F-type centres and hydrogen anions in MgO: Hartree–Fock ground states

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Abstract. Second-neighbour defect clusters, described in the Hartree–Fock approximation, with Kunz–Klein localising potentials out to fourth neighbours, embedded in an infinite shell model lattice, are analysed with consistent distortion and polarisation for F^+, F, $[H^-]^+$, and $[H^{2-}]^0$ defects in MgO. Basis sets for the defects are optimised, and are improved by recontraction for the first and second neighbours. Questions of total energy, nearest-neighbour displacements and localisation are addressed for each defect. For the F^+ centre, its ground state in relation to the valence band is discussed, as is the localisation of its unrelaxed excited state. For the F^+ and $[H^{2-}]^0$ centres, spin densities are evaluated at each step of the calculation, and compared with experiment. Calculations that completely neglect the ion-size effect of all ions except at the defect centre give some qualitatively plausible results. The full-cluster results are used to derive short-range shell model parameters for H^- and H^{2-} in MgO. The method and results are critically reviewed.

1. Introduction

In MgO, a single electron bound in an oxygen vacancy is called an F^+ centre and two such electrons constitute an F centre. The F^+ centre can be optically excited and this is followed by relaxation of the surrounding lattice with the bound electron in its excited state, and subsequently by de-excitation through photon emission. While a similar sequence may occur for the F centre, it is not the dominant process that arises from optical excitation. The most recent indication (Orera and Chen 1987c) is that some defect complex involving an H^- ion plays an intermediary role between excitation and emission processes. Specifically, excitation is followed by spontaneous thermal ionisation of the F centre, to become an F^+ centre, with the liberated electron migrating through the conduction band to be trapped by the H^- complex, denoted $[H_x^-]^+$, where x indicates the presently unidentified defect element associated with an H^- ion, and the superscript $^+$ indicates that the complex has net charge $(+e)$ relative to the rest of the crystal lattice. The electron trapping converts $[H_x^-]^+$ to $[H_x^-]^0$. The $[H_x^-]^0$ defect can be thermally ionised, with the liberated electron migrating to an F^+ centre, which traps it in an excited state, thereby becoming an F centre, and subsequently de-exciting through photon emission. This stage of the process is the characteristic thermoluminescence of the F centre in MgO.

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Before the recent work of Orera and Chen, it was thought (Summers *et al* 1983) that an H^- ion alone (denoted $[H^-]^+$) was involved in the F-centre luminescence in MgO, through electron trapping to form $[H^{2-}]^0$, and subsequent thermal ionisation. Other recent work by Orera and Chen (1987a) indicates that this is indeed the case in CaO. Although it may not be of principal importance for F-centre luminescence in MgO, the H^{2-} ion can exist in that crystal, and its spin density has been determined experimentally both at the hydrogen nucleus (Tombrello *et al* 1984) and at the nearest-neighbour Mg^{2+} nuclei (Orera and Chen 1987b).

The optical excitation and emission processes of the F centre in MgO are well established (Chen *et al* 1969, Kappers *et al* 1970), and its corresponding electronic states have been analysed theoretically (Wilson and Wood 1976, Summers *et al* 1983). The optical processes of the F^+ centre in MgO are also well established (Henderson and King 1966, Chen *et al* 1969, Kappers *et al* 1970), and the present authors with collaborators have done preliminary theoretical work on the corresponding electronic states (Vail *et al* 1984, 1987, Vail and Pandey 1985).

We have undertaken a theoretical study of the defects F, F^+, $[H^-]^+$, and $[H^{2-}]^0$, aware that ultimately $[H_x^-]^+$ and $[H_x^-]^0$ must also be understood for a clear picture of the F-centre optical cycle in MgO. We believe that these centres provide a very sensitive test of any method of simulating defects in ionic crystals. They include the following features: (i) charged (F^+ and $[H^-]^+$) and uncharged (F and $[H^{2-}]^0$) defects; (ii) spin-paired electrons (F and $[H^-]^+$); (iii) unpaired electrons, inducing spin polarisation (F^+ and $[H^{2-}]^0$); (iv) vacancy-centred electrons (F^+ and F) and nuclear-centred impurity defects ($[H^-]^+$ and $[H^{2-}]^0$); and (v) diffuse states for the outer electron of $[H^{2-}]^0$ and for the excited state of the F centre. Because the energies of different states of a given defect, and of different combinations of defects, need to be compared to reasonably high accuracy ($\leqslant 0.1$ eV) in analysing the defect processes, the total energy of the defect and its embedding crystal lattice needs to be estimated accurately and consistently. This requires that we take into account (i) the effect of the defect in significantly perturbing the detailed electronic structure of nearby ions; (ii) the electronic structure of the embedding lattice; (iii) the lattice distortion in terms of nuclear displacement from perfect lattice equilibrium positions; (iv) long-range dielectric polarisation of the lattice in the case of charged defects such as F^+ and $[H^-]^+$. In addition, particularly for the case of diffuse defect electrons, dynamic electron–lattice correlation is likely to be significant.

In this paper we report results from the first stage of investigation of the four related defects F, F^+, $[H^-]^+$, and $[H^{2-}]^0$ in MgO, incorporating all the aspects of defect–lattice interaction mentioned above, except for dynamic electron–lattice correlation. Our approach is to describe the defect and a small number of its surrounding ions as a molecular cluster, treated quantum-mechanically, embedded in a crystal lattice that is described by the classical shell model. The quantum-mechanical treatment of the molecular cluster is based on the unrestricted Hartree–Fock self-consistent field approximation with many-body Rayleigh–Schrödinger perturbation theory correlation correction. In the present work the correlation correction is not included. In § 2 the method is described in more detail.

In § 3 our calculations and results are described in detail. Since they are quite extensive, § 3 is subdivided as follows. In § 3.1 a minimal basis set of O^{2-} in MgO is derived. In § 3.2 optimal basis sets are determined for each of the four defect centres in a fixed nearest-neighbour molecular cluster. In § 3.3 quantum mechanical features of the embedding lattice are refined by (i) optimising the nearest-neighbour Mg^{2+} basis sets for a given set of primitive functions, and (ii) enlarging the molecular cluster to

include second-neighbour O^{2-} ions as derived in § 3.1, and also taking into account the electronic structure of the lattice to fourth neighbours. Our calculated F^+-centre results are here compared with those of other authors. In § 3.4 the minimum energy of the entire lattice, including the defects, is estimated, taking account of nuclear displacements from perfect lattice equilibrium positions, as well as dipole polarisation of ions that are not included in the molecular cluster. Also in this section, total energies and orbital radii are summarised. Our calculated results for the F, $[H^-]^+$, and $[H^{2-}]^0$ centres are then compared with those of other authors. In § 3.5 spin densities at the hydrogen nuclei in $[H^{2-}]^0$, and at nearest-neighbour Mg^{2+} nuclei in both $[H^{2-}]^0$ and F^+, are calculated and compared with experimental values. In § 3.6 a preliminary analysis of the optically excited unrelaxed excited state of the F^+ centre is presented. In § 3.7 a single-site description of the defects is presented, ignoring all quantum-mechanical features of the surrounding lattice. In § 3.8 short-range shell model parameters are derived for H^- and H^{2-} interactions with both Mg^{2+} and O^{2-} in MgO. The results given in § 3.1, and all results for the F^+ centre, are taken from Pandey (1988).

The calculations of § 3 illustrate how most of the essential features of a defect system can be systematically incorporated into a theoretical simulation. Furthermore, they establish the necessary foundation for further analysis of these particular defects, and correctly represent some of their properties. Nevertheless, they are incomplete, and in § 4 their limitations are discussed critically to indicate what an ideal, complete analysis would entail. Finally, in § 5 the useful results obtained in this work are summarised.

2. Method

We apply the minimum energy principle to an infinite crystal containing a defect. This consists of two parts: the defect cluster, which incorporates the molecular cluster, and the embedding classical shell model lattice (see for example Catlow *et al* 1982). The defect cluster will contain all ions that are significantly affected by the defect, including if necessary some shell model ions. The harmonic distortion and polarisation of the embedding lattice are determined by simulating the molecular cluster by a set of point charges whose low-order electrostatic multipole moments match those of the molecular cluster. We denote the energy of the embedding lattice containing these cluster point-charge simulators by E_H. We denote by E_A the energy of the molecular cluster electrons interacting among themselves and with: (i) the point charges of bare cluster nuclei, (ii) shell model ions of the defect cluster and of the embedding lattice, and (iii) any potentials that are added to shell model ions near the defect. The total energy is then

$$E = (E_H + E_A + E_C - E_S) \tag{2.1}$$

where E_C includes the Coulomb energy of bare nuclei of the cluster, and subtracts the Coulomb interaction energy among the point-charge molecular cluster simulators. Also in equation (2.1) E_S consists of any short-range shell model ion interactions in E_H that are included quantum-mechanically in E_A. Thus E_C and E_S eliminate double counting of energies in E_H and E_A.

The total energy E in equation (2.1) is minimised with respect to all shell and core positions and simultaneously with respect to variational parameters in the molecular cluster wavefunction. This minimisation is updated while the nuclear positions of the molecular cluster are varied to give overall minimisation of E. This variation may be extended to ions outside the molecular cluster if the multipole matching has not been

carried to a high enough order. The entire process is carried out in a single calculation by a program named ICECAP, described by Harding *et al* (1985). We believe that without the flexibility and automated nature of this program, investigations of the sort reported here would be impractical. ICECAP has two major components: the Harwell HADES program (Norgett 1974, Catlow 1982), which evaluates the classical energy E_H variationally, and a Hartree–Fock program by Kunz (unpublished) that evaluates E_A in a given configuration of molecular cluster nuclei and lattice point charges.

The classical calculation of E_H here requires knowledge of the lattice structure (MgO, rocksalt structure), the nearest-neighbour lattice spacing, denoted a (2.106 Å), and the ionic charges for both host ions and defect centres. Thus we have charge $(-e)$ for F^+ and H^-, and $(-2e)$ for F and H^{2-}. Also required are shell model parameters, which we have taken from Sangster and Stoneham (1981), in which Mg^{2+} is unpolarisable and has negligible second-neighbour short-range interaction, in contrast to O^{2-}. For further details see § 3.8.

The quantum-mechanical molecular cluster energy E_A is evaluated in unrestricted Hartree–Fock self-consistent field approximation in this work. The shell and core positions of the embedding lattice are taken from the calculation of E_H. In this work ions were included only to 5.6 nearest-neighbour distances from the defect centre. It is preferable (Vail and Woodward 1988) to ensure that this point-charge array has only the net charge of the defect, or even better to include the infinite lattice by an adaptation of the Ewald method (Ewald 1921, Norgett 1974). Nevertheless, we do not believe that our results are affected by this limitation, because the Madelung potential in our molecular cluster is reasonably accurate (Vail *et al* 1984), and our wavefunctions are reasonably localised within the embedding region.

In the Hartree–Fock approximation a many-electron wavefunction is a Slater determinant of one-electron functions (φ_1, φ_2, ... φ_N) that spans a Hilbert space manifold of N dimensions, if there are N electrons. When this manifold is determined variationally by minimising the N-electron energy, we obtain the Fock equation for the one-electron functions:

$$F\varphi_j = \varepsilon_j\varphi_j \qquad j = 1, 2, \ldots N \tag{2.2}$$

where φ_j are spin eigenstates in the unrestricted Hartree–Fock approximation. For a ground state, the solutions corresponding to the N lowest Fock eigenvalues ε_j are normally appropriate. For excited states, and for the perturbation theory correlation correction (Goalwin and Kunz 1986, Kunz *et al* 1988), additional Fock eigenstates will be required. Thus, in general, we seek a non-minimal set of the lowest eigenstates of equation (2.2). This in turn can be done variationally. We follow the approach of Roothaan (1951) and expand φ_j as a linear combination of atomic-like orbitals:

$$\varphi_j = \sum_{k=1}^{N'} C_{kj}\chi_k \tag{2.3}$$

where, ignoring the spin dependence, χ_k is Gaussian localised with spherical harmonic angular dependence:

$$\chi_k(\boldsymbol{r}) = n_k \exp(-\alpha_k|\boldsymbol{r} - \boldsymbol{R}_i|^2)Y_l^m(\Omega_i). \tag{2.4}$$

Such a function is called a primitive. In equation (2.4), n_k is a normalisation factor, $\boldsymbol{R}_i$ is the centre of localisation, Ω_i is the angular position of $(\boldsymbol{r} - \boldsymbol{R}_i)$, Y_l^m is a spherical harmonic, and l, m and i depend on k.

Suppose we have a given set of N' exponential coefficients α. If there were no self-consistent field term in F (equation (2.2)), then minimising ε_j with respect to coefficients C_{kj} of equation (2.3) would give a matrix eigenvalue equation of order N'. Since there is a self-consistent field, however, the matrix equation must be solved iteratively to give N' eigenvalues ε_j and N' eigenvectors C_j with elements C_{kj} ($k = 1, 2, \ldots N'$). The N-electron energy is a function not only of these coefficients C_{kj}, but also of the exponential coefficients α_k (equation (2.4)). In principle, these should also be treated variationally, with a sufficient number of them determined for a given molecular cluster so that the overall enegy minimisation cannot be significantly improved by adding more. This procedure is illustrated in § 3.2 for the central site of the defects. When the process is impractical because of computational limitations, one may use, and possibly augment, primitive sets that have been determined in other calculations, as we do in §§ 3.1 and 3.3.

Since molecular cluster calculations are typically large in terms of computer space and time, it is sometimes advantageous to reduce the number of linearly independent functions χ_k in equation (2.3). This is done by performing a preliminary analysis and then fixing the ratios of sets of coefficients, corresponding to sets of exponential αs. Then equation (2.3) would be replaced by

$$\varphi_j = \sum_k C_{kj}\chi'_k \tag{2.5}$$

where

$$\chi'_k = \sum_\lambda a_{\lambda k}\chi_\lambda. \tag{2.6}$$

The χ_λ are given by equation (2.4) and the fixed coefficients $a_{\lambda k}$ are taken from the preliminary analysis. This procedure, called contraction, will be used in §§ 3.1 and 3.3. The effect is to have a smaller-order matrix problem for a given set of primitives, since not all the primitives will now have independently variable coefficients. Those functions with independent coefficients, χ'_k in equation (2.5), are called basis functions. If the sum in equation (2.6) contains more than one primitive, then χ'_k is called a contracted basis function.

When a molecular cluster is embedded in a crystal, the question of appropriate boundary conditions arises. For a cluster that is strongly localised, it may be valid simply to treat the surrounding ions as point charges, as occur in the shell model. If the cluster is not so localised, then the electronic structure of the surrounding ions needs to be taken into account. This can be done by introducing Kunz–Klein localising potentials (Kunz and Klein 1978, Gilbert 1964, Kunz and Vail 1988) on the relevant sets of embedding lattice ions. The method has the following advantages.

(i) It is rigorously a part of the Hartree–Fock approximation, applied to the molcular cluster as part of an all-electron consideration of the whole crystal.

(ii) It participates in the entire variational process described above for the Hartree–Fock solution. It therefore avoids the unphysical effects of cluster–lattice orthogonalisation procedures, which either reduce the variational manifold spanned by the basis functions χ'_k, equation (2.6), or project the solution out of the iteratively converged manifold, or project the representation of cluster-ion electronic structure out of the manifold determined for it by perfect-lattice calculations.

(iii) Being an effective potential, it does not contribute to the self-consistent field of the molecular cluster. It therefore does not increase the two-electron integral list, nor

enlarge the dimensionality of the Fock matrix. A localising potential is determined for each ionic species by self-consistent perfect-lattice molecular cluster calculations centred on each species, using a program by Kunz (unpublished). The resulting potentials are then fitted to a set of Gaussian primitives (equation (2.4)) using a program by Keegstra and Kunz (unpublished). They lead to a modified Fock equation, requiring a different total-energy algorithm (Kunz and Vail 1988) from that of the original molecular cluster Hartree–Fock problem. They are applied in § 3.3.

For some processes, we need to determine states for which the lattice is not relaxed to minimum energy self-consistently with the defect. An example is the final state of an optical transition, which occurs faster than the ability of the lattice to respond. It may be that, in terms of the shell model, only the cores remain fixed in their ground state positions, while the shells adjust instantaneously to the transition. The other extreme is where neither cores nor shells readjust at all during the transition. Both approaches are options in the ICECAP program, and the second approach is applied in § 3.6.

3. Calculations and results

3.1. O^{2-} in MgO

A guiding attitude in our work is to contribute to a body of results that can be meaningfully assessed because they all derive from the same kind of model, treated by the same methods, using the same approximations. Currently, one necessary approximation is that the primitive sets and their contractions (equation (2.6)) cannot always be determined optimally for all the ions of a molecular cluster. We must then rely on the work of others, and the most extensive compilations of Gaussian basis sets are those of Huzinaga and co-workers (1971, 1984) for free atoms and ions. Now because Mg^{2+} is a tightly bound cation, we believe that the primitive sets of Huzinaga (1984) for neutral Mg^0 or for Mg^{2+} should be useful in the MgO crystal. However, O^{2-} is not a bound ion in free space, and therefore it requires special attention.

We have analysed an oxygen-centred nearest-neighbour molecular cluster $(Mg^{2+})_6(O^{2-})_1$ embedded in MgO, with perfect lattice spacing. Second-neighbour O^{2-} ions and third-neighbour Mg^{2+} ions have Kunz–Klein localising potentials associated with them. The Mg^{2+} basis set was the (4, 3/4) contraction of Huzinaga (1984), meaning two s-type contactions of four and three primitives, respectively, and a p-type contraction of four primitives. The O^{2-} ion is based on the (4, 3/4) contaction for O^0 of Huzinaga (1984). First, the total energy is minimised with respect to independent variations of the coefficients of all the oxygen primitives (we say the O^0 basis set is decontracted). The exponential coefficients of longest range of both s- and p-type primitives were then optimised. The coefficients of the s-type primitives are obtained for the oxygen 1s- and 2s-like eigenstates from that calculation, and are then fixed in relative magnitudes (contracted), and the calculation is repeated with p-type primitives treated independently. For this second calculation, the basis set is (7, 7/1, 1, 1, 1) contraction. The resultant coefficients for the oxygen 2p-like states are then contracted, resulting in a (7, 7/4) basis set of contractions. In going from the O^0 (4, 3/4) contraction to the totally decontracted O^{2-}, the energy dropped by 10.78 eV. On recontracting, the net rise in energy was 0.10 eV.

Table 1. Contracted basis sets for free O^0 (Huzinaga 1984), and for O^{2-} in MgO (present work). For the primitive functions, exponential coefficients α are in Bohr atomic units a_0^{-2}, and ranges R (equation (3.1)) are in units of MgO nearest-neighbour distances.

Orbital	α	R	O^0 coeff.	O^{2-} coeff.
1s	821.83934	0.006	0.0355522	0.040206
	123.68182	0.016	0.2469282	0.282368
	27.66617	0.034	0.8622483	0.946149
	7.29957	0.066	1.0	1.0
	10.60696	0.055		0.110281
	0.91764	0.185		0.091509
	0.28	0.336		−0.027930
2s	821.83934	0.006		−0.008556
	123.68182	0.016		−0.064242
	27.66617	0.034		−0.230668
	7.29957	0.066		−0.253617
	10.60696	0.055	−0.1515865	−0.161864
	0.91764	0.185	1.0	1.0
	0.28	0.336	0.8450905	1.377273
2p	17.75035	0.042	0.0788796	0.092957
	3.86468	0.090	0.4367318	0.514539
	1.04772	0.174	1.0	1.0
	0.28	0.336	0.8677474	1.648566

In table 1, we show the $(4, 3/4)$ contraction coefficients for free O^0 and the $(7, 7/4)$ contraction coefficients for O^{2-} in MgO with the corresponding exponential coefficients α, with α re-expressed in terms of a range R which we define by

$$R = (2\alpha)^{-1/2}. \tag{3.1}$$

This range is the distance at which the squared magnitude of an s-type primitive drops to e^{-1} of its maximum, and of a p-type primitive is a maximum. We note from table 1 that the 1s- and 2s-like orbitals of O^{2-} in MgO take up significant contributions from the 2s and 1s primitive sets, respectively, of O^0. Furthermore, we note a significant increase in the coefficients of the longest-range 2s and 2p primitives in going from free O^0 to O^{2-} in MgO, an effect that seems reasonable in view of the Coulomb and Pauli repulsions associated with the two extra electrons. A significant consequence of improving the contractions as in table 1 is described at the end of § 3.3. For completeness, we mention that Causa *et al* (1986) have developed an $(8, 6/6)$ contracted set for O^{2-} in MgO.

3.2. Defect basis sets

The basis functions centred on the defect site, an O^{2-} vacancy in the case of F^+ and F centres, and substitutional at an O^{2-} site for H^- and H^{2-} ions, need to be determined. We have done this by using a nearest-neighbour molecular cluster $(Mg^{2+})_6(d)_1$, where d stands for F^+, F, $[H^-]^+$, or $[H^{2-}]^0$. The approach seems to be justified by the results as we shall see, except for the case of H^{2-}. At this stage of the analysis, the $(3, 3, 3/3)$ contracted basis set for neutral Mg^0 from Huzinaga (1984) has been used, with the 3s orbital eliminated, leaving $(3, 3/3)$, and these nearest-neighbours have been kept at their perfect lattice sites.

Table 2. Optimal sets of primitives for defects in MgO: exponential coefficients α (units a_0^{-2}); ranges R (units nearest-neighbour distances), equation (3.1); relative coefficients C_{kj}, equation (2.3); and energy lowering, ΔE (eV).

Defect	α	R	C_{kj}	1s(+)	1s(−)	2s(+)	ΔE
F^+	0.079485	0.63	1.0				—
F	0.095888	0.57	1.0				—
	0.066706	0.69	−0.14052				0.15
$[H^-]^-$	0.18012	0.42	1.0				—
	1.42032	0.14	0.18834				—
	9.87980	0.06	0.03001				0.27
	0.45093	0.26	0.12976				0.14
	0.066706	0.69	0.05386				0.10
	0.025563	1.11	0.01667				0.01
$[H^{2-}]^0$	0.17615	0.42		1.0	1.0	0.15330	—
	0.0070458	2.12		−0.00349	−0.00358	1.0	—
	2.22684	0.12		0.15621	0.15554	−0.00039	1.84
	0.057517	0.74		0.08598	0.08662	−0.39274	0.67
	23.00685	0.04		0.01360	0.01354	−0.00082	0.12
	0.45093	0.26		0.28589	0.28275	−0.08463	0.26[a]

[a] α_1 iterated.

The procedure has been to begin with a simple s-type primitive, except in the case of $[H^{2-}]^0$, and to vary its exponential coefficient α until the total energy of the defect crystal was minimised to an accuracy of the order of 0.01 eV. This includes polarisation of the embedding shell model lattice, which is negligible for the electrically neutral defects F and $[H^{2-}]^0$, but definitely not negligible for F^+ and $[H^-]^+$. One then adds a second s-type primitive, optimising its α in the same way, holding the first α fixed, and then iterating until both αs are simultaneously optimised self-consistently. In practice, very little energy lowering ensues from the iteration, and so with one or two exceptions no further iteration was carried out as additional primitives were introduced and optimised. The process was terminated when the point was reached where adding a new primitive lowered the total energy by only about 0.01 eV. In the case of $[H^{2-}]^0$, the two initial primitives, roughly representing the doubly occupied 1s state and the singly-occupied 2s state respectively, were determined self-consistently, and then the same procedure was followed as for the other defects.

In table 2 the results of these calculations are given. They include (i) exponential coefficients α, (ii) the ranges R, equation (3.1), (iii) their relative coefficients which, apart from a normalisation factor are the C_{kj} of equation (2.3), with j referring to molecular orbitals that are dominated by the defect-centred primitives labelled k, and (iv) the magnitude ΔE by which the total energy is lowered by introducing each additional primitive. In table 2 we note that three sets of coefficients are given for $[H^{2-}]^0$. They correspond to the two 1s-like states of opposite spin, (+) and (−) respectively, and to the 2s-like state (+). Comparing the two 1s-like states, we clearly see the spin polarisation effect, which contributes to the spin density, discussed in § 3.5.

3.3. Embedding lattice: quantum features

We now wish to introduce details of the electronic structure of the surrounding lattice into the defect calculation. In § 3.2 the nearest-neighbour Mg^{2+} were fully contracted

Table 3. Contracted basis sets for free Mg^{2+} (Huzinaga 1984), and for Mg^{2+} nearest-neighbours of F^+ centres in MgO (present work). Exponential coefficients α in units a_0^{-2}.

Orbital	α	Free Mg^{2-} coeff.	Mg^{2+} coeff. (MgO)
1s	654.890970	0.1010905	0.122050
	98.727577	0.5836748	0.681394
	21.335201	1.0	1.0
	28.128657		0.175827
	2.295112		0.153987
	0.799752		−0.059163
2s	654.890970		−0.028544
	98.727577		−0.174623
	21.335201		−0.300956
	28.128657	−0.1444224	−0.134815
	2.295112	1.0	1.0
	0.799752	0.7939727	0.793789
			axial
2p	23.805108	0.1953710	0.195149
	5.116593	0.7848047	0.783230
	1.231392	1.0	1.0
			non-axial
			0.195777
			0.786754
			1.0

with coefficients appropriate to the free atom or ion. They were therefore largely unable to respond to the embedding lattice and defect. We have therefore decontracted and recontracted them in the same way as described for O^{2-} in § 3.1, but now in the $(Mg^{2+})_6(d)_1$ cluster, with the defect basis sets of table 2 left uncontracted. In this way, the defect and its nearest neighbours adjust to each other optimally for the given primitive sets in the embedding lattice. At this stage, the nearest neighbours were still held at their perfect lattice sites, and the embedding shell model lattice was allowed to polarise. The results are exemplified by the F^+ centre in table 3, where 'axial' and 'non-axial' refer to p-type functions with axes directed along and transverse to the line joining the Mg^{2+} ion to the defect, respectively. The difference between axial and non-axial basis functions represents polarisation of the Mg^{2+} ions by the defect. Similar results were obtained with the other defects, in all cases producing a total energy reduction of approximately 15 eV. This alone indicates the importance of such a correction, and the conclusion is borne out by the spin density analysis of § 3.5.

Since the nearest neighbours are significantly perturbed by the defect, and the defects themselves are not very strongly localised at their central sites (see § 3.4), we next increased the cluster size in two ways simultaneously. First, we added the twelve second-neighbour O^{2-} ions to the Hartree–Fock cluster, which now becomes $(Mg^{2+})_6(O^{2-})_{12}(d)_1$. The Mg^{2+} and O^{2-} basis functions (90 in all, for a total of 180 electrons) are kept fully contracted because of the size of the calculations. Second, we added Kunz–Klein potentials to third-neighbour Mg^{2+} ions and to fourth-neighbour O^{2-} ions. In this way, the electronic structure is taken into account for all nearest neighbours of the Mg^{2+} ions which themselves are nearest neighbours of the defect. Since the defect

Table 4. F^+ centre in MgO, ground-state properties calculated with free O^0 basis, and with O^{2-} basis for MgO (table 1). Range R and orbital radius $\langle r^2 \rangle^{1/2}$ in units of lattice spacing.

			Mulliken population		
	R	$\langle r^2 \rangle^{1/2}$	F^+	Mg^{2+}	O^{2-}
O^0 basis	0.53	0.87	1.71	10.0000	9.9409
O^{2-} basis (MgO)	0.50	0.85	1.08	9.9993	9.9940

basis sets were kept uncontracted throughout this work, they now respond to the 12 rather large second-neighbour O^{2-} ions at a distance of $\sqrt{2}$ times that of the six nearest-neighbour Mg^{2+} ions. They, of course, respond to the third- and fourth-neighbour Kunz–Klein potentials as well. The effect is again well illustrated by the spin density results of § 3.5.

These calculations also lead to a significant example of the importance of an appropriate basis set, as shown in table 4. With the O^{2-} basis set of § 3.1 optimised to the MgO crystal lattice by recontraction, one finds the Mulliken population of the vacancy-centred F^+ orbital to be 1.08. Since this orbital is a 1s-type Gaussian with $\langle r^2 \rangle^{1/2} = 0.85a$, it is fair to interpret this by saying that almost exactly one electron is trapped in the vacancy. On the other hand, with the original contractions of O^{2-}, appropriate to the free neutral oxygen atom, one finds a Mulliken population of 1.71, with similar localisation. In this case one must say that there is considerable charge transfer to the vacancy, about $0.71e$, seen in table 4 to come essentially from the second-neighbour O^{2-} ions. Furthermore, an examination of the Fock eigenstates shows that with our best O^{2-} basis set, the F^+ centre lies above the valence band (i.e., above the occupied Mg^{2+} and O^{2-} molecular orbitals), while for the inferior O^{2-} basis set there are equal spin-up and spin-down contributions from the vacancy at a level in the gap below the O^{2-} 2p-like states, with some contribution from one spin at the top of the valence band. This same charge transfer effect (about $0.75e$) has been found in an F^+ centre calculation for MgO by Klein *et al* (1987), and also for Al_2O_3 by Choi and Takeuchi (1983), who locate the localised state in the valence band gap below the O^{2-} 2p-like states. In both of these works, lattice polarisation is neglected. One might then guess that the question of charge transfer hinges upon a competition between two screening mechanisms for the excess charge of the defect: one by long-range lattice polarisation and the other by short-range charge transfer. In our work, where long-range polarisation is always included, the charge transfer does not occur with our best O^{2-} basis set, but does occur with an inferior set. For Klein *et al* (1987) and Choi and Takeuchi (1983), without long-range polarisation, the screening can occur only by charge transfer, and is observed in their calculations. Since our O^{2-} basis sets are minimal, fully contracted sets, we do not consider the question to be definitively resolved here. Rather, we would like to see whether or not the system resists charge transfer when the second-neighbour O^{2-} ions are made more flexible by decontraction. Furthermore, the effect of correlation correction should be investigated, since it might be crucial in determining whether the vacancy tends to trap two electrons associated with a nearby hole, or simply traps a single electron.

3.4. Lattice relaxation

For the $(Mg^{2+})_6(O^{2-})_{12}(d)_1$ clusters with third- and fourth-neighbour Kunz–Klein potentials, we now minimise the total energy of the defect lattice by explicitly varying

Table 5. Defect lattice relaxation energies ΔE (eV) for F^+, F, $[H^-]^+$, and $[H^{2-}]^0$ centres in MgO after successive steps of first and second neighbour displacements to relaxed positions d (units: fraction of perfect lattice distance).

	F^+		F		$[H^-]^+$		$[H^{2-}]^0$	
	d	ΔE	d	ΔE	d	ΔE	d	ΔE
Mg^{2+}	1.03	0.35	0.985	0.05	1.06	1.12	1.07	1.41
O^{2-}	0.97	1.75	0.98	0.30	0.97	0.96	0.97	1.12
Mg^{2+}	1.03	0.66			1.03	0.24	1.03	0.29

the nearest- and second-neighbour positions, and allowing the HADES part of ICECAP to determine the positions of all other ions in response to shell model forces. ICECAP will perform this procedure automatically, but because of the size of the calculation we were forced to perform it a step at a time. This was done by optimising the Mg^{2+} positions with the O^{2-} ions held fixed, then optimising the O^{2-} positions with Mg^{2+} fixed at the optimum positions of the first step, and then iterating the Mg^{2+} optimisation. The successive improvements in total energy with each of these three steps are shown in table 5 for each defect. From the results we conclude that ionic positions have been determined to within about 0.01 lattice spacings, and total energies to within 0.2 eV.

Qualitatively, the near-neighbour displacements of table 5 are plausible. For each of the four defects the short-range repulsion is expected to be weaker than for the O^{2-} ion that it replaces. For the positively charged defects F^+ and $[H^-]^+$, the polarisation effect succeeds in pushing nearest-neighbour cations outwards, while drawing second-neighbour anions inwards. The same thing happens with $[H^{2-}]^0$, to the same extent as for the other two, because the third 2s-like electron is so diffuse that the first and second neighbours lie well within its orbit, and are unaffected by its net charge. For the electrically neutral F centre, on the other hand, there is no Coulomb effect, and the weakened short-range force compared to that of O^{2-} results in contraction of the surrounding lattice. This result disagrees with the conclusion of Summers *et al* (1983), who found a 3% outward relaxation for the nearest-neighbour Mg^{2+} ions of the F centre in MgO. While their treatment of the problem included most of the important features of the system, their modelling of ion-size and interionic effects was less systematic and extensive than in the present work.

In table 6 the results for each defect are summarised, including (i) total energy reductions due to defect basis optimisation, nearest-neighbour Mg^{2+} basis recontraction, and lattice relaxation, (ii) total energy, (iii) nearest-neighbour Mg^{2+} and second-neighbour O^{2-} positions, and (iv) orbital radius $\langle r^2 \rangle^{1/2}$, defined by

$$\langle r^2 \rangle^{1/2} = \langle \varphi_d | r^2 | \varphi_d \rangle^{1/2} \tag{3.2}$$

where φ_d is the Fock molecular orbital eigenstate that is dominated by defect-centred basis functions. In the case of $[H^-]^+$, φ_d lies between the O^{2-} 2s and 2p bands, and contains significant components of these O^{2-} orbitals, so that in this case $\langle r^2 \rangle^{1/2}$ is less meaningful than for the other defects. We note from table 6 that the orbital radius of the $[H^{2-}]^0$ 2s-like state extends well beyond the last (fourth) neighbours whose electronic structure has been included, and that its total calculated energy is greater than for $[H^-]^+$, a result that does not seem reasonable. We shall see that the spin density results of § 3.5 further indicate the inadequacy of our treatment of $[H^{2-}]^0$,

Table 6. Summary of results for F^-, F, $[H^-]^+$, and $[H^{2-}]^0$ centres in MgO: energy reductions (eV) due to defect basis optimisation ΔE_1, Mg^{2-} basis recontraction ΔE_2, and lattice relaxation ΔE_3; total energy E (eV), nearest Mg^{2-} and second O^{2-} neighbour positions d_1 and d_2, respectively (units: fraction of perfect lattice distance); orbital radius $\langle r^2 \rangle^{1/2}$ (units: nearest-neighbour distances).

	F^+	F	$[H^-]^+$	$[H^{2-}]^0$
ΔE_1	—	0.15	2.72	2.89
ΔE_2	15.13	14.90	15.13	15.03
ΔE_3	2.76	0.35	2.33	2.82
E	−56535.66	−56533.78	−56553.81	−56552.48
d_1	1.03	0.985	1.03	1.03
d_2	0.97	0.98	0.97	0.97
$\langle r^2 \rangle^{1/2}$	0.85	0.79	1.0^a	2.95^b

[a] Between O^{2-} 2s- and 2p-like bands.
[b] H^{2-} 2s-like state.

Table 7. Spin densities (units A^{-3}) for defects (d) F^+ and $[H^{2-}]^0$ in MgO, evaluated at various stages of approximation, and compared with experiment, at sites s.

	$(Mg^{2-})_6(d)_1$		$(Mg^{2+})_6(O^{2-})_{12}(d)_1$		
d(s)	Contracted	Recontracted	Unrelaxed	Relaxed	Experiment
$F^+(Mg^{2+})$	0.660	0.420	0.525	0.171	0.274^a
$[H^{2-}]^0(p)$	—	0.027	0.123	0.093	0.238^b
$[H^{2-}]^0(Mg^{2+})$	—	0.010	0.017	0.013	0.754^c

[a] Unruh and Culvahouse (1967).
[b] Orera and Chen (1987b).
[c] Tombrello *et al* (1984).

which will be discussed there. The theoretical analysis of $[H^{2-}]^0$ by Tombrello *et al* (1984) obtained an average radius of 1.85 lattice spacings: less than our result, but still significantly diffuse. Tombrello *et al* included the ion-size effect only to nearest neighbours (by orthogonalisation), and ignored lattice relaxation and spin polarisation. An explanation of our larger calculated radius may be that our wider, but still inadequate, ion-size barrier causes 'spilling' of the 2s-like orbital to be more spread out. The mechanism is described in § 3.5.

3.5. Spin densities

In the unrestricted Hartree–Fock approximation, spin-up and spin-down electrons are treated separately, so that if there is an unpaired electron, as in the F^+ and $[H^{2-}]^0$ centres, the Mg^{2+} and O^{2-} ions in the defect cluster will be spin polarised. We have calculated the net many-electron spin density at nearest-neighbour Mg^{2+} nuclei for both defects, and at the proton for $[H^{2-}]^0$. The results are given in table 7 for three stages of the calculations described in §§ 3.2, 3.3 and 3.4, namely (i) with an unrelaxed $(Mg^{2+})_6(d)_1$ cluster, first with the original basis, and then with the Mg^{2+} basis recontracted, (ii) with an unrelaxed $(Mg^{2+})_6(O^{2-})_{12}(d)_1$ cluster, and (iii) with the cluster

relaxed. In this way we can see the effects of recontracting the Mg^{2+} basis, of second-neighbour O^{2-} ions, and of first- and second-neighbour relaxations consistent with the embedding lattice. We see that the spin densities are very sensitive to all three effects. The calculated results can also be compared with experimental values obtained from measured isotropic hyperfine constants (Unruh and Culvahouse 1967, Orera and Chen 1987b, Tombrello *et al* 1984). From table 7 we see that the final calculated value for the F^+ centre is 62% of the experimental value, which is quite good agreement considering the sensitivity to basis set, cluster size, and cluster relaxation. For the $[H^{2-}]^0$ centre the final agreement at the proton site (p) is 39%, again not bad. Incidentally, it is very close to the value of 0.095 $Å^{-3}$ (40%) calculated by Tombrello *et al* (1984). However, at the nearest-neighbour Mg^{2+} nuclei the agreement is negligible, only 2%. We have noted in table 6 that the unpaired 2s-like electron in $[H^{2-}]^0$ has a calculated orbital radius of about three lattice spacings (a), while the electronic ion-size effect has only been carried out to a distance of ($2a$). It may be that because this potential barrier is cut off at ($2a$), the 2s-like electron spills over (or tunnels through) into the surrounding lattice, and if the ion-size effect were extended further, it might force the electron back into a more localised state. This spurious effect is quite common in calculations of this type and will be illustrated explicitly in the next section.

The spin polarisation effect can be clearly seen in the two 1s-like electronic states of $[H^{2-}]^0$. If the 2s-like electron is given spin up, then the 1s-like states of spin up and down have orbital radii $1.0251a$ and $1.0237a$, respectively, with an energy separation 0.0279 eV.

3.6. F^+-centre excited state

Optical excitation of the F^+ centre is not accompanied by instantaneous relaxation of the lattice. In the Franck–Condon approximation, the lattice does not relax at all during the transition. We may assume that this applies at least to the nuclei, and to shell model cores. At one extreme, one might assume that it applies to all but one electron, including the shells of shell model ions. At the other extreme, one might assume that shells and all electrons of the cluster respond instantaneously to the transition. We have carried out a preliminary analysis on the basis of the former assumption, namely that shell model shells as well as cores are frozen in the ground-state configuration during the transition, as are nuclei of the cluster, and that furthermore the contractions used for Mg^{2+} and O^{2-} cluster ions in the ground state are maintained throughout the transition. Thus there is very little flexibility in the cluster electronic configuration, and it cannot adjust significantly to the change of defect state in the transition.

Our procedure was to minimise the unrelaxed excited state energy with respect to variations in α (see equation (2.4)) for a vacancy-centred p-type function. The results are worth describing in detail. Four calculations were performed. First the entire lattice was described by the shell model: the Hartree–Fock 'cluster' consisted of a single electron. The range of the excited-state p-type function (see equation (3.1)) was found to be approximately half the lattice spacing (a). Then an $(Mg^{2+})_6(d)_1$ cluster was analysed, with d = F^+, and the optimum range was found to be approximately $1.5a$, with a subsidiary energy minimum occurring for a range of about $0.5a$. (In this calculation, an augmented Mg^{2+} basis set was used, rather than the recontracted set of § 3.3.) This effect represents the wavefunction spilling referred to at the end of

Table 8. Nearest-neighbour positions d (units: perfect lattice spacing), of F^+, F, $[H^-]^+$, and $[H^{2-}]^0$ defects in MgO, with and without ion-size effect.

	F^+	F	$[H^-]^+$	$[H^{2-}]^0$
With	1.03	0.985	1.03	1.03
Without	1.03	0.92	1.02	0.97

§ 3.5, due to the limited extent of the ion-size-effect barrier. Where Kunz–Klein potentials were added to second, third, and fourth neighbours to simulate their electronic structures, the stabilisation energy of the spilt solution compared to the more localised subsidiary solution was reduced, but its range was somewhat increased, to almost $2a$. Then, when the second-neighbour Kunz–Klein O^{2-} ions were replaced by the all-electron description and incorporated into the Hartree–Fock cluster, the spilling effect disappeared, and only one minimum persisted, at a range of approximately $0.5a$. (In this calculation, the $(3, 3/3)$ contractions for O^0 given by Huzinaga (1984) were used for O^{2-}.) One conclusion from this result is that the Kunz–Klein ion-size effect as evaluated in this work is significantly weaker than that of a Hartree–Fock O^{2-} ion.

Finally, the last calculation described above was repeated with the presumably superior Mg^{2+} and O^{2-} basis sets obtained in §§ 3.3 and 3.1, respectively. The localisation persisted. The calculated excitation energy was 7.59 eV, compared with the experimental value of 4.95 eV (Henderson and King 1966). We attribute the discrepancy mainly to the fact that the electronic structure of the lattice was largely incapable of responding to the transition of these calculations. Particularly, we would like to optimise the second-neighbour O^{2-} basis set, and to allow shells to relax in the presence of the excited-state defect. This is probably more important than the nearest-neighbour Mg^{2+} ions, partly because the anions are more polarisable than the cations, but also because eight second-neighbour anions overlap relatively strongly with the defect's p-type wavefunction, compared to only two nearest-neighbour cations. While this would lower the excited-state energy, it remains to be seen whether it accounts for the 2.64 eV discrepancy.

3.7. Single-centre treatment of the defect

It is commonly known that single-centre treatment of F-type centres, in which all ions of the crystal are described by the shell model, usually gives quite good results for calculated optical excitation energies (see for example Gourary and Adrian 1957). It is probably also widely understood that the corresponding states of the centre are not accurately described by such an approach. In this section we describe such calculations for the ground states only of the four defects F^+, F, $[H^-]^+$, and $[H^{2-}]^0$.

We have used the procedure of § 3.2 to obtain optimal defect basis sets. They turn out to be quite similar to those obtained in § 3.2, where full Hartree–Fock treatment of nearest-neighbour Mg^{2+} ions was included, while here these neighbours are shell model ions. Thus what is neglected here is the ion-size effect of the nearest (and all) neighbours. The positions of the nearest neighbours were then determined using ICECAP, which automatically varied them until total-energy minimisation was achieved, consistent with the defect centre and with the rest of the lattice. The nearest-neighbour positions obtained are given in table 8, along with those obtained in § 3.4, where ion-

size effects were included in detail. The result is that for the two positively charged defects, namely F^+ and $[H^-]^+$, neglect of the ion-size effect (i.e., short-range repulsion) of nearest neighbours has little effect, since the system is dominated by Coulomb interaction. Correspondingly, for the electrically neutral F centre, which has a small inward nearest-neighbour displacement with ion-size effect, there is a significantly larger contraction without it. For the $[H^{2-}]^0$ centre, the results with and without ion-size effect give opposite directions of nearest-neighbour displacement. The spin polarisation effect in the present case is extreme. If the 2s-like electron has spin up, it has orbital radius $1.04a$, while the two 1s-like electrons have radii $0.48a$ for spin up and $0.16a$ for spin down, with an energy separation of 3.016 eV. These differences are much greater than those found with ion-size correction in § 3.5. The fact that the 2s-like electron is much more localised in this case than in the presence of ion-size effect $(2.95a)$ no doubt accounts for the difference in nearest-neighbour relaxation. In view of our earlier discussions of $[H^{2-}]^0$ in §§ 3.4 and 3.5, the present result could even be qualitatively correct.

Finally, we give the calculated total defect energies for a shell model lattice. For F^+, F, $[H^-]^+$, and $[H^{2-}]^0$ they are respectively 18.47, 10.79, 1.80 and 0.63 eV. We note that the ordering here, unlike that obtained in § 3.4, table 6, has the F-centre energy lower than the F^+, and $[H^{2-}]^0$ lower than $[H^-]^+$, as we would expect on the simple argument that the vacancy (or proton) trapping an additional electron would lower the system's total energy. If this argument is correct, it indicates that further accuracy is required in the cluster calculations in order to obtain absolute comparability among the defects.

3.8. Short-range shell model parameters

In the course of evaluating the lattice relaxation in § 3.4 we essentially obtained the total energy E as a function of nearest- and second-neighbour positions, d_1 and d_2 respectively, as fractions of their distances from a central O^{2-} site in the perfect lattice. This can be used to estimate short-range shell model parameters for H^- and H^{2-} ions interacting with Mg^{2+} and O^{2-} in MgO.

The argument is as follows. We assume that the approximation of pairwise inter-ionic forces is valid. For a large variety of ionic crystals, this is borne out by the success of shell model simulation of a wide range of properties (see for example Mackrodt 1982). We then assume that our quantum-mechanical description of host–lattice ion interactions (in the clusters used in § 3.4) is approximately equivalent to the corresponding shell model interactions. The work of Vail *et al* (1987) tends to support this assumption, although more work on the question would be useful. We then imagine a shell model of the MgO crystal containing a single H^{n-} substitutional anion, for $n = 1$ or 2. We let the short-range (H^{n-})–(Mg^{2+}) nearest-neighbour and (H^{n-})–(O^{2-}) second-neighbour interactions be denoted by subscripts $k = 1$, 2, respectively, and represent them by Buckingham potentials $B_{nk}(A_{nk}, \rho_{nk}, C_{nk}; d_k)$, where

$$B(A, \rho, C; d) = A \exp(-d/\rho) - Cd^{-6} \tag{3.3}$$

where (A, ρ, C) are constants, characteristic of the pair of ion species nk, and the separation distances d_k are variable. Now if we use HADES to evaluate the total energy

Table 9. H^{n-} ion ($n = 1, 2$) in MgO: ranges of first- and second-neighbour positions d_1 and d_2 (units: fraction of perfect lattice distances) used to determine shell model short-range potentials.

Fixed		Variable
$n = 1$	$d_1 = 1.06$	$d_2 = 1.0, 0.98, 0.96, 0.94$
	$d_2 = 0.97$	$d_1 = 1.06, 1.05, 1.03, 1.01$
$n = 2$	$d_1 = 1.07$	$d_2 = 1.0, 0.98, 0.96, 0.94$
	$d_2 = 0.97$	$d_1 = 1.07, 1.05, 1.03, 1.01$

$E_n^{(0)}$ for given values of d_k while *omitting* B_{nk} for the defect, then the true shell model energy $E^{(c)}$, where (c) refers to classical, will be

$$E_n^{(c)}(d_1, d_2) = E_n^{(0)} + \sum_k N_k B_{nk}(d_k) \tag{3.4}$$

where N_k is the number of kth neighbours. In MgO, $N_1 = 6$ and $N_2 = 12$. Apart from an additive constant a_n that qualitatively expresses internal quantum-mechanical energy of the ions, $E_n^{(c)}$ should be approximately equal to the lattice energy $E_n^{(Q)}$ evaluated with the quantum-mechanical cluster. Thus

$$E_n^{(Q)} \simeq E_n^{(c)} + a_n. \tag{3.5}$$

Then, from equations (3.4) and (3.5),

$$E_n^{(Q)}(d_1, d_2) - E_n^{(0)}(d_1, d_2) - 6B_{n1}(d_1) - 12B_{n2}(d_2) - a_n = 0. \tag{3.6}$$

Thus for a fixed value of d_2, if we know $E_n^{(Q)}$ and $E_n^{(0)}$ for four values $d_{1,j}$ ($j = 1, 2, 3, 4$) of d_1, we should be able to solve for the four unknowns $x_1 = A_{n1}$, $x_2 = \rho_{n1}$, $x_3 = C_{n1}$, $x_4 = a_n' = [a_n + 12B_{n2}(d_2)]$. In this case, equation (3.6) is of the form

$$f_{nj}(x_1, x_2, x_3, x_4) = 0 \qquad j = 1, 2, 3, 4. \tag{3.7}$$

Similarly, for a fixed value of d_1, if we know $E_n^{(Q)}$ and $E_n^{(0)}$ for four values $d_{2,j}$ of d_2, we can solve for $y_1 = A_{n2}$, $y_2 = \rho_{n2}$, $y_3 = C_{n2}$, $y_4 = a_n'' = [a_n + 6B_{n1}(d_1)]$. In this case, equation (3.6) is of the form

$$g_{nj}(y_1, y_2, y_3, y_4) = 0 \qquad j = 1, 2, 3, 4. \tag{3.8}$$

We have used a library routine that minimises

$$S = \sum_j |f_{nj}|^2 \tag{3.9}$$

and similarly for g_{nj}, reporting the converged values of S. Since we require energies accurate to about 0.05 eV, we have defined convergence to be for $S \leqslant 4(0.05)^2 = 10^{-2}$ eV. In practice, we renormalised $E_n^{(Q)}$ to be approximately equal to $E_n^{(c)}$, so that large values of a_n' and a_n'' would not emerge, and we used starting values of A, ρ and C equal to host–lattice anion–cation and anion–anion values.

In table 9, we show the fixed and variable values of d_1 and d_2 that were used. They include fairly large distortions in order to reproduce the anharmonic features of the

Table 10. Shell model short-range parameters in MgO : H^{n-} ($n = 1, 2$): see equation (3.3).

Ion pair	A(eV)	ρ(Å)	C(eV.Å^6)
O^{2-}–$Mg^{2+\,a}$	1275.2	0.3012	0
O^{2-}–$O^{2-\,a}$	22 764.3	0.1490	20.37
H^-–Mg^{2+}	538.14	0.2854	0
H^-–O^{2-}	48 262.72	0.3067	3734.79
H^{2-}–Mg^{2+}	1856.41	0.3132	0
H^{2-}–O^{2-}	77 143.25	0.2977	4936.64

[a] Sangster and Stoneham (1981).

Table 11. H^{n-} in MgO ($n = 1, 2$): first- and second-neighbour equilibrium positions d_1 and d_2 (fraction of perfect lattice distance) in the shell model and molecular cluster respectively.

		Shell model	Cluster
$n = 1$	d_1	1.02	1.03
	d_2	0.97	0.97
$n = 2$	d_1	1.03	1.03
	d_2	0.97	0.97

short-range interactions. In table 10, the values obtained for A, ρ and C are given for H^{n-} in MgO, along with those for host–lattice species that were used throughout this work (Sangster and Stoneham 1981).

This method has been previously applied by Meng *et al* (1988) for Cu^+ in NaF and in KCl. In those cases, it is reasonable to neglect Cu^+ short-range interactions with second-neighbour cations, and to assume that Cu^+ is essentially unpolarisable. It is then possible to apply the resultant shell model to analyse Cu^+ diffusion by the vacancy mechanism, not only in the original hosts, but assuming transferability, to the other fluorides and chlorides. In the present work, the polarisability of H^{n-} is not likely to be negligible, so that before any applications can be made the shell parameters (core coupling and charge) would need to be determined. However, as a check on the consistency of the method we have used the shell model results of table 10 to calculate the first- and second-neighbour relaxations to equilibrium. They are given in table 11, and are found to be comparable with the full-cluster values obtained in § 3.4. In all cases but one, the small discrepancies (less than $0.01a$) are a measure of the accuracy of the approximations described at the beginning of this section. Clearly, because of the reservations expressed earlier about our quantum-cluster results for $[H^{2-}]°$, the present results for that ion should not be relied upon.

The method described in this section derives shell model parameters from a series of large, accurate calculations. Since shell model calculations are so much less time-consuming than quantum-cluster calculations, if the kind of applications made by Meng *et al* (1988) turns out to be valid by comparison with experiment, it will provide a very efficient extension of a single defect analysis to a large number of configurations, systems and processes.

4. Perspective

The central feature of this work has been to describe and analyse the ground states of point defects in MgO. The excited states which, with the exception of the F^+ centre (§ 3.6), have been ignored, could be dealt with by the same methods. These methods include quantum-mechanical treatment of the defect center, the ion-size effect of the nearby ions, polarisation and distortion of the surrounding lattice, and both physical and mathematical consistency among all elements of the model calculation. Basic assumptions that we shall not discuss here are the static-lattice approximation, and the assumption that the shell model can adequately represent the embedding lattice. We now discuss the extent to which our calculations have implemented the methods listed above.

The quantum-mechanical treatment of the defect centre requires a correlation correction in order to be complete. The Rayleigh–Schrödinger perturbation theory has been shown to be effective for such work (Goalwin and Kunz 1986) and has been adapted to the present methods (Kunz *et al* 1988). The ion-size effect includes both Hartree–Fock ions and Kunz–Klein potentials in a mathematically consistent formulation (Kunz and Klein 1978, Kunz and Vail 1988). The Hartree–Fock treatment of nearby ions could be improved by optimising the Gaussian exponential coefficients α in the presence of the defect, and by using less restrictive contractions in the basis functions. The accuracy of the Kunz–Klein potentials could also be improved. In the present work, we believe that such corrections would have little effect, except in the case of $[H^{2-}]^\circ$, where a larger Kunz–Klein region is called for, and in the case of the F^+-centre excited state, where improved basis functions for second-neighbour O^{2-} ions are needed. While total consistency among all elements of the calculation would require more iteration than we have given it, from defect basis optimisation, to near-neighbour optimisation, to enlarging the cluster, to relaxing the cluster, we believe that our results are substantially converged to an accuracy that gives a true qualitative picture of most of the defect features. The exceptions are $[H^{2-}]^0$ and F^+ excited state as mentioned above and, in addition, further refinement of second-neighbour O^{2-} ions in the F^+-centre ground state seems necessary, as mentioned in § 3.3, to resolve the question of where the state lies relative to the valence band. None of the improvements to the present work described in this paragraph has any intrinsic theoretical or computational difficulty. However, the present work, and to a greater extent any follow-up, requires access to quite liberal computing facilities.

5. Summary

We now briefly review what has been achieved by the present work. First, a basis set contraction for O^{2-} in MgO has been derived by the cluster method of ICECAP. The same method could be used to develop improved basis sets for host–lattice ions in a variety of crystals. Second, the Hartree–Fock ground states of F and $[H^-]^+$ centres have been determined in calculations that are both mathematically and physically consistent. The same can be said of the F^+ centre, except that while casting further light on the question of the location of the ground state relative to the valence band, the issue has not been definitely resolved. The corresponding analysis of the $[H^{2-}]^0$ centre is incomplete, requiring more extensive treatment of ion-size effects to determine the extent of localisation of the defect. The spin density analysis of F^+ and $[H^{2-}]^0$

centres clearly illustrates the sensitivity of the results to basis set, cluster size, and lattice relaxation, thereby demonstrating how essential all three elements are to a correct description of such defects. Preliminary analysis of the F^+ centre's excited state graphically demonstrates how inadequate treatment of the ion-size effect can lead to qualitatively wrong results, by spurious electron spilling, or tunnelling. While the single-centre treatment of such defects is shown once again to be unreliable in some respects, its very simplicity may give qualitatively correct features such as $[H^{2-}]^0$ localisation and relative energies of the different defects. Finally, it is demonstrated how cluster calculations can be used to derive shell model parameters for impurities, and could be applied to host–lattice interactions as well.

In summary, this work demonstrates the practicality of the ICECAP methodology in simulating rather subtle physical features of electronic defects, and clearly identifies details of the procedure that need refinement or extension.

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