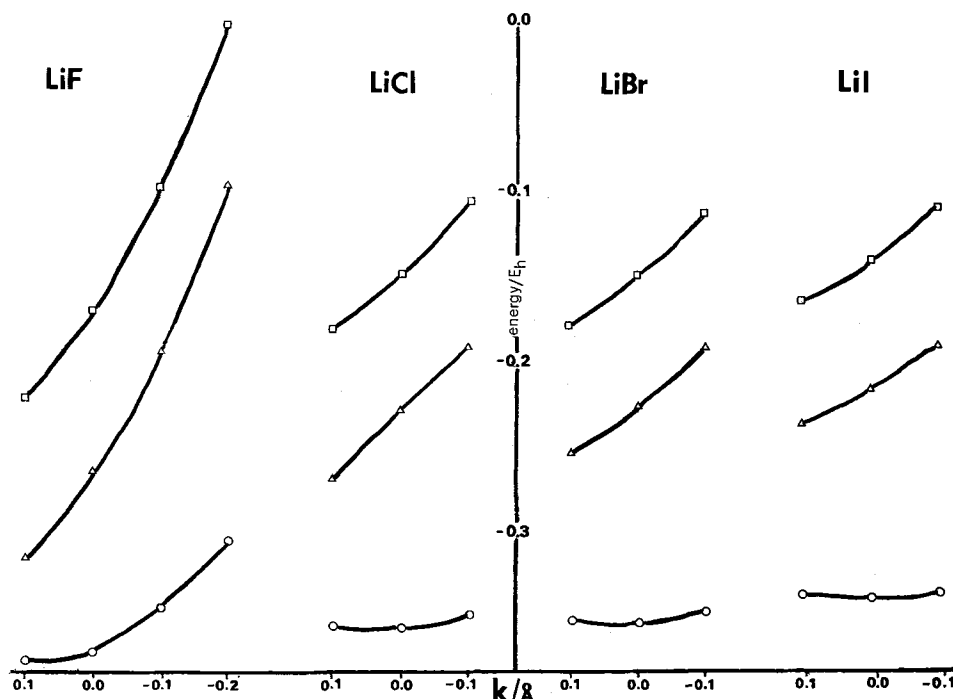
## 5. LATTICE DISTORTION

A complete treatment of the lattice relaxation around an  $F$  centre is a lengthy problem. Firstly, ionic displacements around a vacancy are not confined to the nearest neighbours, and secondly for the  $^2P$  state they are not totally symmetric, as the  $^2P$  state is subject to a Jahn-Teller distortion. In this study we consider only totally symmetric displacements of the nearest neighbour ions. The potentials are therefore calculated as a function of a parameter  $k$ , which is the displacement *outwards* of a nearest neighbour  $\text{Li}^+$  ion. Calculations were made in the first neighbour approximation ( $L = 1$ ) using model 1 for the  $F_a$ ,  $^2S$  and  $^2P$  states. For the  $F_a$  state we can make an independent estimate of the potential curve from empirical functions and this allows us to test the reliability of the molecular SCF calculations.

In this approximation, in which only the defect basis functions and nearest neighbour  $\text{Li}^+$  functions are used, it is possible to calculate the relaxation in all the lithium halides by using appropriate values for the lattice parameters. Table 3 gives the diffuse  $p$  functions optimized at the four lattice parameters relevant to LiF, Cl, Br and I respectively. The figure shows the results of these calculations. We note that for lattices except LiF the  $^2S$  state potential is very flat and in all cases the potential curves for the  $F_a$  and  $^2P$  states are nearly parallel.

The potential curves arise from a balance between an outward force on the  $\text{Li}^+$  ions from the Coulomb potential of the lattice and an inward force arising from the electron. For the  $F_\alpha$  state only the Coulomb force is present and as the odd electron in the  $^2P$  state is only weakly bound the inward force in this case is also small.

We can see from table 2 that model 1 underestimates the Coulomb potential at the nearest neighbour sites and this deficiency becomes worse as the distance from the centre increases. However, this error is partly compensated by the absence of exchange repulsion between the  $\text{Li}^+$  ions and their neighbouring anions. A consequence of this omission is that the outward displacement of the  $\text{Li}^+$  in the  $F_\alpha$  state would continue until there is coincidence with an anion centre. Thus calculations with only nearest neighbours included in the SCF procedure will not give a correct equilibrium position for the  $F_\alpha$  state. The important question, however, is whether the potential is correct for small displacements from the undistorted lattice.



SCF energies of  $F_\alpha(\square)$ ,  $^2S(\circ)$  and  $^2P(\triangle)$  states calculated for model 1,  $L=1$ , as a function of the outward displacement  $k$  of nearest neighbour  $\text{Li}^+$  ions. Calculations have been made for lattice spacings appropriate to each lithium halide crystal.

Empirical pair potentials give a good representation of the properties of perfect crystals. It is possible to use these to calculate the relaxation in the  $F_\alpha$  state, assuming that the pair potential is unchanged by the formation of the defect. We used the pair potential first suggested by Huggins and Mayer [24] which separates Coulombic and exponential repulsive terms. The repulsive term for a separation  $r$  is written

$$bC_{ij} \exp [(r_i + r_j - r)/\rho], \quad (1)$$

where  $r_i$  and  $r_j$  are the effective radii of the two ions, and  $C_{ij}$  is the so-called Pauling coefficient [25] which depends on the charge and number of outer electrons of the

Table 7. Parameters for the Huggins–Mayer repulsive potential (1), as deduced by Fumi and Tosi [26].

	Li <sup>+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I
$r_i/a_0$	1.727	2.566	3.039	3.281	3.636
	$b=0.00583 E_n$		$\rho=0.6414 a_0$		

two ions. The parameters  $b$  and  $\rho$  have been optimized for the alkali halides and in table 7 we give values deduced by Fumi and Tosi [26]. We have investigated the use of other published parameters but they made little difference to the final results.

To determine the Coulomb energy for the  $F_\alpha$  state we start with the potential experienced by one ion within its Wigner–Seitz cell which arises from the rest of the perfect crystal. At the cell centre the potential is  $\pm 1.7476/a$ ; the sign depending on the charge of the ion. The problem of calculating the summed contribution from all ions in a NaCl lattice at a general point within the cell has been solved by Hajj [27]. This potential, written  $M(q)/a$  is a slowly varying function of  $q$  near the site centre ( $q=0$ ) and for small values it can be approximated by

$$M(q) = \pm [1.7476 + 3.6q^4]. \quad (2)$$

In the relaxed lattice we are considering six Li<sup>+</sup> ions moving simultaneously; hence we must subtract from (2) the contribution from the other five Li<sup>+</sup> ions and replace it by the full Coulomb potential of the cluster of six. We must also remove the contribution from the anion which is missing at the centre. The full expression for the Coulomb potential of the defect for a relaxation  $k$  is

$$6 \left[ -\frac{M(k)}{a} + \frac{1}{a+k} - \left( \frac{1}{2a+k} + \frac{4}{(a^2 + (a+k)^2)^{1/2}} \right) + \frac{1}{2} \left( \frac{1}{2a+2k} + \frac{4}{\sqrt{2(a+k)}} \right) \right] \quad (3)$$

plus terms independent of  $k$ .

The total energies of the  $F_\alpha$  state which are obtained from the empirical potential and the SCF calculation cannot be compared because they refer to different sized fragments. However, the relevant quantity for determining the equilibrium position is the slope of the potential. In this respect we find almost exact agreement between the empirical and SCF calculations, the two being indistinguishable on the scale of the figure. This perhaps implies that we have a fortuitous cancellation of errors between our model Coulomb potential and the Li<sup>+</sup>–X<sup>-</sup> exchange repulsion terms. We therefore assumed that the corrections which should be made to the SCF curves for the <sup>2</sup>S and <sup>2</sup>P states are negligible compared with other errors in our calculations.

Our calculations predict an outward displacement of the Li<sup>+</sup> ions ( $k$  positive) of 0.09  $a_0$  in LiF. This is 2.5 per cent of the lattice parameter. Because the <sup>2</sup>S state potentials are so flat for the other halides our predicted movements are subject to large uncertainties in view of the approximations of our model. There is a small movement outward (0.02  $a_0$ ) for LiCl and inward for LiBr (0.02  $a_0$ ) and LiI (-0.04  $a_0$ ). Kojima calculated a much larger displacement for LiF of the opposite sign. Our results are, however, in reasonable agreement with those of Korrynga [11] and Bartram *et al.* [6].



## 6. CONCLUSIONS

To obtain variationally accurate results on the LiF *F* centre has proved to require a rather heavy calculation by molecular standards. Only model 2 with  $L=3$  gives a good excitation energy but it can be seen from table 6 that it is the  ${}^2P$  state which is slow to converge. As we have underestimated the excitation energy any variational improvement would have to be more in the  ${}^2S$  than the  ${}^2P$  state; perhaps reoptimization of the diffuse orbitals in the model 2,  $L=3$  calculation.

It is generally expected that electron correlation (beyond the SCF level) has a small effect on the difference in energy between states which have the same number of electron pairs. Recent calculations [28] on the  ${}^2\Pi$  and  ${}^2\Sigma$  states of  $\text{HCN}^+$  show that configuration interaction stabilizes the  ${}^2\Sigma$  more than the  ${}^2\Pi$  by 0.3 eV. For  $\text{HNC}^+$ , however the  ${}^2\Sigma$  is stabilized by 1.3 eV. We can therefore expect errors of up to  $\sim 1$  eV in our calculations due to neglect of correlation and in that respect our  ${}^2S \rightarrow {}^2P$  excitation energy must be considered quite satisfactory.

The authors thank Dr. P. D. Townsend for stimulating discussions on this topic.

## REFERENCES

- [1] INUI, T., and UEMURA, Y., 1950, *Prog. theor. Phys.*, **5**, 252.
- [2] KOJIMA, T., 1957, *J. phys. Soc. Japan*, **12**, 908, 918.
- [3] GOURARY, B. S., and ADRIAN, F. J., 1957, *Phys. Rev.*, **105**, 1180.
- [4] WOOD, R. F., and JOY, H. W., 1964, *Phys. Rev. A*, **136**, 451.
- [5] MARTINO, F., 1968, *Int. J. quant. Chem.*, **2**, 217, 233.
- [6] BARTRAM, R. H., STONEHAM, A. M., and GRASH, P., 1968, *Phys. Rev.*, **176**, 1014.
- [7] OPIK, V., and WOOD, R. F., 1969, *Phys. Rev.*, **179**, 772.
- [8] WOOD, R. F., and OPIK, V., 1969, *Phys. Rev.*, **179**, 783.
- [9] CHANEY, R. C., and LIN, C. C., 1976, *Phys. Rev. B*, **13**, 843.
- [10] BEALL FOWLER, W., 1964, *Phys. Rev. A*, **135**, 1725.
- [11] WOOD, R. F., and KORRINGA, J., 1961, *Phys. Rev.*, **123**, 1138.
- [12] SAUNDERS, V. R., and GUEST, M. F., ATMOL3, documented by the Atlas Computing Division, Rutherford Laboratory.
- [12a] MURRELL, J. N., and TENNYSON, J., 1980, *Chem. Phys. Lett.*, **69**, 212.
- [13] VAN DUJNEVELDT, F. B., 1975, *IBM JI Res. Dev.*, **945**, 1.
- [14] WILLIAMS, J. E., and STREITWIESER, A., JR., 1974, *Chem. Phys. Lett.*, **25**, 507.
- [15] RAFFENETTI, R. C., 1973, *J. chem. Phys.*, **59**, 5936.
- [16] MCLEAN, A. D., and YOSHIMINE, M., 1967, *IBM JI Res. Dev. Suppl.*
- [17] Computed from data in MCLEAN, A. D., 1963, *J. chem. Phys.*, **39**, 2653.
- [18] GUEST, M. F., and SAUNDERS, V. R., 1974, *Molec. Phys.*, **28**, 819.
- [19] TANG KAI, A. H., 1980, Dissertation, University of Uppsala.
- [20] APKER, L., and TAFT, E., 1959, *Phys. Rev.*, **79**, 964.
- [21] HOLTON, W. G., and BLUM, H., 1962, *Phys. Rev.*, **125**, 89.
- [22] DAWSON, R. K., and POOLEY, D., 1969, *Phys. Stat. Sol.*, **35**, 95.
- [23] GRASSANO, U. M., MARGITONDO, G., and ROSEI, R., 1970, *Phys. Rev. B*, **2**, 3319.
- [24] HUGGINS, M. L., and MAYER, J. E., 1933, *J. chem. Phys.*, **1**, 643.
- [25] PAULING, L., 1928, *Z. Kristallogr.*, **67**, 377.
- [26] FUMI, F. G., and TOSI, M. P., 1964, *J. Chem. Phys. Solids*, **25**, 31.
- [27] HAJJ, F. Y., 1972, *J. chem. Phys.*, **56**, 891.
- [28] MURRELL, J. N., and AL-DERZI, A., 1980, *J. chem. Soc., Faraday II*, **76**, 319.