MOLECULAR SCF CALCULATIONS ON THE F CENTRE OF LiF

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A molecular ab initio SCF program has been used to calculate the energy levels of the F centre in LiF using a model crystal potential which includes explicitly the electrons of up to third neighbours to the defect and a truncated point-charge representation of the rest of the lattice. The most complete calculations underestimate the $^2S \rightarrow {}^2P$ excitation energy by 35% and this suggests that the model potential needs to be further extended for this technique to be successful.

If the energy levels associated with defects in a solid are well separated from the band energies of the ideal lattice then one expects the defect properties to be interpretable through calculations on a small fragment surrounding the defect. The key questions are how small has the fragment to be and how does one make the calculation.

The problem has been tackled by several groups, with particular reference to the optical properties of the F centre in alkali halides [1–10]. All of these are variational calculations which employ model or pseudo potentials for the ions surrounding the anion vacancy. The agreement with experimental data that is reached in these calculations may be due to the excellence of the variational wavefunction or to a fortunate choice of potentials. In fact the variational wavefunctions of all except ref. [10] are modest by present standards of small-molecule calculations, and this exception is a once-iterated LCAO scheme using the Slater exchange approximation.

In this paper we investigate the use of a molecular ab initio SCF MO program to make such calculations. These programs in standard form have a maximum size to the basis (N) and to the number of centres (C). The one we use in this work (ATMOL 3 [11]) has max $N = 127$ and max $C = 50$.

The F centre in an alkali halide is obtained by replacing a halide ion by an electron. We first assume that the rest of the lattice is unrelaxed. We shall represent the first (6 Li^+), second (12 F^-) and third (8 Li^+) neighbours either explicitly (i.e. include all their electrons in the calculation) or represent them by point charges. The remainder of the lattice is replaced by a charge $-\delta$ at the position of the six fourth neighbours so as to reproduce the Madelung potential at the centre of the defect. δ is independent of the lattice parameter for a rock-salt structure and has the value 0.1286.

Having the correct Coulomb potential at the centre of the defect does not guarantee that the potential is correct over the whole defect region. The symmetry of the potential (point group O_h) is of course retained by our approximation. Table 1 compares the exact and model electrostatic potentials at points along the (100) direction. It is seen that the two potentials are very similar at $q = a/2$ but show a significant difference at $q = 3a/2$. The implications of this are discussed later.

Atomic basis functions for the calculations were developed from the gaussian basis of van Duijneveldt [12], (8s, 4p) contracted to (3s, 2p) for F and (8s) contracted to (3s) for Li, together with a (4p) contracted to (2p) for Li as given by Williams and Streitwieser [13]. Using this valence double-zeta basis for a calculation on the diatomic LiF gave $r_e = 2.99\ a_0$ (1% greater than experimental). Calculations were also made at the minimal basis level by further contractions, these being based upon atomic calculations for Li^+ and F^-. The 2s and 2p contractions for Li^+ were taken as the lowest energy s and p virtual orbitals in an Li^+ calculation.

For the functions which span the space of the miss-

Table 1
The electrostatic potential $V(q)$ as a function of q the displacement from the centre of the defect along (100), a line directed towards a nearest neighbour Li^+; a is the lattice constant

q	Exact		Model	
	$V(q)$	$V(q)+\lvert a-q\rvert^{-1}$	$V(q)$	$V(q)+\lvert a-q\rvert^{-1}$
0	$1.7476/a$	$0.7476/a$	$1.748/a$	$0.748/a$
$a/2$	$2/a$	0	$2.0015/a$	$0.0015/a$
a	$+\infty$	-0.7476	$+\infty$	$-0.7099/a$
$3a/2$	$2/3a$	$-4/3a$	$0.8252/a$	$-1.1748/a$

ing halide ion we took the double-zeta (3s, 2p) set for F^- with the addition of some diffuse gaussian functions. These were chosen by minimizing the energy of ^2S and ^2P states for a calculation at the LiF lattice spacing using only nearest-neighbour (Li^+) orbitals at the minimal basis level. Three even-tempered [14] 1s gaussian functions were investigated and their optimum exponents were found to be 0.1370, 0.1849 and 0.2496. For the diffuse p gaussian functions, we found no significant improvement for three even-tempered functions over a single 2p gaussian of exponent 0.0166.

Separate SCF calculations were made on the vacancy without an electron (this is usually called an F_α centre) and with an electron in an s or p orbital (the F centre). The energies we report are for restricted Hartree–Fock wavefunctions with symmetry equivalencing [15] for the ^2P state. Table 2 shows calculations for successive inclusion of neighbouring ion electrons.

With all neighbours replaced by point charges, the model is essentially that of Gourary and Adrian [3]. In this model the lowest ^2P state is concentrated mainly on the lithium centres (where the Coulomb potential is negative), but the second ^2P state is more strongly localized at the defect centre. It is this state which becomes the lowest ^2P state when the 1s electrons of the lithium ions are explicitly included in the calculations.

The second series of calculations which include the first-neighbour 1s electrons add two features to the calculation. Firstly the effective nuclear charge for electrons in orbitals which are orthogonal to these 1s orbitals is greater than one by virtue of a penetration effect. Thus electrons in the lithium 2p orbitals are stabilized. In contrast, the requirement of orthogonality raises the energy of electrons in any orbital, such as a diffuse basis

Table 2
Calculated total energy of the F_α state and the binding energy of the F centre electron in ^2S and ^2P states. All calculations are for LiF (lattice parameter a = 2.009 Å). Min.: minimal basis; DZ: valence double-zeta basis, dif.: diffuse functions at defect centre

	Basis		Energies E_h			ΔE_{sp} (eV)
	ions	defect centre	F_α	^2S	^2P	
model 1, point charges	Li2s + 2p	F^-DZ + dif.	−5.4710	0.2990	0.1295 0.0978	4.6 5.5
model 2, nearest neighbours	min	F^-min.	−48.5861	0.1285	0.0329	2.6
	min	F^-DZ	−48.5862	0.1536	0.0353	3.2
	min	F^-DZ + dif.	−48.5862	0.2001	0.0945	2.9
	DZ	F^-DZ	−48.5864	0.1885	0.1022	2.3
	DZ	F^-DZ + dif	−48.5865	0.2022	0.1007	2.8
model 3, first and second neighbours	min	F^-min.	−1237.4186	0.1097	0.0009	3.0
	min.	F^-DZ	−1237.4261	0.1371	0.0019	3.7
	min	F^-DZ + dif.	−1237.4453	0.1856	0.0879	2.7
model 4, first, second and third neighbours	min.	F^-DZ + dif.	−1295.2286	0.1800	0.0623	3.2

function, which is not orthogonal to the 1s orbitals. A number of calculations were made with different defect basis functions as summarized in table 2.

To examine the extent to which the above calculations have a saturated variational basis, we extended the lithium basis to double zeta. Both the ^2S and ^2P states were stabilized by approximately $0.002E_h$ which is relatively little. However, for a calculation without the diffuse basis functions such an extension gave an appreciable stabilization of approximately $0.05E_h$ for both states.

Above the ^2P state we find a state of E_g symmetry (in O_h) whose wavefunction consists of Li^+ orbitals alone. This state is stabilized by adding orbitals of d symmetry at the centre of the defect to the basis. The optimum exponent for a single set of gaussian d functions is 0.0093 and the resulting state then has an energy 1 eV above the ^2P state but it is 1.5 eV below the F_α state.

To include the electrons of the twelve second-neighbour F^- in the variational calculation and remain within the maximum size of basis for the computer program, it was necessary to take all Li^+ and F^- at the minimal basis level. The defect functions were added as before. The effect of second neighbours was to destabilize the ^2S state by approximately $0\ 015E_h$. Without the diffuse basis functions, the ^2P state was destabilized by a larger amount ($\approx 0.03E_h$) thus increasing the $^2S \rightarrow {}^2P$ excitation energy. However, with diffuse basis functions the second neighbours have a smaller effect on the ^2P state energy so that in our most extensive variational calculations the $^2S \rightarrow {}^2P$ excitation energy is almost unaffected by second neighbours.

An important effect of including second neighbours is to stabilize a second ^2S state. Examination of the virtual levels of the F_α state gives the first three at -0.175, -0.063 and $-0\ 012E_h$. The first two of these are s levels and the third a p level. From this calculation we would predict that a $^2S \rightarrow {}^2S$ transition should lie below the $^2S \rightarrow {}^2P$ transition

Our most extensive calculations included the electrons of third neighbour Li^+ but due to restrictions on the size of the basis we took only the 1s contracted function referred to earlier for each of these. Inclusion of these electrons raises the energies of both ^2S and ^2P states (an effect which can be attributed to exchange with the Li^+ core), more so for the ^2P state. The $^2S \rightarrow {}^2P$ excitation energy is now calculated to be 3.2 eV which however is still appreciably lower than the experimental value 5.1 eV [16]. The second ^2S state is now found to be less stable than the ^2P state by 1.6 eV as judged by the virtual levels of the F_α state.

Calculations in model 2 as a function of lattice spacing are valid for all alkali halides because second neighbours are replaced by point charges. Our calculated $^2S \rightarrow {}^2P$ excitation energies in the min Li^+ basis with F^-DZ + dif. (see table 2) and with the diffuse p orbitals optimized for each lattice parameter gave 3.5, 3.5 and 3.4 eV for LiCl, LiBr and LiI respectively. These are in much better agreement with the experimental values (3.3, 2 8 and 3.2 eV [16]) than the LiF calculation

A complete treatment of the lattice distortion for the F centre is a lengthy problem. We have considered only totally symmetric distortions of the first neighbour ions in model 2. Calculations have been made for the ^2S, ^2P and F_α states In the latter case we can make an independent estimate of the potential curve using empirical crystal potentials [17] and a knowledge of the electrostatic potential over the lattice cell [18]. This shows that for small displacements from the unrelaxed lattice, the SCF calculations agree with the empirical potential function.

The minimum of the ^2S state is predicted to be at an outward displacement of the Li^+ by 0.05 Å in LiF, which is 2.5% of the lattice parameter. Wood and Joy [4] obtained 0.006 Å in the same sense but Kojima [2] predicted an inward displacement of 0.15 Å, much larger and in the opposite sense to our value.

The most disappointing aspect of the calculations was the underestimate of the $^2S \rightarrow {}^2P$ excitation energy for LiF. We believe that our calculations show that this is not a result of a poor basis and it must therefore be due to an inadequate crystal potential. Our model potential is too attractive away from the centre of the defect and this becomes appreciable at second neighbours. As the ^2P state is more diffuse than the ^2S it is stabilized by a relatively greater amount. We are hoping to extend the calculations by including more distant neighbours in the lattice as point charges This however requires some modification of the program at present available

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