

# The Cohesion of Solid Magnesium and Calcium Oxide: The Role of in-Crystal Modification of the Oxide ion and Electron Correlation

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# The cohesion of solid magnesium and calcium oxide: the role of in-crystal modification of the oxide ion and electron correlation

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The cohesive properties of solid MgO and CaO are investigated using the fully ionic description calculating exactly, after generating the electronic wavefunctions of the ions, those portions of each inter-ionic potential energy function that do not arise from electron correlation. Three major new refinements are introduced. The modifications of each anion wavefunction that arise from the crystalline environment are described using two new methods in which the environmentally generated contribution to the potential energy acting on an anion electron is related to the cation electron density. These methods improve substantially on earlier models, shown to be inadequate for solid oxides, in which the environmental potential energy has the form of that generated by a spherical shell of charge. Density functional theory is used to evaluate the contribution of electron correlation to the oxide-ion rearrangement energy, that is the energy required to convert a free  $O^-$  ion to an in-crystal  $O^{2-}$  ion. For any oxide, this correlation term varies appreciably with crystal geometry, as well as differing significantly between different oxides at their equilibrium geometries. The present models for the in-crystal environment of the oxide ion require a new way of deriving the parameters that govern the damping of the dispersive attractions between the ions, this damping originating from ion-wavefunction overlap being too large to neglect.

The lattice energies, closest equilibrium cation–anion separations and bulk compressibilities, predicted for both MgO and CaO using all of the improvements presented here, agree very well with experiment. There is no evidence for any significant covalent contribution to the cohesion of these two oxides.

## 1. Introduction

There are many reasons (Catlow *et al.* 1977; Pyper 1986, 1991) for non-empirically studying the electronic structures and properties of polar solids. Oxides are scientifically and technologically important;  $CeO_2$ ,  $ZrO_2MgO$ , and CaO being ceramics (De Vita *et al.* 1992; Mackrodt & Woodrow 1986; Butler *et al.* 1983). The two latter are also of geophysical interest as major constituents of the mantle of the Earth (Stacey 1969; Cohen & Gordon 1976; Hemley *et al.* 1985; Jackson & Gordon 1988; Wolf & Bukowinski 1988);  $ThO_2$  is a nuclear material (Colbourn & Mackrodt 1983), while  $UO_2$  and  $PuO_2$  are reactor fuels (Catlow 1977; Catlow & Pyper 1979).

The recent extensions of standard electronic band-structure computations to the calculation of cohesive energies, inter-atomic spacings and elastic properties have been reviewed (Srivastava & Weaire 1987). Although these calculations have the

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advantage of avoiding any assumptions concerning ionicity, this is offset by the resulting complexity necessitating the use of various approximations, particularly the local density-functional description of both exchange and correlation. However, a local correlation approximation cannot yield the full dispersive attraction between the ions because this is still appreciable at large separations where the overlap of their electron densities is negligible. Since dispersion contributes significantly (Pyper 1986) to the cohesion of many polar solids, the local correlation approximation needs refinement. Problems in calculations using pseudo-potentials, local exchange and correlation are revealed by the underestimation (3.94 au (De Vita *et al.* 1992)) of the MgO cation–anion separation (3.974 au at 0 K (Touloukian *et al.* 1977)); this would be accentuated on accurately including the dispersion energy.

The crystal Hartree–Fock method (Harris & Monkhorst 1969, 1971; Euwema *et al.* 1973) avoids the uncertainties of pseudo-potentials or local exchange while making no ionicity assumptions. However, its prediction for the lattice energy of LiF of  $1076 \text{ kJ mol}^{-1}$  (Euwema *et al.* 1974) is larger than the experimental  $1036 \text{ kJ mol}^{-1}$  (Weast 1979) despite the absence of correlation which would increase the discrepancy. There is also evidence (Pyper 1991) that it overestimates the prediction (Causa *et al.* 1986, 1987) for the MgO lattice energy derived without including electron correlation. The evaluation of the correlation energy as an expectation value of a functional (Causa *et al.* 1987) fails to describe the dispersive attractions between ions of negligibly overlapping electron densities. However, despite this failure, the crystal Hartree–Fock-plus-correlation prediction (Causa *et al.* 1987) of  $3074 \text{ kJ mol}^{-1}$  for the lattice energy of MgO is greater than the experimental  $3038 \text{ kJ mol}^{-1}$  (Cohen & Gordon 1976). Although analysis of the electron density (Causa *et al.* 1986) shows MgO to be essentially fully ionic, the contribution to the binding energy predicted (Causa *et al.* 1987) from the correlation energy functional is significantly less than that reliably derived (Pyper 1986, 1991) assuming full ionicity. These discrepancies all show that the crystal Hartree–Fock approach is not free from difficulty.

There is good evidence that many solids are essentially fully ionic with oxides containing the doubly charged  $\text{O}^{2-}$  ion. X-ray crystallographic electron-density determinations (Hosoya 1969; Linkoaho 1969; Castman *et al.* 1971) show full ionicity in alkali halides, which is also indicated for MgO and CaO by analysis (Redinger & Schwarz 1981) of the electron densities resulting from local density-functional band-structure computations in agreement with a similar study (Causa *et al.* 1986) of the crystal Hartree–Fock wavefunction for MgO. The magnetic properties of  $\text{UO}_2$  indicate a uranium  $5f^2$  configuration (Dawson & Lister 1952), while analysis of the experimental phonon dispersion curves, treating the uranium charge as an adjustable parameter, predicts this to be four (Dolling *et al.* 1965). The fully ionic model not only affords a transparent breakdown of the cohesive energy into pair potentials and the rearrangement energies needed to convert an isolated ion into its in-crystal state, but also straightforwardly incorporates the inter-ionic dispersive attractions while avoiding many uncertainties of computations not assuming full ionicity.

An advantage of fully ionic models is the ability to compute exactly, given wavefunctions for the individual ions, the major portions of each inter-ionic potential, namely those not arising from electron correlation. Their common evaluation by density-functional theory (Lenz 1932; Jensen 1932, 1936; Massey & Sida 1955; Gordon & Kim 1972; Kim & Gordon 1974; Wedepohl 1977; Cohen & Gordon 1975, 1976; Muhlhausen & Gordon 1981; Hemley *et al.* 1985; Jackson & Gordon 1988; Wolf & Bukowinski 1988) loses this advantage, there being evidence (Wood & Pyper 1981a;

Pyper 1986) that even improved methods (Rae 1973, 1975; Lloyd & Pugh 1977; Waldman & Gordon 1979*a, b*; Cohen & Gordon 1976; Muhlhausen & Gordon 1981) can contain appreciable errors. The more occasional density-functional evaluation (Boyer *et al.* 1985; Mehl *et al.* 1986) of the entire rearrangement energy of oxides is quite unsatisfactory, introducing errors comparable with the lattice energy. Other early approximate non-empirical calculations (Hylleraas 1930; Landshoff 1936, 1937; Löwdin 1950, 1956; Froman & Löwdin 1962; Mansikka & Bystrand 1966; Vallin *et al.* 1967; Petterson *et al.* 1967, 1968; Calais *et al.* 1967, 1971; Haynes & Calais 1973) not based on density-functional theory contained inaccuracies reviewed elsewhere (Pyper 1986, 1991). Although the non-correlated terms were subsequently computed exactly (Abarenkov & Antonova 1970; Andzelm & Piela 1977, 1978; Wood & Pyper 1981*b*), none of these calculations simultaneously included two other important effects.

Satisfactory calculations must consider damping of the inter-ionic dispersive attractions from their standard multipolar form in the presence of non-negligible ion-wavefunction overlap. Furthermore, the interaction between anion electrons and the environment must be described by a model potential which is physically realistic in reducing to the interaction generated by a point-charge lattice where the electron density of other ions is negligible but which includes, in regions of non-negligible cation electron density, a repulsion dependent on cation and crystal geometry. Although the simple radius variable Madelung–Watson (RVMW) model contains these features and satisfactorily describes the fluorides and chlorides considered (Pyper 1986), the greater environmental sensitivity of the  $O^{2-}$  ion may need a more sophisticated model. Furthermore, electron correlation contributes significantly to the large rearrangement energy needed to convert a free  $O^-$  ion into an in-crystal  $O^{2-}$  ion. However, taking this contribution as constant (Cohen & Gordon 1976; Abarenkov & Antonova 1979*b*; Mulhausen & Gordon 1981; Pyper 1986), equal to the value deduced (Clementi & McLean 1964) by extrapolation along the neon isoelectronic sequence, may be inadequate in neglecting any dependence on cation and crystal geometry.

This paper presents the three refinements of previous theory (Pyper 1986) needed to describe oxides, namely an improved model of the crystalline environment, inclusion of the dependence on both cation and crystal spacing of the correlation contribution to the  $O^{2-}$  rearrangement energy and the modification of the dispersion damping needed with the improved environmental model. These refinements are tested on MgO and CaO and shown to rectify the slightly less good description of MgO compared with the halides shown by the previous calculations (Pyper 1986).

## 2. Basic theory

### (a) Overview

For uniform expansions or contractions from the equilibrium six-coordinated cubic structure, the spatial positions of all the nuclei in an MgO or CaO crystal, that is the crystal geometry, is uniquely defined by the spacing  $R$  between any cation and its six closest anion neighbours. The binding energy  $U_L(R)$  is defined as the heat change on forming one mole of the crystal from free cations, free singly charged ( $O^-$ ) ions and free electrons, the observed  $R$  value,  $R_e$ , being that minimizing  $U_L(R)$ . This definition ensures that the lattice energy ( $D_e$ ), the heat required to convert the crystal with  $R$  value  $R_e$  into these dissociation products and equal to  $-U_L(R_e)$ , can be derived from experiment using a Born–Haber cycle (Cohen & Gordon 1976). The energy needed to convert the crystal into free cations and  $O^{2-}$  ions is not experimentally measurable

because a free  $O^{2-}$  ion is unstable with respect to decomposition to an  $O^-$  ion and a free electron. For crystals such as MgO and CaO having the rock-salt structure, the bulk compressibility, denoted  $B$ , can be computed from  $U_L(R)$  through the result (7) of Pyper (1991) with the constant  $k_v$  equal to two.

The basic assumption of the present study is that solid MgO and CaO are fully ionic containing doubly charged alkaline earth cations and doubly charged oxide ions ( $O^{2-}$ ). This is expressed quantitatively (Abarenkov & Antonova 1970; Pyper 1986, 1991) by writing the wavefunction for all the electrons in the crystal as an antisymmetrized product of the wavefunctions of the individual ions, each of which is taken to be spherically symmetric. Although this procedure neglects the correlation of the motions of electrons on different ions (the inter-ionic electron correlation), the correlation of the motions of electrons belonging to the same ion (the intra-ionic electron correlation) can be included by using a multi-determinantal description for each of the individual ion wavefunctions. A perturbation-theory treatment of the inter-ionic electron correlation then yields the final result for  $U_L(R)$ .

(b) *Formulation exclusive of electron correlation*

In the approximation, denoted by a 0 superscript, in which electron correlation is entirely neglected, the crystal binding energy  $U_L^0(R)$ , is derived by writing the crystal wavefunction as an antisymmetrized product of Hartree–Fock, or, in a relativistic theory, Dirac–Fock, wavefunctions for the individual ions and then taking the expectation value of the the total electronic Hamiltonian of the crystal. This yields, as discussed elsewhere (Abarenkov & Antonova 1970; Pyper 1986, 1991),

$$U_L^0(R) = N_f \{ E_{\text{re}}^0(R) - 6.990\,258\,24/R + 6[V_{\text{sCA}}^0(R) + V_{\text{sAA}}^0(\sqrt{2}R) + V_{\text{sCC}}^0(\sqrt{2}R)] \}. \quad (2.1)$$

Here all the terms inside the braces are expressed in atomic units on a scale where electrons and nuclei have zero energy if stationary and isolated. The constant  $N_f$ , equal to 2625.5, converts an energy per ion in atomic units into an energy per mole of crystal.

The quantity  $E_{\text{re}}^0(R)$  is the Hartree or Dirac–Fock prediction for the rearrangement energy required to convert one free singly charged  $O^-$  ion into an  $O^{2-}$  ion having the wavefunction considered appropriate for describing the crystal having closest cation–anion separation  $R$ . Thus,

$$E_{\text{re}}^0(R) = E_A^0(R) - E_{O^-}^0. \quad (2.2)$$

Here,  $E_{O^-}^0$  is the Hartree–Fock or Dirac–Fock prediction for the energy of a free  $O^-$  ion and  $E_A^0(R)$  is the energy of an  $O^{2-}$  ion computed in the orbital approximation using the free-ion Hamiltonian, but with the wavefunction considered appropriate for the ion in the crystal. The environment of an  $O^{2-}$  depends not only on  $R$  but also on the counter cation and, hence,  $E_A^0(R)$  and  $E_{\text{re}}^0(R)$  depend on both these variables. There is abundant evidence that light highly charged cations such as  $Mg^{2+}$  and  $Ca^{2+}$  are essentially unaffected by their environment in the crystal, having the same polarizabilities (Fowler & Madden 1984, 1985; Fowler & Pyper 1985), electron densities and, hence, inter-ionic potentials (Pyper 1986) as the free cations. The cations will therefore be taken to remain unchanged from their free state and, hence, there is no cation rearrangement energy in (2.1).

In the absence of overlap between the wavefunctions of the ions, the interaction between every pair of ions would have the purely coulombic form  $q_a q_b / (x_{ab} R)$ , where  $q_a$  is the net charge of ion a, equal to  $-2$  for an oxide ion, and  $x_{ab}$  is a purely

geometrical constant which yields the separation of the pair of ions a and b as  $x_{ab}R$ . The sum of all such purely coulombic interactions enters (2.1) as the Madelung term  $-6.990\,258\,24/R$ . If the overlap between the wavefunctions of two ions is not negligible, the purely coulombic interaction is augmented by a correction  $V_{sab}^0(x_{ab}R)$ , of short range as denoted by the s subscript, given by

$$V_{sab}^0(x_{ab}R) = V_{ab}^0(x_{ab}R) - q_a q_b / (x_{ab}R). \quad (2.3)$$

Here,  $V_{ab}^0(x_{ab}R)$  is the total interaction energy of the pair of ions a and b separated by a distance  $x_{ab}R$  and measured relative to the sum ( $E_a^0(R) + E_b^0(R)$ ) of the energies that the two ions would have if each retained its in-crystal wavefunction while not interacting. For MgO and CaO, the only non-negligible short-range interactions are those ( $V_{sCA}^0(R)$ ) between a cation and its six nearest anions, those  $V_{sAA}^0(\sqrt{2}R)$  between an anion and its closest anion neighbours at a distance  $\sqrt{2}R$  and the corresponding cation terms  $V_{sCC}^0(\sqrt{2}R)$ . The recently reviewed (Pyper 1991) evidence suggests that the only terms neglected in deriving (2.1), three-body and higher-order multibody terms are only a very minor portion of  $U_L^0(R)$  although they may make an important contribution to some of the elastic constants.

The in-crystal  $O^{2-}$  ion wavefunctions determining the rearrangement energy and short-range inter-ionic interactions are generated using the Oxford atomic Dirac–Fock program (Grant *et al.* 1980) adding to the term describing the potential energy acting on each electron a representation of the interaction between this electron and the environment generated by all the other ions in the crystal, including their attendant electrons. The development, described in §3, of significantly more accurate representations of this potential energy, constitutes the first of the three major refinements of the computations of crystal cohesion to be presented in this paper.

Dirac–Fock wavefunctions for the free cations and in-crystal  $O^{2-}$  ions were input to the relativistic integrals program (RIP) (Wood & Pyper 1981*b, c*, 1986) to yield interaction energies  $V_{ab}^0(x_{ab}R)$  and, hence, the short-range terms  $V_{sab}^0(x_{ab}R)$ , which are exact once the wavefunctions of the interacting ions have been specified. This avoids the uncertainties that would arise if these interactions were computed using density-functional theory. Although relativistic effects would be expected to be very small for MgO and CaO, the RIP computations take full account of relativity by using four-component wavefunctions for the individual orbitals and a relativistic Hamiltonian containing the Dirac kinetic energy operator. Non-relativistic computations with the Oxford Dirac–Fock and RIP programs differ from their relativistic counterparts solely by using an artificially large value for the velocity of light and thus offer no economies.

### (c) *Crystal cohesion including electron correlation*

#### (i) *The total crystal cohesion*

The discussions (Pyper 1986, 1991) of the derivation of  $U_L(R)$ , including the contributions from electron correlation, suggested that three- and higher-order multibody terms are small. After neglecting both these terms and a very small effect of intra-ionic electron correlation, one finds

$$U_L(R) = N_f \{ E_{re}(R) - 6.990\,258\,24/R + 6[V_{sCA}^T(R) + V_{sAA}^T(\sqrt{2}R) + V_{sCC}^T(\sqrt{2}R)] \} + U_{disp}(R). \quad (2.4)$$

Here,  $E_{re}(R)$  is the total rearrangement energy which differs from  $E_{re}^0(R)$  by containing a term  $E_{re}^{corr}(R)$  originating from intra-ionic electron correlation and evaluated

through (2.8). Thus,

$$E_{\text{re}}(R) = E_{\text{re}}^0(R) + E_{\text{re}}^{\text{corr}}(R). \quad (2.5)$$

The perturbation treatment of inter-ionic electron correlation yields two corrections to  $V_{\text{ab}}^0(x_{\text{ab}}R)$ , a term  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$  discussed in § 2 c (iii) and the dispersive attraction. The first term is conveniently incorporated into  $U_L(R)$  through the definition

$$V_{\text{sab}}^{\text{T}}(x_{\text{ab}}R) = V_{\text{sab}}^0(x_{\text{ab}}R) + V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R), \quad (2.6)$$

while the pairwise sum of all the dispersions yields the total crystal dispersion energy  $U_{\text{disp}}(R)$ .

(ii) *The intra-ionic electron correlation contribution*

Electron correlation lowers both the energy  $E_{\text{O}^-}^0$  of the free  $\text{O}^-$  ion as well as that  $E_{\text{A}}(R)$  of the  $\text{O}^{2-}$  ion by contributions, denoted  $E_{\text{O}^-}^{\text{corr}}$  and  $E_{\text{A}}^{\text{corr}}(R)$ , respectively, so that

$$E_{\text{O}^-} = E_{\text{O}^-}^0 + E_{\text{O}^-}^{\text{corr}}, \quad E_{\text{A}}(R) = E_{\text{A}}^0(R) + E_{\text{A}}^{\text{corr}}(R). \quad (2.7)$$

Here  $E_{\text{A}}(R)$ , which is the analogue of that  $E_{\text{A}}^0(R)$  in the treatment in which correlation is neglected, is the expectation value of the Hamiltonian for an isolated  $\text{O}^{2-}$  ion computed using the correlated wavefunction for the in-crystal ion. The term  $E_{\text{re}}^{\text{corr}}(R)$  is given by

$$E_{\text{re}}^{\text{corr}}(R) = E_{\text{A}}^{\text{corr}}(R) - E_{\text{O}^-}^{\text{corr}}, \quad (2.8)$$

and is therefore known after evaluating both the correlation energies in (2.7).

It is now well established (Cohen & Gordon 1976; Abarenkov & Antonova 1979*b*; Muhlhausen & Gordon 1981; Pyper 1986) that  $E_{\text{re}}^{\text{corr}}(R)$  is an important contributor to oxide lattice energies. Hitherto it has been calculated using for the  $\text{O}^{2-}$  ion correlation energy  $E_{\text{A}}^{\text{corr}}(R)$  a value derived (Clementi & McLean 1964) by extrapolating experimental data on ions which, unlike  $\text{O}^{2-}$ , are stable in the free state. However, this approach can be questioned not only because it neglects the  $R$  dependence of the wavefunction of the in-crystal  $\text{O}^{2-}$  ion which must make  $E_{\text{re}}^{\text{corr}}(R)$  vary with  $R$ , but also because it is not clear that the correlation energy of an  $\text{O}^{2-}$  ion in a crystal is the same as that deduced for a hypothetical free  $\text{O}^{2-}$  ion. These questions motivate the development of the second of the three major refinements of the computations of crystal cohesion to be presented in this paper, namely a method for computing  $E_{\text{re}}^{\text{corr}}(R)$  including its  $R$  dependence.

(iii) *The inter-ionic electron correlation contributions*

The first,  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$ , of the two contributions of inter-ionic electron correlation to the interaction between a pair of ions arises from the exchange of electrons between them. It is therefore of short range, depending on the overlap of the wavefunctions of the two ions, and vanishes for sufficiently large distances  $x_{\text{ab}}R$ , where this overlap is negligible (Boehm & Yaris 1971). The only non-negligible interactions are those ( $V_{\text{sCA}}^{\text{corr}}(R)$ ) between a cation and its six nearest anions, those  $V_{\text{sAA}}^{\text{corr}}(\sqrt{2}R)$  between an anion and its closest anion neighbours and the corresponding cation terms  $V_{\text{sCC}}^{\text{corr}}(\sqrt{2}R)$ . These terms are too complicated to calculate exactly and were evaluated as already discussed (Wood & Pyper 1981*a*; Pyper 1990, 1991) from the Dirac-Fock electron densities of the free cations and in-crystal  $\text{O}^{2-}$  ions by using a density-functional theory (Gordon & Kim 1972) based on electron correlation in a uniform electron gas.

The second contribution of inter-ionic correlation to the interaction energy of a

pair of ions does not involve the exchange of electrons between them and, therefore, does not vanish for large separations at which the overlaps between the ion wavefunctions are negligible. This long-range term is the dispersive or Van der Waals attraction between the two ions (Kreek & Meath 1969; Boehm & Yaris 1971). For large separations ( $x_{ab}R$ ) at which the overlap of the wavefunction of ion a with that of ion b is negligible, this attraction can be expanded into the familiar multipole series whose leading term is the dipole–dipole interaction  $-C_6(ab)/[(x_{ab}R)^6]$  (Kreek & Meath 1969). For separations ( $x_{ab}R$ ) sufficiently small that overlap between the ion wavefunctions is not negligible, each term in the multipole series is multiplied by a damping function (Jacobi & Csanak 1975; Koide 1976; Pyper 1986). For ion wavefunctions generated using the RVMW model for the crystalline environment, the appropriate damping functions describe well the dispersive attractions in solid ionic halides (Pyper 1986). Ion wavefunctions computed using the improved models for the crystalline environment developed here require slightly different damping functions; the derivation of which constitutes the third of the three major refinements of the computation of crystal cohesion to be presented in this paper.

### 3. The environmental potential

#### (a) *Exact analysis*

An anion in a crystal with geometry specified by  $R$  differs from the corresponding isolated ion because an anion electron at a position  $\mathbf{r}_a$  relative to the anion nucleus experiences a potential energy, called the environmental potential and denoted  $F_{\text{env}}(\mathbf{r}_a; R)$ , generated by the nuclei and electrons of all the other ions. This potential has three contributions (Mahan 1980; Pyper 1986, 1991), the first being that generated when all the other ions b ( $\neq a$ ) are replaced by point charges of size  $q_b$ , the second and third being the corrections to this point-lattice description which arise from the spatial extensions of the charge distributions of the ions b. These corrections are of short range, being non-zero only where neighbouring ions have non-negligible electron densities. The third contribution is, in principle, non-local since it arises from exchange with electrons on neighbouring ions. Since no systematic study of the reliability of even local approximations in lattice-energy calculations has been presented hitherto, non-local descriptions will not be considered.

Any local potential  $F_{\text{env}}(\mathbf{r}_a; R)$  can be expanded into a series of the type

$$F_{\text{env}}(\mathbf{r}_a; R) = F_{\text{env}}^{(0)}(\mathbf{r}_a; R) + \sum_{L=1}^{\infty} F_{\text{env}}^{(L)}(\mathbf{r}_a; R). \quad (3.1)$$

The first term depends only on the radial distance  $r_a$  of the electron from nucleus a, the angular variation of  $F_{\text{env}}^{(L)}(\mathbf{r}_a; R)$  being that of a rank  $L$  spherical harmonic centred on the a nucleus. This paper uses the conventional description of a closed-shell ion, where all the orbitals have the standard central-field form and are either completely filled with electrons or entirely empty. Only the spherically symmetric term  $F_{\text{env}}^{(0)}(\mathbf{r}_a; R)$  is added to the potential energy in the Fock Hamiltonian when computing the in-crystal  $O^{2-}$  wavefunctions because the remainder of (3.1) contributes zero to the total energy of the ion a (Pyper 1986). This approach is self-consistent in that it still generates central-field orbitals; there being no evidence that this introduces any shortcomings. Furthermore, for a cubic lattice, retention of only  $F_{\text{env}}^{(0)}(\mathbf{r}_a; R)$  in (3.1) is a good approximation because parity eliminates all terms of odd  $L$  while the



$L = 2$  terms also vanish leaving, as the leading correction, the  $L = 4$  terms whose effect on an s or p orbital would be expected to be small.

In the first of the two broad groups of environmental models considered here, the short-range contributions to  $F_{\text{env}}^{(0)}(r_a; R)$  are modelled separately from the point-lattice term. The second group, in which  $F_{\text{env}}^{(0)}(r_a; R)$  is described by a single function, has two subdivisions depending on whether  $F_{\text{env}}^{(0)}(r_a; R)$  has the form of a potential generated by a shell of positive charge.

(b) *Separate modelling of the point-lattice and short-range terms*

(i) *The point-lattice environmental potential*

The contribution to  $F_{\text{env}}^{(0)}(r_a; R)$  arising from a point-charge lattice is constant ( $= -\phi_{\text{env}}/R$ ) from  $r_a = 0$  to  $r_a = R$  (Mahan 1980; Pyper 1990, 1991), with  $\phi_{\text{env}}$  equal to 3.495 129 for rock-salt structure oxides. It rises at larger  $r_a$  to reach zero around  $r_a = \sqrt{2}R$  after which there occur several smaller oscillations associated with distances between the anion a and other ions greater than  $\sqrt{2}R$ . Such an environmental potential contracts anions reducing both their polarizabilities (Fowler & Madden 1983, 1984, 1985) and short-range interactions  $V_{\text{sCA}}^0(R)$  with cations (Pyper 1986).

The derivative with respect to  $r_a$  of the point-lattice environmental potential is discontinuous where  $r_a$  equals an anion-ion distance. Since, in the Oxford Dirac-Fock program, the radial wavefunctions are tabulated numerically, the grid must be sufficiently dense for  $r_a$  in the vicinity of  $R$  where the point-lattice approximation to  $F_{\text{env}}^{(0)}(r_a; R)$  is varying most rapidly. The MgO binding energies computed with four different grids were not grossly inaccurate with discrepancies (in au) in  $E_{\text{re}}^0$  (3.981),  $V_{\text{sCA}}^0$  (3.981) and  $V_{\text{sAA}}^0$  (3.981 $\sqrt{2}$ ) in the fourth decimal combining to produce uncertainties in  $U_L^0$  (3.981) in the third. However, such an error is only marginally acceptable.

The second and third contributions to  $F_{\text{env}}(r_a; R)$  cause the entire  $F_{\text{env}}^{(0)}(r_a; R)$  to differ greatly from the point-lattice term where the electron density of neighbouring ions is appreciable. Hence, there is no need to model the gradient discontinuities in the exact point-lattice contribution, thus justifying the Madelung Fermi smoothed (MFS) function  $F_{\text{MFS}}(r_a; R)$  as a model for the latter

$$F_{\text{MFS}}(r_a; R) = -(\phi_{\text{env}}/R)\{1 + \exp[g(r_a - r_0)]\}^{-1}. \quad (3.2)$$

The centre  $r_0$  is chosen such that (3.2) reproduces the point-lattice result where the latter equals  $-\phi_{\text{env}}/(2R)$  while  $g$  is fixed by requiring that (3.2) reproduces the point-lattice expression half way between  $R$  and  $r_0$ , at  $r_a = R + (r_0 - R)/2$ . For a rock-salt lattice, the resulting values  $r_0 = 1.170\,45R$  and  $g = 11.6921/R$  ensure that (3.2) accurately reproduces the point-lattice result ( $-\phi_{\text{env}}/R$ ) for small  $r_a$ , where cation electron density is negligible. The evidence to be discussed shows that the numerical problems encountered with the exact point-lattice potential arise from the gradient discontinuities.

(ii) *Short-range contributions to the environmental potential*

The second contribution to  $F_{\text{env}}(r_a; R)$  is the correction arising when the purely electrostatic potential generated by the electrons on each ion b ( $b \neq a$ ) is calculated taking account of the spatial extension of their charge distributions. This contribution introduces into  $F_{\text{env}}^{(0)}(r_a; R)$  a deep attractive well around the nuclei of these cation neighbours (Pyper 1986, 1990, 1991) which acts to expand the anion. The most dominant of several effects in the third contribution to  $F_{\text{env}}(r_a; R)$  (Pyper 1986, 1991)

is a repulsion originating from the Pauli principle which forces the wavefunction of ion a to be orthogonal to the occupied orbitals of ion b, thereby introducing an extra node into the orbitals of ion a increasing their kinetic energies. This third contribution thus acts to contract the anion in opposition to the second. It would be ill-advised to try to model the sum of these two terms by calculating the second exactly while introducing local approximations to the third. Since the latter term far more than outweighs the former to produce orbitals considerably more contracted than those predicted using only the point-lattice term,  $F_{\text{env}}^{(0)}(r_a; R)$  is written as the sum of the MFS function plus a model for the repulsion generated as the sum of the second and third contributions.

The electron density of each closest cation neighbour decreases exponentially at large distances from the cation nucleus, which is located at a distance  $R$  from the anion, thus justifying the ‘optimized hyperbolic secant Madelung Fermi smoothed’ model potential  $F_{\text{OHSMFS}}(r_a; R)$

$$F_{\text{OHSMFS}}(r_a; R) = F_{\text{MFS}}(r_a; R) + A \operatorname{sech}[k(r_a - R)]. \quad (3.3)$$

The model  $A \operatorname{sech}[k(r_a - R)]$  for the sum of the second and third contributions to  $F_{\text{env}}^{(0)}(r_a; R)$  reaches its maximum value of  $A$  at  $r_a = R$ , corresponding to the position of the cation nuclei and decreases exponentially at large  $r_a$ . The variation principle shows that the better the approximation to the wavefunction of the entire crystal, the lower is the predicted value of its total energy. This shows that, in the approach where electron correlation is neglected, improving the description of the in-crystal  $\text{O}^{2-}$  ion will predict a more negative cohesive energy  $U_L^0(R)$  because the Dirac–Fock energies of a free cation and free  $\text{O}^-$  ion are independent of the crystalline environment. Thus, for any  $R$ , the best values for  $A$  and  $k$  are those minimizing  $U_L^0(R)$ . Such parameters could, in principle, be optimized by minimizing the total crystal energy predicted including the contributions from electron correlation. However, this procedure is very dubious if the correlation contribution is not calculated exactly from a trial wavefunction but is derived approximately using density-functional theory. Hence, in this paper, the minimization of  $U_L^0(R)$  is used as the criterion for optimizing parameters in environmental potentials. The continuity of (3.3) and its derivatives explains why the results are free from the difficulties encountered using the exact point-lattice potential. Thus, the results derived using (3.3) are accurate to at least four decimal places (in au), corresponding to uncertainties of just a few tenths of  $\text{kJ mol}^{-1}$ , which is more than acceptable.

Another model for the sum of the second and third contributions to  $F_{\text{env}}^{(0)}(r_a; R)$  is based on Phillips–Kleinman pseudo-potential theory (Phillips & Kleinman 1959). The effects on a valence orbital of energy  $\varepsilon_v$  ( $< 0$ ) which arise from its orthogonality to other filled orbitals  $\phi_i(\mathbf{r})$  of energies  $\varepsilon_i$  are described by adding a potential  $F_{\text{PK}}$  to the Fock operator for the valence electron without demanding that the valence orbital is orthogonal to the orbitals  $\phi_i(\mathbf{r})$ . The potential  $F_{\text{PK}}$  is defined as a sum over the filled orbitals by

$$F_{\text{PK}} = - \sum_i (\varepsilon_i - \varepsilon_v) |\phi_i(\mathbf{r})\rangle \langle \phi_i(\mathbf{r})|. \quad (3.4)$$

In relativistic theory,  $\phi_i(\mathbf{r})$  is a column vector of four rows (Sakurai 1967) having a four-column row-vector adjoint  $\phi_i^+(\mathbf{r})$  ( $= \langle \phi_i(\mathbf{r})|$ ), the non-local potential (3.4) depending quadratically on the  $\phi_i(\mathbf{r})$ . The ‘optimized with eigenvalues Madelung Fermi

smoothed' (OEMFS) potential  $F_{\text{OEMFS}}(r_a; R)$  results by replacing these quadratic terms by the local approximations  $\phi_i^+(\mathbf{r})\phi_i(\mathbf{r}) = \rho_i(\mathbf{r})$ :

$$F_{\text{OEMFS}}(r_a; R) = F_{\text{MFS}}(r_a; R) - A \sum_b \sum_{i \in b} (\varepsilon_i - \varepsilon_0) \{[\rho_i(\mathbf{r}_b)]^k\}^{(0)}. \quad (3.5)$$

The sum over  $b$  is over the six cations adjacent to anion  $a$  while the sum over  $i$  is over all the orbitals containing an electron in the ion  $b$ , the position  $\mathbf{r}_b$  being measured relative to the  $b$  nucleus. The superscript (0) in (3.5) denotes the spherically symmetric term in the series of the type (3.1) that results when  $[\rho_i(\mathbf{r}_b)]^k$  is expanded about the nucleus of the anion  $a$ . The generation of  $\{[\rho_i(\mathbf{r}_b)]^k\}^{(0)}$  uses techniques in the RIP program already described (Wood & Pyper 1986). Since the same Fock operator must be used for all the anion orbitals to ensure that these are orthogonal,  $\varepsilon_v$  in (3.4) is replaced in (3.5) by an average  $\varepsilon_0$ . This was taken to be the energy of a stationary electron subject to just the constant portion  $-(\phi_{\text{env}}/R)$  of  $F_{\text{env}}^{(0)}(r_a; R)$ . If Phillips–Kleinman theory was exact, and only negligible errors were introduced by approximating (3.4) as (3.5), the variational parameters  $A$  and  $k$ , introduced for greater flexibility, would be unity when optimized by minimizing  $U_L^0(R)$ . Since the spacings between points on the grid used to define the Dirac–Fock atomic orbitals increase with increasing distance, a contracted cation orbital is appreciable at only a small number of points when expanded about the anion. Possible numerical inaccuracies were avoided by omitting all orbitals with mean radius less than 0.3 au from the  $i$  sum in (3.5). This only introduces insignificant errors because compression of anion orbitals arises almost entirely from overlap with the outermost cation orbitals. These calculations are as numerically accurate as those performed using the ODMFS model, which is described next.

The major factor rendering the sum of the second and third contributions to  $F_{\text{env}}^{(0)}(r_a; R)$  repulsive is the increase in the kinetic energy of an anion electron in spatial regions of appreciable cation electron density. In the density-functional theory of electronic structure, the total kinetic energy of a species  $S$  is expressed as the integral over all space of the product of the local total electron density  $\rho_{\text{TS}}(\mathbf{r})$  of the system  $S$  at position  $\mathbf{r}$  multiplied by a kinetic-energy functional (Hohenberg & Kohn 1964). For an electron density varying slowly in space, this functional can be taken to equal at each  $\mathbf{r}$  the value  $(= \frac{3}{10}(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{2/3})$  for a non-relativistic infinite electron gas having a uniform density equal to that of the system at that point in space (March *et al.* 1967). This shows that if an anion electron has a small probability  $\Delta(\mathbf{r})$  of entering a region of space where the total electron density of the cation is  $\rho_{\text{TC}}(\mathbf{r})$ , a contribution of  $\frac{3}{10}(3\pi^2)^{2/3}[\rho_{\text{TC}}(\mathbf{r}) + \Delta(\mathbf{r})]^{5/3}$  to the kinetic energy is generated compared with one of  $\frac{3}{10}(3\pi^2)^{2/3}[\rho_{\text{TC}}(\mathbf{r})]^{5/3}$  for vanishing  $\Delta(\mathbf{r})$ . After expressing  $[\rho_{\text{TC}}(\mathbf{r}) + \Delta(\mathbf{r})]^{5/3}$  in the form  $[\rho_{\text{TC}}(\mathbf{r})]^{5/3}[1 + (\Delta(\mathbf{r})/\rho_{\text{TC}}(\mathbf{r}))]^{5/3}$  and making a Taylor expansion to lowest order in the small quantity  $\Delta(\mathbf{r})/\rho_{\text{TC}}(\mathbf{r})$ , the kinetic energy is seen to increase by  $\frac{1}{2}(3\pi^2)^{2/3}[\rho_{\text{TC}}(\mathbf{r})]^{2/3}\Delta(\mathbf{r})$ . This suggests adding the term  $\frac{1}{2}(3\pi^2)^{2/3}[\rho_{\text{TC}}(\mathbf{r})]^{2/3}$  to the potential energy in the anion Dirac–Fock equations to describe the effects of overlap with filled cation orbitals. This justifies introducing for  $F_{\text{env}}^0(r_a; R)$  the 'optimized with density Madelung Fermi smoothed' (ODMFS) model  $F_{\text{ODMFS}}(r_a; R)$

$$F_{\text{ODMFS}}(r_a; R) = F_{\text{MFS}}(r_a; R) + A \sum_b \{[\rho_{\text{Tb}}(\mathbf{r}_b)]^k\}^{(0)}, \quad (3.6)$$

where the  $b$  sum is over the six cations closest to anion  $a$  and  $\rho_{\text{Tb}}(\mathbf{r}_b)$  is the total

electron density of ion b. This density is spherically symmetric about its nucleus and given in Dirac–Fock theory as the sum of the densities  $\rho_i(\mathbf{r}_b)$  of the orbitals occupied on ion b. The superscript (0) in (3.6) denotes the term which is spherically symmetric with respect to the nucleus of ion a in the series of the form (3.1) generated by expanding  $\rho_{Tb}(\mathbf{r})$  about the a nucleus. The parameters  $A$  and  $k$  are optimized by minimizing  $U_L^0(R)$ ; the results would be 4.785 and  $\frac{2}{3}$  if (3.6) described  $F^{0_{env}}(r_a; R)$  exactly. Contracted cation orbitals having mean radii less than 0.3 au were omitted from the ODMFS potential for the same reasons that they were not included in the OEMFS function. Tests show that calculations using (3.6) are as accurate as those using the OHSMFS method, even though generation of the ODMFS potential requires an expansion of the type (3.1) absent from (3.2).

(c) *Single-function models of the environmental potential*

(i) *General models*

The Abarenkov & Antonova (1979a) (OAA) model  $F_{OAA}(r_a; R)$  for the entire spherically symmetric part of the environmental potential is

$$F_{OAA}(r_a; R) = \{-\phi_{env}/R\}\{1 - [1 - \exp(-Ar_a)]^k\}, \quad (3.7)$$

where  $A$  and  $k$  are variational parameters. The justification of this model is that it reduces to the point-lattice result  $\{-\phi_{env}/R\}$  at small  $r_a$  but rises to zero for  $r_a$  significantly greater than  $A^{-1}$ .

The optimized Fermi function (OFFM) model  $F_{OFFM}(r_a; R)$  defined by

$$F_{OFFM}(r_a; R) = -\{\phi_{env}/R\}\{1 + \exp[A(r_a - r_k)]\}^{-1}, \quad (3.8)$$

with  $A$  and  $r_k$  chosen variationally, is also suggested by the above argument. Although (3.8) becomes identical with the FMS model (3.2) of the point-lattice potential when  $A = g$  and  $r_k = r_0$ , the two functions are physically distinct because (3.2) is a model for just the potential generated by a point-charge lattice, whereas (3.8) is a model for the entire function  $F_{env}^{(0)}(r_a; R)$ . It is clear that, with the appropriate choice of parameters, the OAA and OFFM models are rather similar.

(ii) *Models having the form of a potential generated by a shell of charge*

The reasoning behind the introduction of the OAA and OFFM models also suggests (Pyper 1986) the RVMW  $F_{RVMW}(r_a; R)$  model for  $F_{env}^{(0)}(r_a; R)$ :

$$F_{RVMW}(r_a; R) = -k_{env}/R_W, \quad \text{for } r_a \leq R_W, \quad (3.9a)$$

$$F_{RVMW}(r_a; R) = -k_{env}/r_a, \quad \text{for } r_a \geq R_W, \quad (3.9b)$$

$$\text{where} \quad k_{env}/R_W = \phi_{env}/R. \quad (3.10)$$

This definition of  $k_{env}$  ensures that, for  $r_a \leq R_W$ , the RVMW function reproduces the potential generated by the point-charge lattice with spacing  $R$  ( $> R_W$ ). The form (3.9b) is introduced because, in spatial regions where the electron density of neighbouring cations is non-negligible, an anion electron will experience a repulsive potential acting to reduce the constant stabilization of the point lattice. It is thus reasonable to take  $R_W$ , the maximum distance  $r_a$  from the anion nucleus at which the spherical average of the electron density of neighbouring species is still negligible, to be  $R - R_C$ , where  $R_C$  is either the cation radius or some closely related combination of cation properties. This model acceptably describes (Pyper 1986) environmentally induced modifications of inter-ionic potentials involving halide ions,

as well as performing not unreasonably for MgO. The previous value  $R_C = 1.285$  au is used for MgO (Pyper 1986), while for CaO,  $R_C$  is taken to be 1.871 au, the ionic radius (0.99 Å) of  $\text{Ca}^{2+}$  (Johnson 1968). The ‘optimized radius variable Madelung Watson’ (ORVMW) model differs from the RVMW model in determining  $R_W$  variationally. Numerical errors in using both these models are slightly greater than those arising with the OHSMFS or OEMFS models, but are less than those occurring with the exact point-charge-lattice potential. This almost certainly occurs because the RVMW model has only one gradient discontinuity compared with none in the OHSMFS and OEMFS models and several in the exact point-lattice potential.

The RVMW and ORVMW potentials are just those generated by uniformly distributing a total charge  $k_{\text{env}}$  au over a shell of radius  $R_W$ . Although the introduction of these two potentials owes nothing to this observation, Watson (1958) argued that the true environmental potential is generated by uniformly distributing two units of positive charge over the surface of a sphere with radius equal to that of the  $\text{O}^{2-}$  ion. If this radius is taken to be 1.42 Å (Johnson 1968), the resulting potential, to be called the Watson potential, is independent of  $R$  and given by setting  $k_{\text{env}} = 2$  and  $R_W = 2.683$  in (3.9). This model predicts the wrong value for the constant part of the potential at  $r_a \leq 2.683$  au for all  $R$  values excepting 4.68956 au. This difficulty is rectified in the model, to be called the Watson–Madelung (WM) model, which has been used in density-functional calculations of crystal cohesion (Muhlhausen & Gordon 1981; Hemley *et al.* 1985). Here, one still accepts the Watson (1958) argument that an anion electron sees two units of charge distributed over the surface of a sphere but also demands that the depth of well is the same as that generated by the point-charge lattice. The resulting potential has the form (3.9) with  $k_{\text{env}} = 2$ , which fixes  $R_W$  as  $2R/\phi_{\text{env}}$ . The WM potential cannot be entirely correct because it is independent of the nature of the cations.

#### (d) Tests of environmental potentials

##### (i) Comparison with previous basis-expansion calculations

Optimization of an environmental potential has previously been attempted only for the OAA model (Abarenkov & Antonova 1979*a, b*; Antonova 1979). These non-relativistic calculations differed from those presented here in using a basis-set expansion for the radial parts of the atomic orbitals and in including an approximation to the negative short-range three-body contribution to  $U_L^0(R)$ . The magnitudes of these three-body terms are almost certainly too large (Pyper 1991) because comparison with exact results (Andzelm & Piela 1977; Andzelm & Piela 1978) shows them to be several times too great for both LiF and NaF. For MgO, it is only for  $R = 3.981$  au that the uncorrelated short-range potentials and rearrangement energy have been presented explicitly using an environmental potential reported by Abarenkov & Antonova (1979*b*) as optimized: they claim 0.74 as the best value for  $A$  in (3.7) while taking  $k$  to be 10 without optimization on the grounds that this parameter is of only minor importance. Their predictions (table 1) for  $E_{\text{re}}^0(3.981)$ ,  $V_{\text{sCA}}^0(3.981)$  and  $V_{\text{sAA}}^0(3.981\sqrt{2})$ , as well as the value of  $U_L^0(3.981)$  calculated from (2.1), agree reasonably with the corresponding RIP results. However, the present calculations do not substantiate the claimed (Abarenkov & Antonova 1979*a*) unimportance of  $k$  since  $|U_L^0(3.981)|$  is increased to 2692 kJ mol<sup>-1</sup> on using the value (16), which is found to be optimal when  $A$  is fixed as 0.74. Furthermore, optimization of both  $A$  and  $k$  yields values of 3.0 and 30 000 which produce the even larger prediction (table 2) of 2716 kJ mol<sup>-1</sup> for  $|U_L^0(3.981)|$ .

Table 1. Comparison of RIP and basis-expansion results using the same OAA environmental potential<sup>a,b</sup>

	MgO				CaO		
	$E_{\text{re}}^0(R_e)$	$V_{\text{sCA}}^0(R_e)$	$V_{\text{sAA}}^0(\sqrt{2}R_e)$	$-U_L^0(R_e)$	$V_{\text{sCA}}^0(R_e)$	$V_{\text{sAA}}^0(\sqrt{2}R_e)$	$-U_L^0(R_e)$
basis	0.477 64	0.038 46	0.005 95	2656	0.054 67	0.000 09	
RIP	0.481 18	0.037 38	0.005 60	2669	0.060 89	0.000 21	2053

<sup>a</sup>Basis results for  $E_{\text{re}}^0(R_e)$ ,  $V_{\text{sCA}}^0(R_e)$  and  $V_{\text{sAA}}^0(\sqrt{2}R_e)$  are from Abarenkov & Antonova (1979b) for MgO and from Antonova (1979) for CaO; RIP results present work calculated using the numerical non-relativistic Hartree–Fock wavefunctions generated with the same OAA environmental potential (3.7), with the  $A$  and  $k$  parameters reported as being optimal for the basis-set calculations (see text).

<sup>b</sup>All quantities in au, except  $U_L^0(R_e)$  in  $\text{kJ mol}^{-1}$ , calculated by substituting the previous three quantities into (2.1).  $R_e = 3.981$  au (MgO) and  $4.544$  au (CaO), both at room temperature (Landolt–Börnstein 1973). Basis set  $E_{\text{re}}^0(R_e)$  not reported (Antonova 1979) for CaO.

Table 2. Crystal binding energies predicted without including electron correlation<sup>a,b</sup>

method <sup>c</sup>	MgO		CaO	
	$-U_L^0(3.25)$	$-U_L^0(3.981)$	$-U_L^0(3.5)$	$-U_L^0(4.544)$
Watson	1544	2670	−402	2073
WM	1672	2679	−158	2082
RVMW	1671	2681	−159	2078
ORVMW <sup>d</sup>	1671	2684	−144	2090
OAA		2716		2164
OFFM	1870	2716	276	2160
OHSMFS	1889	2712	618	2181
OEMFS	1887	2714	574	2176
ODMFS	1887	2714	598	2175

<sup>a</sup>In  $\text{kJ mol}^{-1}$ .

<sup>b</sup>All predictions derived from  $U_L^0(R)$  (2.1).

<sup>c</sup>Methods differ only in the model used for the environmental potential. The models are defined in § 3b, c.

<sup>d</sup>Optimum  $R_W$  values are 1.963, 2.500, 1.828 and 2.349 for MgO,  $R = 3.25$  and  $3.981$  and CaO  $R = 3.5$  and  $4.544$ , all in au

For CaO, the previous Antonova (1979) and RIP results do not agree (table 1). Furthermore, with the values ( $A = 0.51$ ,  $k = 10$ ) reported as being optimal, the RIP prediction for  $|U_L^0(4.544)|$  of  $2053 \text{ kJ mol}^{-1}$  is less than any of the results in table 2. The optimum values ( $A = 3.0$  and  $k = 24\,000$ ), found using the RIP program and predicting  $|U_L^0(4.544)|$  to be  $2164 \text{ kJ mol}^{-1}$ , are quite unlike those presented previously (Antonova 1979). Since tests (Pyper 1986) have demonstrated that the RIP program is correct, the discrepancies between the present and previous results (Abarenkov & Antonova 1979b; Antonova 1979) must arise from basis-set inadequacies in the latter. There are no OAA predictions for  $R$  less than  $R_e$  because the parameters could not

Table 3. Predictions for oxide ion properties at the equilibrium geometries<sup>a,b</sup>

method <sup>c</sup>	$\langle r \rangle_{2p}$		$\langle r^2 \rangle_{2p}$		$-\varepsilon_{2p}$		$E_{re}^0(R_e)$	
	MgO	CaO	MgO	CaO	MgO	CaO	MgO	CaO
Watson	1.591	1.591	3.447	3.447	0.3941	0.3941	1040	1040
WM	1.519	1.577	3.077	3.372	0.4553	0.4057	1151	1058
RVMW	1.570	1.585	3.319	3.414	0.5124	0.4137	1072	1047
ORVMW	1.547	1.549	3.202	3.233	0.4877	0.3743	1106	1098
OAA	1.495	1.498	2.894	2.911	0.4597	0.3527	1257	1248
OFFM	1.491	1.496	2.876	2.908	0.4515	0.3461	1260	1239
OHSMFS	1.489	1.476	2.877	2.788	0.4454	0.3330	1254	1351
OEMFS	1.492	1.468	2.887	2.761	0.4518	0.3160	1253	1365
ODMFS	1.492	1.472	2.888	2.775	0.4524	0.3248	1254	1344

<sup>a</sup>All quantities in au except for the rearrangement energies  $E_{re}^0(R_e)$  expressed in  $\text{kJ mol}^{-1}$ .  $R_e$  taken as 3.981 au (MgO) and 4.544 au (CaO).

<sup>b</sup>The properties reported for the 2p orbitals are averages with weights of  $\frac{1}{3}$  and  $\frac{2}{3}$  over those for the relativistic orbitals  $2p_{1/2}$  and  $2p_{3/2}$  having  $j = \frac{1}{2}$  and  $\frac{3}{2}$ , respectively.

<sup>c</sup>See note c to table 2.

be fully optimized. Thus, for MgO, the largest  $|U_L^0(3.25)|$  was generated for  $A = 10.0$  and  $k = 10^{11}$ , further optimization requiring a larger  $k$  value producing computer overflow. This result, as well as the  $A$  and  $k$  values found to be optimal at  $R = R_e$ , show the OAA potential to be mathematically inconvenient. It will not be considered further, except to compare it with the OFFM function which can be expected to contain similar physics while appearing in a preferable form.

### (ii) Comparison of environmental models

The cohesive energies (table 2) show that, as judged by the variational criterion, the different models for  $F_{env}^{(0)}(r_a; R)$  fall into the same three groups as those already used for classification. Thus, the Watson, WM, RVMW and ORVMW models predict significantly less cohesion than the other approaches. Although the former four methods yield comparable results at  $R = R_e$ , the Watson is much poorer at smaller  $R$ . None of these four models predicts CaO at  $R = 3.5$  au to be stable with respect to  $\text{Ca}^{2+}$ ,  $\text{O}^-$  ions and free electrons. The energy improvement on passing from the RVMW to the ORVMW model is not large while  $E_{re}^0(R)$ ,  $V_{sCA}^0(R)$  and  $V_{sAA}^0(\sqrt{2}R)$  are not greatly changed. The ORVMW approach produces a smaller  $R_W$  than the RVMW model for all  $R$ , excepting those very much less than  $R_e$  where the situation is reversed. These smaller  $R_W$  values generate a slightly more contracted anion as shown (table 3) by smaller 2p orbital mean radii and mean-square radii and slightly larger  $E_{re}^0(R)$ . This increase is more than offset by smaller  $V_{sCA}^0(R)$  in the ORVMW method, which therefore predicts a greater cohesion.

The OFFM predictions for  $|U_L^0(R)|$  are greatly enhanced over those of the ORVMW model, being 32 and 70  $\text{kJ mol}^{-1}$  larger for MgO and CaO, respectively, at  $R = R_e$ . At the smaller  $R$  of 3.25 au for MgO and 3.5 a.u for CaO, the OFFM method improves on the ORVMW results by no less than 199 and 420  $\text{kJ mol}^{-1}$ . This shows that the OFFM function (3.8) describes  $F_{env}^{(0)}(r_a; R)$  significantly better than any of the four methods where this has the form of the potential generated by a shell of charge. Since

Table 4. Crystal cohesion predicted without including electron correlation<sup>a</sup>

method <sup>b</sup>	MgO			CaO		
	$D_e$	$R_e$	$B$	$D_e$	$R_e$	$B$
Watson	2700	4.182	19.4	2164	4.999	4.95
WM	2699	4.156	17.2	2158	4.952	8.69
RVMW	2704	4.167	17.0	2147	4.940	8.34
ORVMW	2713	4.202	18.4	2161	4.940	8.91
OEMFS	2725	4.117	17.0	2206	4.821	8.66
expt <sup>c</sup>	3038	3.974	17.5	2644	4.537	11.3

<sup>a</sup> $D_e$  in  $\text{kJ mol}^{-1}$ ,  $R_e$  in au and  $B$  in  $10^{10} \text{ N m}^{-2}$ .

<sup>b</sup>See notes b and c to table 2.

<sup>c</sup> $D_e$  values from Cohen & Gordon (1976),  $R_e$  values at 0 K from Touloukian *et al.* 1977,  $B$  value for MgO is the average of three different results reported by La & Barsch (1968) and the  $B$  value for CaO is from Weir (1956).

the OFFM function, like the latter four, cannot be positive at any  $r_a$ , it can differ from these in only two respects. These are, first, the region of space in which the function hardly deviates from the constant point-lattice result  $-\phi_{\text{env}}/R$ , and, second, the rate at which it increases towards zero when  $r_a$  has values greater than the largest at which it is still almost constant. For both MgO and CaO at both distances ( $R$ ) considered in table 2, each of the OFFM functions remains almost constant ( $= -\phi_{\text{env}}/R$ ) up to significantly larger values of  $r_a$  than either the RVMW or ORVMW function. Thus, for MgO at  $R = 3.25$  and  $3.981$  au the OFFM potentials have centres ( $r_k$ ) at  $2.64$  and  $3.63$  au, respectively, while those for CaO at  $R = 3.5$  and  $4.544$  au are centred at  $2.55$  and  $3.54$  au. Not only is each of these four centres located at a distance from the anion nucleus significantly greater than  $R_W$  in the corresponding ORVMW potential (see table 2), but also each of the OFFM potentials increases much more rapidly towards zero. Thus, for both MgO at  $R = 3.25$  au and CaO at  $R = 3.5$  au,  $F_{\text{OFFM}}(r_a; R)$  deviates only insignificantly from  $-\phi_{\text{env}}/R$  right up to  $r_a$  values of around  $2.26$  au, while for both MgO at  $R = 3.981$  au and CaO at  $R = 4.544$  au, this essentially constant region of  $F_{\text{OFFM}}(r_a; R)$  extends up to around  $r_a = 2.8$  au. These environmental potentials have all risen to reach essentially zero for  $r_a = R$ . Thus, the OFFM potential increases much more rapidly than the Watson, WM, RVMW or ORVMW functions, the rise in the former being roughly exponential with a high exponent compared with an  $r_a^{-1}$  variation in each of the latter four models. This coupled with the much larger OFFM binding energies shows that these four models poorly describe the repulsive portion of  $F^{0_{\text{env}}}(r_a; R)$ . The OFFM potential generates an anion electron density which is much more contracted than those produced by the Watson, WM, RVMW or ORVMW models, as shown by significantly smaller  $2p$  orbital mean radii and  $E_{\text{re}}^0(R_e)$  values for MgO and CaO that are greater than the ORVMW predictions by  $154$  and  $141 \text{ kJ mol}^{-1}$ , respectively. The OFFM and OAA models predict very similar  $U_L^0(R_e)$  values and  $\text{O}^{2-}$   $2p$  orbital properties.

The OHSMFS, OEMFS and ODMFS functions differ from the present single-function models since  $F_{\text{env}}^{(0)}(r_a; R)$  is always negative in the latter. However, the former three potentials become positive around  $r_a = R$  if optimization of  $A$  and  $k$  generates sufficiently large  $A$ . Each of these three functions predicts very similar  $U_L^0(R)$  (table 2) and anion properties (table 3) and is a significant improvement, as judged



by the variational criterion, over the OAA and OFFM models, except for MgO at  $R = 3.981$  au. Here all five descriptions produce similar results because the OHSMFS, OEMFS and ODMFS potentials remain negative at all  $r_a$ , hardly differing from the OAA and OFFM functions. However, at  $R = 3.5$  and  $4.544$  au for CaO, as well as for MgO at  $R = 3.25$  au, the large maxima around  $r_a = R$  in  $F_{\text{env}}^{(0)}(r_a; R)$  of 16.2, 3.6 and 1.8 au, respectively, coupled with  $|U_L^0(R)|$  predictions enhanced over the OAA and OFFM results, show that the true environmental potential is positive in spatial regions of high-cation electron density. These values should be compared with Madelung well depths ( $\phi_{\text{env}}/R$ ) in the range 0.75–1.1 au. The improvement afforded by the OHSMFS, OEMFS or ODMFS descriptions over the OAA and OFFM models is especially marked for CaO at  $R = 3.5$  au, where the former yield a cohesive energy larger by at least  $300 \text{ kJ mol}^{-1}$ . Even at  $R = R_e$ , each of the former three models predicts the  $\text{O}^{2-}$  ion in CaO to be significantly more compressed than either the OAA or OFFM descriptions, as manifested by the smaller 2p orbital mean radii and mean-square radii as well as rearrangement energies larger by at least  $96 \text{ kJ mol}^{-1}$ .

For the OHSMFS and ODMFS models,  $U_L^0(R)$  was not calculated at further  $R$  values because both their predictions are very similar to those of the OEMFS method. No further calculations were performed using the OFFM approach since this has been shown to be inferior to the OEMFS description. Since the optimization of environmental potentials containing two variables is a considerable task, attention was restricted to the OEMFS method and those in which  $F_{\text{env}}^{(0)}(r_a; R)$  has the form generated by a charged shell. The latter methods are considered further because they have been used most extensively, particularly in density-functional descriptions of ionic solids. It is therefore worthwhile to conclusively demonstrate the shortcomings of such descriptions for ionic oxides. The predictions of each of these four methods for  $D_e$ ,  $R_e$  and  $B$  are compared in table 4 with the corresponding results of the OEMFS method. The latter predicts  $D_e$  to be enhanced by at least 12 and  $45 \text{ kJ mol}^{-1}$  for MgO and CaO, respectively, while reducing the overestimations of  $R_e$  by at least 0.04 and 0.12 au. These reductions in the discrepancies between theory and experiment confirm the deduction drawn from tables 2 and 3 that the OEMFS approach is much better than the Watson, WM, RVMW or ORVMW models. Theory and experiment are compared only after describing the new refinements introduced into the calculation of the contributions arising from electron correlation.

#### 4. The electron correlation contribution to the crystal cohesion

(a) *The correlation contribution to the rearrangement energy*

(i) *Density functional formulation*

The only methods currently feasible for computing the correlation energy of an in-crystal anion seem to be those based on density-functional theory. These rely on the Hohenberg–Kohn theorem (1964) which shows that the correlation energy ( $E_S^{\text{corr}}$ ) of a species  $S$  depends only on its total electron density  $\rho_{\text{TS}}(\mathbf{r})$  and a universal correlation-energy functional  $F^{\text{corr}}[\rho(\mathbf{r})]$  through

$$E_S^{\text{corr}} = \int \rho_{\text{TS}}(\mathbf{r}) F^{\text{corr}}[\rho_{\text{TS}}(\mathbf{r})] d\mathbf{r}. \quad (4.1)$$

The exact form of  $F^{\text{corr}}[\rho(\mathbf{r})]$  is unknown. In the widely used local density approximation, it is assumed that  $\rho_{\text{TS}}(\mathbf{r})$  varies sufficiently slowly with  $\mathbf{r}$  such that at

each point in space the functional  $F^{\text{corr}}[\rho(\mathbf{r})]$  can be taken to equal that of a non-relativistic infinite electron gas having a uniform density equal to that of the system at that point (March *et al.* 1967). For such an electron gas,  $F^{\text{corr}}[\rho(\mathbf{r})]$  is known exactly in the limits of low (Carr *et al.* 1961) and high (Carr & Maradudin 1964) densities, while for intermediate densities it can be evaluated by interpolation. The resulting functional presented as equations (20)–(22) of Gordon & Kim (1972), to be called the GK functional, is used here. Dirac–Fock theory is used to construct all total electron densities  $\rho_{\text{TS}}(\mathbf{r})$ .

A one-electron system is spuriously predicted to have a non-zero correlation energy if this is calculated using the GK functional in (4.1). This shows that such an evaluation of  $E_S^{\text{corr}}$  for a many-electron system introduces unphysical terms describing the correlation of each electron with itself (Cowan 1967). There are several ways (Carroll *et al.* 1987; Cowan & Wilson 1991) of modifying this calculation of  $E_S^{\text{corr}}$  to remove these spurious self-correlations. The original Cowan (1967) modification, to be used here, yields a prediction, denoted  $E_S^{\text{Ccorr}}$ , as

$$E_S^{\text{Ccorr}} = \sum_{i \in s} \int \rho_i(\mathbf{r}) F^{\text{corr}}[\rho_{\text{TS}}(\mathbf{r}) - \rho_i(\mathbf{r})] d\mathbf{r}, \quad (4.2)$$

where the sum is over all the orbitals  $\phi_i(\mathbf{r})$  occupied in the Dirac–Fock description of species  $S$ .

### (ii) *Tests of density-functional predictions of total correlation energies*

For a variety of atomic species, table 5 presents the total correlation energy defined as the exact non-relativistic energy minus the non-relativistic Hartree–Fock energy. For any species containing more than two electrons, the most accurate value for the exact non-relativistic energy is derived by subtracting the computed contributions from relativity, Breit interaction, Lamb shift and nuclear motion from the total energy evaluated as the sum of all its experimentally measured ionization potentials. The same results (table 5) for three- and four-electron systems have been independently deduced (Clementi 1963*a, b*; Clementi & McLean 1964; Vosko & Wilk 1983; Pyyper 1985; Savin *et al.* 1986; Carroll *et al.* 1987) despite the use of slightly different experimental data and different methods of evaluating the four corrections. However, for isoelectronic sequences with  $2p^5$  or  $2p^6$  outermost electronic configurations, these differences mean that it is not always clear whether increased nuclear charge increases or decreases the correlation energy. The Clementi results, derived using relativistic corrections computed by perturbation theory, differ from those of Carroll *et al.* (1987) because the latter use the slightly different Lamb shift corrections of Veillard & Clementi (1968). The Vosko & Wilk (1983) results, differing from those of Carroll *et al.* (1987) in omitting the Lamb shift corrections, are thus less accurate but will still reproduce the trends along an isoelectronic sequence because the Lamb shift is non-negligible only for the innermost electrons. The data of Savin *et al.* (1986) differ in that the relativistic, Breit and Lamb shift corrections were computed using the Oxford Dirac–Fock program (Grant *et al.* 1980; McKenzie *et al.* 1980).

The density-functional expression (4.2) invariably overestimates (table 5) the magnitude of the correlation energy by a factor of between two to four. On traversing any isoelectronic sequence, this overestimation becomes more pronounced with increasing nuclear charge. However, for the two-, three- and four-electron species, (4.2) correctly predicts that the correlation energy is enhanced in magnitude as the nuclear charge is increased along an isoelectronic sequence, even though these enhancements

Table 5. *Density-functional predictions of total correlation energies of mononuclear species*<sup>a,b</sup>

	H <sup>-</sup>	He	Li <sup>+</sup>	Be <sup>2+</sup>	B <sup>3+</sup>		
D Fun	0.0708	0.1073	0.1271	0.1420	0.1540		
best <sup>c</sup>	0.0398	0.0420	0.0435	0.0443	0.0447		
	Li	Be <sup>+</sup>	B <sup>2+</sup>	Li <sup>-</sup>	Be	B <sup>+</sup>	
D Fun	0.1354	0.1575	0.1748	0.1709	0.2144	0.3370	
best	0.0453	0.0474	0.0486	0.0726	0.0943	0.1113	
	O <sup>-</sup>	F	Ne <sup>+</sup>	Na <sup>2+</sup>	F <sup>-</sup>	Ne	Na <sup>+</sup>
D Fun	0.5922	0.6394	0.6779	0.7113	0.6903	0.7397	0.7801
Ex Clem <sup>d</sup>	0.323	0.324	0.328	0.336	0.398	0.393	0.396
Ex Sav <sup>e</sup>	0.331	0.323	0.321		0.400	0.387	
Ex Carr <sup>f</sup>						0.390	
Ex VW <sup>g</sup>					0.394	0.381	0.379
	Cl	Cl <sup>-</sup>	Ar				
D Fun	1.3358	1.3822	1.4342				
Ex Clem	0.712		0.791				
Ex Carr	0.714		0.787				
Ex VW	0.667	0.705	0.732				

<sup>a</sup>All correlation energies are negative and reported as the moduli expressed in au

<sup>b</sup>Density-functional predictions, labelled D Fun, computed from equation (4.2) with the relativistic Dirac–Fock total electron densities  $\rho_{\text{TS}}(\mathbf{r})$ .

<sup>c</sup>Best current values (Pyper 1985) evaluated from exact non-relativistic energies computed by Frankowski & Pekeris (1966).

<sup>d</sup>Experimentally derived values from Clementi (1963a) for first-row neutral atoms, cations and F<sup>-</sup>, from Clementi & McLean (1964) for O<sup>-</sup> and from Clementi (1963b) for second-row species.

<sup>e</sup>Experimentally derived values from Savin *et al.* 1986.

<sup>f</sup>Experimentally derived values from Carroll *et al.* 1987.

<sup>g</sup>Experimentally derived values from Vosko & Wilk 1983.

are grossly overestimated. Density functional theory similarly predicts that increased nuclear charge enhances the magnitude of the correlation energy in an isoelectronic sequence having a 2p<sup>5</sup>, 2p<sup>6</sup> or 3p<sup>6</sup> outermost electronic configuration. Although this agrees with the experimental result that the correlation energy of Ar is greater in magnitude than that of Cl<sup>-</sup>, the disagreement between the Clementi and Savin data for the systems having 2p<sup>5</sup> or 2p<sup>6</sup> outermost electronic configurations means that it is not known whether (4.2) predicts the correct trend in these two isoelectronic sequences. However, for both these sequences, it is clear that (4.2) significantly overestimates the nuclear-charge dependence of the correlation energy since the Clementi and Savin data agree that this depends only weakly on the nuclear charge.

The lack of close agreement between experiment and the predictions of (4.2) cannot be ascribed either to using this rather than some other variant of density-functional theory or to using relativistic electron densities with the non-relativistic GK functionals. The nuclear charges of all the species in table 5 are sufficiently small that these correlation energies differ only marginally from those predicted using non-relativistic

wavefunctions in (4.2). The latter predictions of  $-1.4331$  and  $-1.3812$  au for the Ar and  $\text{Cl}^-$  correlation energies, for example, differ little from those of table 5. The same correlation-energy trends are predicted if Hartree–Fock electron densities are input to the fundamental density-functional formula (4.1). For example, this predicts the Ar and  $\text{Cl}^-$  correlation energies to be  $-1.4586$  and  $-1.4067$  au, less than 2% different from the results of (4.2). The spurious self-correlation thus introduced would be expected to constitute the largest fraction for the two-electron species. However, even for these, the predictions from (4.2) differ from those of (4.1) by less than 10%, the largest difference arising for  $\text{H}^-$ , where the prediction of (4.2) should be compared with that of  $-0.0792$  au, derived using the total Hartree–Fock density in (4.1).

Many approximations for  $F^{\text{corr}}[\rho(\mathbf{r})]$  have been proposed, namely a functional (Vosko *et al.* 1980) containing spurious self-correlations, two alternative methods for removing self-correlations (Stoll *et al.* 1978; Vosko & Wilk 1983) as well as two different functionals (Langreth & Mehl 1983; Perdew 1986) involving the gradient of the electron density but which still contain unwanted self-correlations. However, it seems that there is currently no form of density-functional theory which can always predict the trend of the correlation energy in an isoelectronic sequence. Thus, neither (4.2) with the GK functional, nor any of the functionals just referenced and examined by Savin *et al.* (1986), reproduces the result that  $F^-$  has a correlation energy of very slightly greater magnitude than that of Ne. Here, the functional of Langreth and Mehl (1983) is the least unsatisfactory since it predicts these two correlation energies to be equal, while all the other functionals predict that Ne has a correlation energy of greater magnitude than that of  $F^-$ . Nevertheless, this functional cannot be regarded as better than the others because it erroneously predicts the magnitude of the correlation energy to decrease with increasing nuclear charge in both the He and Be isoelectronic sequences.

The magnitude of the GK correlation-energy functional is enhanced in spatial regions of increased electron density. This explains why (4.2) predicts that, upon contraction of the electron-density distribution, the magnitude of the correlation energy is increased and, hence, why this is predicted to become larger on increasing the nuclear charge in an isoelectronic sequence. However, if the correlation energy is computed by treating the correlation as a perturbation on the Hartree–Fock function, the result depends on both the matrix elements linking the Hartree–Fock ground state to the appropriate excited states as well as the excitation energies from the ground to these excited states. The magnitude of the correlation energy would be expected to be enhanced by either increase of the matrix elements or by decrease of the excitation energies. The contraction of the electron density that occurs on increasing the nuclear charge in an isoelectronic sequence would be expected to generate larger matrix elements, thus enhancing the magnitude of the correlation energy, while this magnitude would be expected to be decreased by the larger excitation energies accompanying a greater nuclear charge. On passing from  $F^-$  to Ne, the increased excitation energies must outweigh the enhanced matrix elements to reduce the magnitude of the correlation energy. Although the GK functional clearly takes account of the enhancement of the matrix elements resulting from contraction of the electron density, it is unclear how this functional or (4.2) incorporates the tendency of increased excitation energies to reduce the magnitude of the correlation energy. This might explain both why (4.2) fails to predict  $F^-$  to have a correlation energy of greater magnitude than Ne and why (4.2) overestimates the increase in the magnitude of the correlation energy occurring on increasing the nuclear charge in the He, Be and Ar isoelectronic sequences.

Table 6. Comparison of experimental and density-functional predictions for electron correlation contributions ( $I_{\text{corr}}(S)$ ) to ionization potentials<sup>a–f</sup>

$S$	Na <sup>+</sup>	Ne	F <sup>−</sup>	K <sup>+</sup>	Ar	Cl <sup>−</sup>	Rb <sup>+</sup>	Kr	Br <sup>−</sup>
outer	1.854	1.674	1.406	1.582	1.458	1.262	1.504	1.395	1.217
all	1.872	1.681	1.402	1.607	1.470	1.261	1.531	1.409	1.214
expt	1.667	1.774	2.066	1.094	1.067	1.091	1.013	0.988	0.989
$A_{\text{corr}}(\zeta)$	0.890	1.055	1.474	0.681	0.726	0.865	0.662	0.701	0.815
$S$	Cs <sup>+</sup>	Xe	I <sup>−</sup>	B <sup>+</sup>	Be	Li <sup>−</sup>	B <sup>2+</sup>	Be <sup>+</sup>	Li
outer	1.421	1.322	1.159	4.075	1.875	1.145	0.0	0.0	0.0
all	1.448	1.330	1.155	4.412	1.549	0.965	0.568	0.432	0.228
expt	1.191	0.917	0.876	1.706	1.278	0.742	0.106	0.084	0.050
$A_{\text{corr}}(\zeta)$	0.823	0.689	0.758	0.387	0.825	0.769	0.187	0.194	0.219

<sup>a</sup>All results in electronvolts.

<sup>b</sup>Experimental  $I_{\text{corr}}(S)$  values for three-electron species taken from table A5 of Pyper (1985).

<sup>c</sup>Experimental  $I_{\text{corr}}(S)$  values for four-electron species calculated from the data presented in table A3 of Pyper (1985) by the method used for the three-electron systems.

<sup>d</sup>Experimental  $I_{\text{corr}}(S)$  values for species having  $np^6$  outermost electronic configurations calculated as  $I_{\text{expt}}(S) - I_{\text{DF}}(S)$  neglecting the small contributions from Breit interaction, Lamb shift and nuclear motion. Experimental ionization potentials  $I_{\text{expt}}(S)$  taken from Moore (1971) for all neutrals and cations, except for the Cs<sup>+</sup> result, which is from Cotton & Wilkinson (1966). Moore (1971) gives  $I_{\text{expt}}(\text{Cs}^+) = 25.1$  eV, which would yield the anomalously large  $I_{\text{corr}}(\text{Cs}^+)$  value of 2.89 eV. For anions taken from the table of recommended electron affinities Hotop & Lineberger (1975). Dirac–Fock ionization potentials  $I_{\text{DF}}(S)$  computed here.

<sup>e</sup>Predictions labelled ‘outer’ and ‘all’ are calculated from (4.3) using the density-functional result (4.2) considering, respectively, just the outermost (outer) electrons (2s for three- and four-electron species otherwise the five or six  $np$  electrons) and all the electrons.

<sup>f</sup> $A_{\text{corr}}(\zeta)$  calculated from (4.4) using the experimental  $I_{\text{corr}}(S)$  values and those  $I_{\text{Ccorr}}(S)$  computed considering in (4.2) all the electrons.

(iii) *Test of density-functional predictions of correlation contributions to ionization potentials*

The correlation contribution ( $I_{\text{corr}}(S)$ ) to the ionization potential of species  $S$  is the difference between the ionization potential predicted using exact non-relativistic wavefunctions and that predicted using non-relativistic Hartree–Fock theory. Although the former can be computed only for the simplest species, it can always be derived by subtracting the contributions from relativity, Breit interaction, Lamb shift and nuclear motion from the experimental ionization potential. If the small relativistic contribution to the correlation energy is neglected, the relativistic contribution to the ionization potential is given by the difference between the Dirac–Fock and Hartree–Fock ionization potential predictions. The experimental  $I_{\text{corr}}(S)$  values thus derived are compared in table 6 with predictions ( $I_{\text{Ccorr}}(S)$ ) of density-functional theory calculated from

$$I_{\text{Ccorr}}(S) = E_{S^+}^{\text{Ccorr}} - E_S^{\text{Ccorr}}. \quad (4.3)$$

Here,  $E_S^{\text{Ccorr}}$  and  $E_{S^+}^{\text{Ccorr}}$  are the predictions of (4.2) for, respectively, the correlation energy of species  $S$  and that of the species  $S^+$  produced by ionization of the most

Table 7. Comparison of different density-functional predictions for  $I_{\text{corr}}(\text{Ne})$  and  $I_{\text{corr}}(\text{F}^-)$ <sup>a,b</sup>

	VWN	SPP	GCL	GCP	(4.1) <sup>c</sup>	(4.2) <sup>d</sup>	expt
$I_{\text{corr}}(\text{Ne})$	1.80	1.03	2.12	1.33	1.68	1.68	1.77
$I_{\text{corr}}(\text{F}^-)$	1.50	0.87	1.82	1.14	1.40	1.40	2.07

<sup>a</sup>All in electronvolts calculated as  $E_{\text{S}^+}^{\text{corr}} - E_{\text{S}}^{\text{corr}}$  with these energies derived as described below.

<sup>b</sup>The results in the first four columns were computed by Savin *et al.* 1987 using methods defined below:

VWN: Vosko *et al.* (1980) using functional without gradient corrections and containing self-correlation;

SPP: Stoll *et al.* (1978) using functional without gradient corrections but with self-correlation eliminated;

GCL: Langreth & Mehl (1983) using functional with gradient corrections and self-correlation.

GCP: Perdew (1986) using functional with gradient corrections and self-correlation.

<sup>c</sup>Present work using GK functional without gradient corrections and containing self-correlation through the use of (4.1) with density  $\rho_{\text{TS}}(\mathbf{r})$  computed from Dirac-Fock wavefunctions.

<sup>d</sup>Present work using (4.3), (4.2), GK functional and Dirac-Fock densities  $\rho_{\text{TS}}(\mathbf{r})$ , thus eliminating self-correlation but with no gradient corrections.

loosely bound electron in  $S$ . The predictions labelled ‘all’ in table 6 were computed from correlation energies derived by substituting into (4.2) the electron densities derived by considering all the electrons of both the species  $S$  and  $S^+$  while those labelled ‘outer’ were derived by considering in (4.2) only the outermost electrons of both  $S$  and  $S^+$ .

The close similarity between the  $I_{\text{Ccorr}}(S)$  values, derived by including all the electrons, and those generated by considering only the outermost electrons shows that the correlation energies of the innermost electrons of  $S^+$  and  $S$  largely cancel in the calculation of  $I_{\text{Ccorr}}(S)$  as the difference (4.3). The results in table 5 show that there will be large errors in the predictions of (4.2) for the correlation energies of these inner electrons. However, the cancellation of the inner-electron contributions in the calculation of  $I_{\text{Ccorr}}(S)$  prevents these large errors from being propagated into the  $I_{\text{Ccorr}}(S)$  result. Furthermore, a similar cancellation of errors occurs in the calculation of  $I_{\text{Ccorr}}(\text{Ne})$ , even when (4.2) is evaluated for Ne and  $\text{Ne}^+$  including all the electrons. Thus, although table 5 shows that (4.2) overestimates the correlation energy of both these species by a factor of about two, the  $I_{\text{Ccorr}}(\text{Ne})$  value derived through (4.3) agrees excellently with the experimental value of  $I_{\text{corr}}(\text{Ne})$ . Although both  $I_{\text{Ccorr}}(\text{Na}^+)$  and  $I_{\text{Ccorr}}(\text{F}^-)$  do not agree so well with experiment, the fractional errors in both these predictions are much less than those in the density-functional values of the total correlation energies of  $\text{Ne}^+$ , Ne,  $\text{F}^-$  or F. However, (4.2) disagrees qualitatively with experiment in predicting that  $I_{\text{corr}}(S)$  decreases with decreasing nuclear charge in the Ne isoelectronic sequence, whereas  $I_{\text{corr}}(\text{F}^-)$  is actually larger than  $I_{\text{corr}}(\text{Ne})$  which is in turn greater than  $I_{\text{corr}}(\text{Na}^+)$ . This difficulty is not a peculiarity of using (4.2) with the GK functional since the results in table 7 show that all other variants of density-functional theory currently available also fail to predict that  $I_{\text{corr}}(\text{F}^-)$  is greater than  $I_{\text{corr}}(\text{Ne})$ . Furthermore, none of these variants predicts  $I_{\text{corr}}(\text{Ne})$  and  $I_{\text{corr}}(\text{F}^-)$  any more accurately than (4.2) with the GK functional.

The difficulties with present density-functional predictions for  $I_{\text{corr}}(S)$  show the need to introduce correlation correction factors  $A_{\text{corr}}(\zeta)$  depending on the species  $S$  and defined by

$$A_{\text{corr}}(\zeta) = I_{\text{corr}}(S)/I_{\text{Ccorr}}(S). \quad (4.4)$$

The factors  $A_{\text{corr}}(\zeta)$  (table 6) are constant neither within nor between isoelectronic sequences. For a given sequence, it is useful to parametrize this variation using a quantity  $\zeta$  which is thus controlled by that facet of the electronic structure which causes the correlation correction factors to deviate from unity. For isolated mononuclear species, there is, within a given isoelectronic sequence, only one independent variable. This variable, denoted  $\zeta$ , will be defined as the negative of the net charge, the variation of  $A_{\text{corr}}(\zeta)$  within an isoelectronic sequence being described by a polynomial in  $\zeta$ . The correlation energy predicted from (4.2) for a free  $\text{O}^{2-}$  ion was derived by computing a series of  $\text{O}^{2-}$  wavefunctions in which the radius  $R_{\text{W}}$  in the RVMW model for the environmental potential was successively increased. This method had to be used because the unbound nature of the free  $\text{O}^{2-}$  ion prevented the direct computation of its wavefunction. After extrapolation to the limit of infinite  $R_{\text{W}}$  and subtraction of the  $\text{O}^-$  correlation energy of  $-0.59222$  au predicted from (4.2), the correlation contribution to the first ionization potential of  $\text{O}^{2-}$  is predicted to be  $0.029229$  au. Comparison of this result with the value of  $0.083$  au, deduced by extrapolation (Clementi & McLean 1964) of experimental data along the Ne isoelectronic sequence, shows  $A_{\text{corr}}(2)$  to be  $2.840$ . This result, taken with the values  $A_{\text{corr}}(-1)$ ,  $A_{\text{corr}}(0)$  and  $A_{\text{corr}}(1)$  for  $\text{Na}^+$ , Ne and  $\text{F}^-$ , shows that the variation of  $A_{\text{corr}}(\zeta)$  along the Ne isoelectronic sequence is reproduced by

$$A_{\text{corr}}(\zeta) = 1.055 + 0.292\zeta + 0.127|\zeta|^{3.241}. \quad (4.5)$$

(iv) *The in-crystal oxide anion*

The correlation contribution ( $E_{\text{re}}^{\text{corr}}(R)$ ) to the rearrangement energy of the  $\text{O}^{2-}$  ion in an ionic crystal having closest cation–anion separation  $R$  is currently best evaluated by using

$$E_{\text{re}}^{\text{corr}}(R) = A_{\text{corr}}(\zeta)[E_{\text{A}}^{\text{Ccorr}}(R) - E_{\text{O}^-}^{\text{Ccorr}}], \quad (4.6)$$

where  $E_{\text{A}}^{\text{Ccorr}}(R)$  is the prediction derived from (4.2) for the correlation energy of the in-crystal  $\text{O}^{2-}$  ion with  $E_{\text{O}^-}^{\text{Ccorr}}$  being the corresponding result for the correlation energy of a free  $\text{O}^-$  ion. For an in-crystal ion,  $\zeta$  is defined as the negative of the net charge of the isolated isoelectronic species for which (4.3) predicts the same fraction of the correlation contribution to the ionization potential. Isolated species having non-integral  $\zeta$  can be treated theoretically, being here merely the ion with nuclear charge  $10 - \zeta$  for the Ne isoelectronic sequence of interest. The abundant evidence that the properties of the  $\text{O}^{2-}$  ion are strongly influenced by its environment in the crystal shows that its  $\zeta$  value is not 2. This must therefore be deduced by considering some in-crystal ionic property, either reliably computed or deduced from experiment, whose variation is controlled by the same factors which underlie the deviations of the  $A_{\text{corr}}(\zeta)$  from unity.

A property suitable for determining  $\zeta$  is the polarizability because, in its quantum-mechanical perturbation-theory description, this, like the correlation energy, is determined by both excitation energies and matrix elements between the ground and excited states. The coupled Hartree–Fock (CHF) prediction of the polarizability is more closely related to the correlation energy than the exact polarizability because the two former arise in perturbation theory at second order while the latter occurs at higher order in a double-perturbation treatment. This probably explains why the contribution of electron correlation to the polarizability, the correlation polarizability, is much more environmentally sensitive than the CHF prediction. Thus, the latter is reduced from  $10.7$  to  $5.39$  au when a free  $\text{F}^-$  ion enters a LiF crystal (Fowler &

Table 8. Ion polarizabilities, electron numbers, dipole–dipole  $C_6(ab)$  dispersion coefficients and anion correlation correction factors<sup>a,b</sup>

$\alpha_{cr}$	cation			anion $O^{2-}$			$O^{2-}$ correlation			
	$\alpha_C$	$P_C$	$C_6(CC)$	$\alpha_A$	$P_A$	$C_6(AA)$	$C_6(CA)$	$\zeta$	$A_{corr}(\zeta)$	
MgO	11.831	0.486	4.455	0.536	11.345	4.455	60.491	4.292	0.944	1.436
CaO	19.289	3.193	6.106	10.574	16.096	4.455	102.226	29.380	1.516	1.987

<sup>a</sup>All polarizabilities and dipole–dipole dispersion coefficients in au

<sup>b</sup> $\alpha_{cr}$  values from Boswarva (1970), other quantities derived as described in text.

Madden 1983) compared with a total polarizability reduction from 15.1 (Nellin *et al.* 1982) to 6.15 au (Wilson & Curtiss 1970; Fowler & Madden 1983) corresponding to reduction of correlation polarizability from 4.4 to 0.76 au. Since, for the in-crystal ions, only total polarizabilities are known, these should be compared with the polarizability that a free anion would have if its large correlation polarizability was reduced to a typical in-crystal result. Thus, one value of the function expressing  $\zeta$  in terms of polarizability  $\alpha$  is  $\zeta = 1$ ,  $\alpha = 11.5$  au corresponding to a free  $F^-$  ion having the correlation polarizability of that in LiF, a second  $\zeta = 2$  arising for a free  $O^{2-}$  ion corresponding to infinite  $\alpha$ . These two points are reproduced by setting  $k_1 = 0.092\,754$ ,  $k_2 = 0.005\,797$  in the relation (in au)

$$\alpha^{-1} = k_1 - k_2\zeta^4, \quad (4.7)$$

suggested by the inverse fourth-power dependence of polarizability on nuclear charge (Pauling 1927). The correlation correction parameters  $\zeta$  and correlation correction factors  $A_{corr}(\zeta)$  presented in table 8 were derived by substituting into (4.7) the experimentally derived values of the oxide-ion polarizability in MgO and CaO and then using (4.5).

### (b) *The dispersion energy*

#### (i) *Basic formalism*

The dispersive attraction between two ions a and b separated by a distance  $r_{ab}$  is an infinite series of terms  $-\chi_n^{ab}(r_{ab})C_n(ab)r_{ab}^{-n}$ , where the  $C_n(ab)$  are dispersion coefficients and  $n$  is an even integer not less than six. The non-negative dispersion damping functions  $\chi_n^{ab}(r)$ , which decrease with decreasing  $r$ , arise from ion-wavefunction overlap reaching their maximum values of unity only for large  $r$ , where overlap is negligible. For distances  $r$  where overlap is appreciable, the  $\chi_n^{ab}(r)$  decrease rapidly with increasing  $n$  thus ensuring that terms with high  $n$  are unimportant. These terms are also unimportant at large  $r$  owing to their  $r^{-n}$  dependence even though the damping function is close to unity. Hence, only the first two terms in the dispersion series need be retained.

The first ( $n = 6$ ) term in the dispersion series arises from the attraction of the dipole induced on one ion by a dipole instantaneously present on the other ion. The corresponding dipole–dipole ( $C_6(ab)$ ) dispersion coefficient can be evaluated (Fowler *et al.* 1985; Pyper 1986) to an accuracy of at least 5% by using the Slater–Kirkwood (1931) formula (equations (2.25) of Pyper 1986) provided that each electron number  $P_a$  for the ion a (table 8) is chosen such that this formula exactly reproduces the  $C_6(ii)$  coefficient for the inert gas ( $i$ ) isoelectronic with ion a from the polarizability



Table 9. Dipole–quadrupole dispersion coefficients and dispersion damping parameters<sup>a–c</sup>

	cation		anion O <sup>2–</sup>		C <sub>8</sub> <sup>DQ</sup> (CA)	C <sub>8</sub> <sup>QD</sup> (CA)
	C <sub>8</sub> (CC)	d <sub>C</sub>	C <sub>8</sub> (AA)	d <sub>A</sub>		
MgO	2.135	3.860	1162.290	1.958	41.234	8.549
CaO	101.530	3.240	1752.438	2.254	251.827	141.051

<sup>a</sup>All dipole–quadrupole dispersion coefficients in au derived using the Starkschall–Gordon formula from the C<sub>6</sub>(ab) coefficients in table 8.

<sup>b</sup>Cation d<sub>C</sub> and anion d<sub>A</sub> dispersion-damping parameters derived as described in text in § 4*b* (ii). d<sub>A</sub> derived from orbital decay using (4.8) and (4.10).

<sup>c</sup>All quantities computed using free-cation wavefunctions and O<sup>2–</sup> wavefunctions generated using the OEMFS model for the crystalline environment.

$\alpha_i$  of that gas. *Ab-initio* quantum chemistry computations (Fowler & Madden 1985) taking account of electron correlation yielded accurate cation polarizabilities ( $\alpha_C$ , table 8)). The total molar polarizabilities ( $\alpha_{cr}$ ) were deduced using the Clausius–Mossotti relation from experimental refractive-index data (Boswarva 1970), the in-crystal O<sup>2–</sup> polarizabilities ( $\alpha_A$ ) being  $\alpha_{cr} - \alpha_C$ .

The second ( $n = 8$ ) term in the dispersion series originates as the sum of two contributions, the first of which, governed by the coefficient C<sub>8</sub><sup>DQ</sup>(ab), arises from the quadrupole induced on the second ion by a dipole instantaneously present on the first ion. The second contribution, arising from the corresponding interaction in which the dipole is instantaneously present on the second ion, is governed by the coefficient C<sub>8</sub><sup>QD</sup>(ab), with C<sub>8</sub>(ab) being equal to the sum C<sub>8</sub><sup>DQ</sup>(ab) + C<sub>8</sub><sup>QD</sup>(ab). These coefficients (table 9) were evaluated from the Starkschall–Gordon (1972) formulae (equations 46 of Pyper 1991) with only the contributions of the six outermost electrons included in the calculation of the expectation values ( $\langle r^n \rangle_i$ ) of the  $n$ th power of the distance of the electrons from the nucleus of ion  $i$ . This approach has been shown (Pyper 1986; Fowler & Pyper 1986) to be the most reliable in the absence of *ab-initio* quantum chemistry computations.

The total crystal dispersion energy  $U_{disp}(R)$  was evaluated from result (2.22) of Pyper (1986). This was derived by summing the dispersive attractions between ion pairs over all the pairs in the crystal, retaining only the dipole–dipole and dipole–quadrupole terms and noting that the only dispersion damping functions differing non-negligibly from unity are those  $\chi_n^{CA}(R)$  for the interactions between a cation and its six closest anion neighbours, those  $\chi_n^{AA}(\sqrt{2}R)$  between an anion and its twelve closest anion neighbours and the corresponding cation terms  $\chi_n^{CC}(\sqrt{2}R)$ .

### (ii) The dispersion damping functions

The  $\chi_n^{ab}(r)$  with  $n = 6$  and  $n = 8$  have been derived (Pyper 1986, 1994) from the general formalism of Jacobi & Csanak (1975). The  $\chi_n^{aa}(r)$  for two like species  $a$  depend only on the internuclear separation  $r$  and a single dispersion damping parameter characteristic of species  $a$ . The parameter entering  $\chi_6^{aa}(r)$ , denoted  $d_{a1}$ , differs, in principle, from that  $d_{a2}$  determining  $\chi_8^{aa}(r)$ . The functions  $\chi_n^{ab}(r)$  for two unlike species  $a$  and  $b$  depend on the same two dispersion damping parameters that control the damping of the interactions between two like species.

Each  $d_{aL}$  ( $L = 1$  or  $2$ ) consists of a ground-state contribution ( $d_{ag}$ ) plus one

contribution ( $d_{aeL}$ ) from the lowest excited state ( $eL$ ), with symmetry correct for contributing to the sum-over-states perturbation description of the corresponding dispersion energy (Lassetre 1965; Csanak & Taylor 1972):

$$d_{aL} = d_{ag} + d_{aeL}. \quad (4.8)$$

The  $d_{aL}$  govern the momentum ( $q$ ) dependence of the  $X_{aL}(q)$ , which are the angular independent parts of the Fourier transforms of the transition matrix elements  $X_{ae}(r, r)$  (Csanak & Taylor 1972) which enter (Jacobi & Csanak 1975) the dispersion energy. The  $d_{aL}$  are determined (Csanak & Taylor 1972) by the exponential decay of the integrand at large distances  $r_a$  in the expression

$$X_{aL}(q) = \int r_a^2 [P_{ag}(r_a)/r_a] [P_{aeL}(r_a)/r_a] j_L(qr_a) dr_a, \quad (4.9)$$

yielding the  $X_{aL}(q)$  in an orbital description of the electronic structure of the species  $a$ . Here  $j_L(qr_a)$  is a spherical Bessel function (Rose 1961), while  $P_{ag}(r_a)/r_a$  and  $P_{aeL}(r_a)/r_a$  are the radial parts of the wavefunctions of the outermost orbital in the ground state and excited state  $eL$ , respectively. The exponential decreases of both these wavefunctions, at distances  $r_a$  from the  $a$  nucleus significantly greater than those at which they attain their maxima, determine  $d_{ag}$  and  $d_{aeL}$  through

$$[P_{ag}(r_a)/r_a] \propto \exp(-d_{ag}r_a), \quad [P_{aeL}(r_a)/r_a] \propto \exp(-d_{aeL}r_a). \quad (4.10)$$

If the potential energy experienced by an electron in species  $a$  varies as  $r_a^{-1}$  at large distances from the nucleus, as is the case for a free atom or cation, the decay of each of these orbitals is determined by the corresponding orbital eigenvalue (in au) according to

$$d_{ag} = \sqrt{-2\varepsilon_{ag}}, \quad d_{aeL} = \sqrt{-2\varepsilon_{aeL}}. \quad (4.11)$$

Since both the ground and excited states  $eL$  of light cations are essentially unaffected by their environment in the crystal, the cation  $d_{aL}$  were evaluated by the previous method (Pyper 1986) of using (4.11). Although the potential energy experienced by an anion electron in the RVMW and ORVMW models varies as  $r_a^{-1}$  at intermediate  $r_a$  in the vicinity of the cation, such variation occurs only at extremely large  $r_a$  in the OEMFS, ODMFS and OHSMFS models. Since for these three models it would therefore be incorrect to derive the  $d_{aL}$  from (4.11), these parameters were evaluated through (4.10) by considering the decay of the wavefunction from an  $r_a$  value just beyond the maximum in the wavefunction to the value at which this was reduced by a factor of about twenty. The resulting range of  $r_a$ , from about 4.5 to 7.0 au, is not only just the range giving rise to a large portion of the overlap with filled cation orbitals, but is also the range making the greatest contribution to (4.9). The  $d_{aL}$  predicted through (4.10) for the OEMFS and ODMFS models are greater than those similarly calculated for the RVMW or ORVMW approaches because the former two models produce anion orbitals that are significantly more contracted. The forms of the  $\chi_n^{ab}(r)$  show that, for given  $r$ , increase of  $d_{aL}$  enhances the corresponding damping function  $\chi_n^{ab}(r)$  with the result that the magnitude of the dispersion energy is reduced less by the damping. It should have been expected that an environmental model producing more contracted anion orbitals and, hence, smaller overlap between the orbitals of two interacting species should predict smaller reduction by damping of the undamped dispersion energy. The OEMFS and ODMFS models predict anion eigenvalues  $\varepsilon_{ag}$  (table 3) and  $\varepsilon_{aeL}$  smaller in magnitude than those of the RVMW or ORVMW models. Consequently, a greater dispersion damping would have been predicted in the two former models

than in the latter had the anion  $d_{aL}$  been (incorrectly) evaluated from (4.11). The calculation of the anion dispersion damping parameters using (4.10) is the third of the three major refinements of the computation of crystal cohesion to be presented in this paper.

In the OEMFS and ODMFS models, the decay of the anion orbitals at very large  $r_a$  of 30 au or more from the nucleus corresponds closely to that predicted from the orbital eigenvalues, being not nearly so rapid as that in the region (4.5–7.0 au) used to evaluate the  $d_{aL}$ . However, since these large  $r_a$  values make only minute contributions both to the overlap between the orbitals of two interacting species as well as to the integral (4.9), it would be quite inappropriate to evaluate the anion  $d_{aL}$  by examining anion orbitals at these very large distances.

For an ion having an  $np^6$  outermost electronic configuration, the same excited state ( $eL$ ) contributes in (4.8) to both  $d_{a1}$  and  $d_{a2}$ , which become equal to a common value denoted  $d_a$ . For both the  $O^{2-}$  and  $Mg^{2+}$  ions, the state  $eL$  in (4.8) is the  $^1P$  term of the  $2p^53s$  configuration but is the  $3p^53d$   $^1P$  term for  $Ca^{2+}$ . For each crystal, the oxide-ion dispersion damping parameter  $d_A$  was derived from the orbitals arising at  $R = R_e$ . Since in all the environmental models, excepting that of Watson, the oxide-ion orbitals in MgO differ from those in CaO, the  $d_A$  values in these two crystals are not the same: table 9 presents those derived from (4.10) using the OEMFS model.

## 5. Prediction of the cohesion of MgO and CaO

### (a) *The importance of the environmental potential and damping of the dispersion energy*

The  $D_e$ ,  $R_e$  and  $B$  values predicted without considering electron correlation showed the OEMFS environmental model to be considerably better than those where  $F_{env}^{(0)}(r_a; R)$  has the form of a potential generated by a shell of charge. This improvement is only fully manifested in calculations (tables 10 and 11) where all the contributions ( $E_{re}^{corr}(R)$ ,  $V_{sab}^{corr}(x_{ab}R)$  and  $U_{disp}(R)$ ) arising from electron correlation are introduced using the most accurate methods currently available. The predictions in the columns labelled ( $P$ ) are preferable to those in the columns headed ( $\varepsilon$ ) because, in the former,  $U_{disp}(R)$  is evaluated using  $d_A$  values calculated by the theoretically correct method of deriving  $d_{ag}$  and  $d_{aeL}$  from the decay (4.10) of the orbital wavefunctions. The predictions labelled ( $\varepsilon$ ), derived using  $d_A$  values calculated through (4.11) from the orbital eigenvalues, are reported solely to illustrate the importance of correctly evaluating the  $d_A$ . Each of the five different environmental models has its own  $d_A$  and  $C_8(ab)$  coefficients involving the  $O^{2-}$  ion because these quantities were derived from the model-dependent outermost anion orbitals. However, the  $C_6(ab)$ ,  $d_C$  and  $C_8(CC)$  values are model-independent because the former were derived from experiment and the latter calculated from free-cation wavefunctions. The OEMFS rearrangement energies and inter-ionic potentials expressed in atomic units are presented in tables 12 and 13. All cation wavefunctions used are those computed for the free cation.

Comparison of tables 10 and 11 with table 4 shows that agreement between theory and experiment is significantly improved for all five environmental models on including electron correlation. Nevertheless, the discrepancies between experiment and the predictions of Watson, WM, RVMW and ORVMW models are still appreciable. Although the Watson model is the least satisfactory, it is interesting that the predictions of these four methods are not that dissimilar despite the theoretical objections,

Table 10. MgO crystal cohesion predicted with inclusion of correlation and using different environmental models<sup>a-d</sup>

	Watson		WM		RVMW		ORVMW		OEMFS		expt
	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	
$D_e$	2980	2974	2992	2985	2997	2987	3002	2994	3002	3038	3038
$R_e$	4.115	4.121	4.068	4.074	4.064	4.077	4.105	4.114	4.034	3.994	3.974
$B$	20.9	20.7	18.9	18.7	19.3	19.1	18.2	18.4	19.1	19.9	17.5

<sup>a</sup>See note c to table 2 and notes a and c to table 4.

<sup>b</sup>All predictions derived with  $U_L(R)$  computed from (2.4) with correlation contribution ( $E_{re}^{corr}(R)$ ) to rearrangement energy calculated using the density-functional expression (4.6) with the best (table 8)  $A_{corr}(\zeta)$  parameters.

<sup>c</sup>The results in columns headed ( $\epsilon$ ) are computed with  $O^{2-}$  dispersion damping parameters ( $d_A$ ) derived from orbital eigenvalues according to (4.8) and (4.11).

<sup>d</sup>The results in columns headed ( $P$ ) are computed with  $O^{2-}$  dispersion damping parameters ( $d_A$ ) derived according to (4.8) and (4.10) from decay of the large components of the orbitals.

Table 11. CaO crystal cohesion predicted with inclusion of correlation and using different environmental models<sup>a</sup>

	Watson		WM		RVMW		ORVMW		OEMFS		expt
	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	( $\epsilon$ )	( $P$ )	
$D_e$	2528	2519	2521	2512	2509	2499	2533	2524	2562	2645	2644
$R_e$	4.846	4.860	4.800	4.813	4.767	4.782	4.783	4.797	4.669	4.536	4.537
$B$	10.2	9.65	10.6	10.5	10.9	10.7	11.2	11.0	10.4	11.7	11.3

<sup>a</sup>See notes from table 10.

discussed in §3, which can be raised against the first two methods. The ORVMW predictions are only marginally better than those of the RVMW model, despite the considerable extra effort needed to optimize  $R_W$  in the former approach. Indeed, neither of these two methods has significantly improved on the predictions of the WM model despite the absence of any cation dependence in the latter environmental potential. It is noteworthy that for both MgO and CaO, the predictions of the theoretically best calculations, those using the OEMFS model with the  $d_A$  given in table 9, agree excellently with experiment. These predictions are more accurate than those of the crystal Hartree–Fock method, as would be expected from the absence of electron correlation in this latter method. Thus, the most recent such calculations (Dovesi *et al.* 1993) predict  $R_e$  and  $B$  for CaO to be 4.601 au and  $12.8 \times 10^{10} \text{ Nm}^{-2}$ , while the MgO results reviewed elsewhere (Pyper 1991) were discussed in the introduction.

The agreement of the present calculations with experiment does not arise simply as the sum of the improvement in the prediction of  $U_L^0(R)$  on replacing the Watson, WM, RVMW or ORVMW models by the OEMFS approach plus an environmentally independent improvement produced on including electron correlation. This agreement depends explicitly on the interplay between the improvement of the environmental model and its consequent effect on the predicted  $U_{disp}(R)$  and  $E_{re}^{corr}(R)$ . Thus, the more contracted anion 2p orbitals predicted by the OEMFS model generate  $d_A$  val-

Table 12. *The OEMFS predictions for MgO*

$R$	$A$	$k$	$E_{\text{re}}^0(R)$	$V_{\text{sCA}}^0(R)$	$V_{\text{sAA}}^0(\sqrt{2}R)$	$E_{\text{re}}(R)$	$V_{\text{sCA}}^T(R)$	$V_{\text{sAA}}^T(\sqrt{2}R)$
3.25	2.54	1.43	0.816 52	0.085 28	0.017 28	0.703 24	0.083 33	0.016 23
3.5	2.00	1.29	0.643 37	0.062 26	0.011 87	0.541 10	0.060 63	0.010 75
3.75	1.54	1.16	0.538 47	0.046 61	0.007 55	0.445 07	0.045 24	0.006 38
3.981	1.21	1.05	0.477 42	0.036 27	0.004 54	0.390 69	0.035 10	0.003 37
4.25	0.90	0.937	0.431 35	0.027 72	0.002 11	0.351 04	0.026 74	0.000 96
4.5	0.74	0.843	0.406 23	0.021 50	0.000 80	0.330 27	0.020 68	-0.000 27
5.0	0.42	0.683	0.372 20	0.013 94	-0.000 63	0.303 75	0.013 34	-0.001 61
5.5	0.25	0.553	0.353 60	0.009 40	-0.001 06	0.290 61	0.008 96	-0.001 93

All  $V_{\text{sCC}}^0(\sqrt{2}R)$  and  $V_{\text{sCC}}^{\text{corr}}(\sqrt{2}R) < 10^{-5}$  for  $R \geq 3.5$ ;  $V_{\text{sCC}}^0(\sqrt{2}R)$  is 0.000 07 and 0.000 01 with  $V_{\text{sCC}}^{\text{corr}}(\sqrt{2}R) = -0.000 03$  and  $-0.000 01$  for  $R = 3.0$  and  $3.25$ , respectively.

Table 13. *The OEMFS predictions for CaO*

$R$	$A$	$k$	$E_{\text{re}}^0(R)$	$V_{\text{sCA}}^0(R)$	$V_{\text{sAA}}^0(\sqrt{2}R)$	$E_{\text{re}}(R)$	$V_{\text{sCA}}^T(R)$	$V_{\text{sAA}}^T(\sqrt{2}R)$
3.5	1.8	1.07	0.945 91	0.132 55	0.003 40	0.784 58	0.128 68	0.003 08
3.75	1.93	1.12	0.794 20	0.088 06	0.002 26	0.644 85	0.084 96	0.001 96
4.0	2.25	1.12	0.692 39	0.058 66	0.001 44	0.552 08	0.056 18	0.001 19
4.25	2.18	0.97	0.609 76	0.040 97	0.001 06	0.476 63	0.039 00	0.000 83
4.544	1.26	0.718	0.519 93	0.030 48	0.001 05	0.395 63	0.028 89	0.000 79
4.75	0.91	0.63	0.474 09	0.025 34	0.000 95	0.356 18	0.023 94	0.000 65
5.0	0.75	0.59	0.438 16	0.019 82	0.000 72	0.326 85	0.018 63	0.000 41
5.5	0.64	0.59	0.394 33	0.012 37	0.000 33	0.293 97	0.011 49	0.000 01
6.0	0.56	0.58	0.368 71	0.008 18	0.000 09	0.276 61	0.007 53	-0.000 21

$R$	$V_{\text{sCC}}^0(\sqrt{2}R)$	$V_{\text{sCC}}^T(\sqrt{2}R)$
3.5	0.00282	0.00250
3.75	0.00101	0.00083
4.0	0.00036	0.00026
4.25	0.00013	0.00008
4.544	0.00004	0.00002
4.75	0.00002	0.00001
5.0	0.00001	0.00001

ues appreciably larger than those derived from the Watson, WM, RVMW or ORVMW models. For MgO, these four models produce  $d_A$  values of 1.295, 1.387, 1.481 and 1.442, respectively, compared with 1.958 in the OEMFS model. This causes the latter to produce significantly greater  $|U_{\text{disp}}(R)|$  values, for example, the OEMFS description predicts  $U_{\text{disp}}(3.981)$  to be  $-60 \text{ kJ mol}^{-1}$  compared with  $-36 \text{ kJ mol}^{-1}$  in the ORVMW model. This trend is accentuated for CaO for which the WM, RVMW and

ORVMW models have  $d_A$  values of 1.315, 1.325 and 1.317 compared with 2.254 in the OEMFS method; the  $U_{\text{disp}}(4.544)$  of  $-113 \text{ kJ mol}^{-1}$  resulting in the latter approach being of much greater magnitude than the corresponding ORVMW result of  $-59 \text{ kJ mol}^{-1}$ . The greater contraction of the OEMFS orbitals causes the Starkschall-Gordon formula to predict smaller  $C_8(\text{ab})$  dispersion coefficients involving the  $\text{O}^{2-}$  ion than those produced in the Watson, MW, RVMW and ORVMW methods. However, this factor is outweighed by the larger  $d_A$  values in the OEMFS model which therefore yields larger  $|U_{\text{disp}}(R)|$  values.

The importance of the environmental modifications of  $U_{\text{disp}}(R)$  and  $E_{\text{re}}^{\text{corr}}(R)$  is shown by considering, for MgO, the  $D_e$  increases of 21 and 12  $\text{kJ mol}^{-1}$  and  $R_e$  decreases of 0.05 and 0.085 au on passing from the RVMW and ORVMW models to the OEMFS predictions of  $U_L^0(R)$ . These improvements are much less than the  $D_e$  increases of 51 and 44  $\text{kJ mol}^{-1}$  and  $R_e$  decreases of 0.083 and 0.120 au on passing from the RVMW and ORVMW calculations of  $U_L(R)$  to those performed using the OEMFS approach. For CaO similarly, the  $D_e$  increases of 59 and 45  $\text{kJ mol}^{-1}$  and  $R_e$  decreases of 0.119 and 0.119 au on passing from RVMW and ORVMW to OEMFS calculations of  $U_L^0(R)$  are less than half the  $D_e$  increases of 146 and 121  $\text{kJ mol}^{-1}$  and  $R_e$  decreases of 0.246 and 0.261 au generated by passing from RVMW and ORVMW to the OEMFS description of  $U_L(R)$ .

The significance of deriving  $d_A$  from the decay of the orbitals using (4.10) rather than from the eigenvalues (4.11) is shown (tables 10 and 11) by comparing the corresponding predictions for the crystal cohesion. For the Watson, WM, RVMW and ORVMW models, these two different methods produce rather similar values of  $d_A$ , thereby generating not dissimilar predictions for  $D_e$ ,  $R_e$  and  $B$ . This might have been expected because in all four of these environmental models,  $F_{\text{env}}^{(0)}(r_a; R)$  varies as  $r_a^{-1}$  over a large part of those spatial regions in which the orbitals are appreciable. However, for the OEMFS model, the  $d_A$  values of 1.154 and 0.795 predicted from (4.11) for MgO and CaO, respectively, are very much less than those (table 9) derived from the orbital decays. These differences arise because  $F_{\text{env}}^{(0)}(r_a; R)$  does not even approximately vary as  $r_a^{-1}$  in spatial regions where the anion orbitals are appreciable. The overestimation of the dispersion damping using  $d_A$  values from (4.11) causes the crystal cohesion to be appreciably underestimated.

(b) *The role of the correlation contribution to the rearrangement energy*

The importance of the  $R$  dependence of both  $E_{\text{re}}^{\text{corr}}(R)$  evaluated through (4.6) and the correction factors  $A_{\text{corr}}(\zeta)$  is shown by the comparison (table 14) of calculations differing only in the evaluation of  $E_{\text{re}}^{\text{corr}}(R)$ . The environment was described using the OEMFS model in all these calculations, which included both the correlation contributions  $V_{\text{sab}}^{\text{corr}}(x_{\text{ab}}R)$  to the short-range interactions as well as  $U_{\text{disp}}(R)$ , evaluated using the best  $d_A$  values (table 9).

The results in the first row of table 14 show that  $R_e$  is overestimated if  $E_{\text{re}}^{\text{corr}}(R)$  is taken to be independent of  $R$ . These calculations, in which  $E_{\text{re}}^{\text{corr}}(R)$  was taken to be  $-218 \text{ kJ mol}^{-1}$ , as deduced by Clementi & McLean (1964), should be compared with the best of the previous (Pyper 1986, 1994) methods which differ by using the RVMW model and in deriving  $d_A$  from (4.11). The latter method predicts  $D_e$ ,  $R_e$  and  $B$  for CaO to be 2463  $\text{kJ mol}^{-1}$ , 4.830 au and  $9.71 \times 10^{10} \text{ Nm}^{-2}$ . These predictions are only changed to 3005  $\text{kJ mol}^{-1}$ , 4.111 au and  $17.8 \times 10^{10} \text{ Nm}^{-2}$  for MgO and 2454  $\text{kJ mol}^{-1}$ , 4.846 au and  $9.54 \times 10^{10} \text{ Nm}^{-2}$  for CaO on replacing the  $d_A$  values of (4.11) with those of (4.10). Although the overestimations of  $R_e$  in the RVMW model

Table 14. Comparison of MgO and CaO crystal cohesion predicted using different methods for incorporating the correlation contribution to the  $O^{2-}$  rearrangement energy into the OEMFS method with inclusion of electron correlation<sup>a</sup>

method <sup>b</sup>	MgO			CaO		
	$D_e$	$R_e$	$B$	$D_e$	$R_e$	$B$
const $E_{re}^{corr}$	3032	4.049	18.3	2541	4.643	9.39
$A_{corr}(\zeta) = 1$	2970	4.010	19.4	2484	4.587	10.4
$F^-$ , i.e. $A_{corr}(1)$	3044	3.992	20.0	2561	4.562	11.0
best $A_{corr}(\zeta)$	3038	3.994	19.9	2645	4.536	11.7
expt	3038	3.974	17.5	2644	4.537	11.3

<sup>a</sup>See notes a and c to table 4. All results calculated from (2.4) with  $O^{2-}$  dispersion-damping parameters having values presented in table 9 and derived according to (4.8) and (4.10) from decay of the large components of the orbitals.

<sup>b</sup>Row labelled const  $E_{re}^{corr}$  has correlation contribution  $E_{re}^{corr}(R)$  to  $O^{2-}$  rearrangement energy taken to be independent of  $R$  and equal to the value of  $-218 \text{ kJ mol}^{-1}$  derived for free  $O^{2-}$  ion by extrapolation (Clementi & McLean 1964). Results in all other rows have  $E_{re}^{corr}(R)$  computed using the density-functional prescription (4.6) and (4.2) and differ only in the values used for the correlation correction factor  $A_{corr}(\zeta)$ . In the second row,  $A_{corr}(\zeta)$  is omitted from (4.6), i.e. taken to be unity; in the third row  $A_{corr}(\zeta)$  is taken from the free  $F^-$  ion (see table 6) and in the fourth row the best (table 8)  $A_{corr}(\zeta)$  values.

of 0.124 and 0.293 a.u for MgO and CaO are almost halved to 0.075 and 0.106 au (first row, table 14) on using the OEMFS model, these remaining errors show that variation of  $E_{re}^{corr}(R)$  with  $R$  must be considered. Although the OEMFS prediction of  $D_e$  for MgO, derived with constant  $E_{re}^{corr}(R)$  ( $= -218 \text{ kJ mol}^{-1}$ ), agrees excellently with experiment,  $D_e$  for CaO is underestimated by  $105 \text{ kJ mol}^{-1}$ . This shows that no single constant  $E_{re}^{corr}(R)$  can reproduce both  $D_e$  values.

The importance of the  $R$  dependence of  $E_{re}^{corr}(R)$  can be demonstrated without accepting the arguments used to derive  $A_{corr}(\zeta)$  for an in-crystal  $O^{2-}$  ion. Thus, the  $R_e$  overestimations produced for MgO and CaO by taking  $E_{re}^{corr}(R)$  to be constant are more than halved (second row, table 14) to 0.036 and 0.050 au on introducing its  $R$  dependence through (4.6), but taking  $A_{corr}(\zeta)$  to be unity even though the resulting  $|E_{re}^{corr}(R)|$  values are too small. This underestimation, deduced from the Ne and  $F^-$   $A_{corr}(\zeta)$  (table 6), is propagated into the results for  $D_e$ . The natural expectation that using the  $A_{corr}(\zeta)$  value correct for a free  $F^-$  ion would generate more realistic predictions is confirmed by the excellent agreement (third row, table 14) between theory and experiment for MgO, although the cohesion of CaO is still slightly underestimated. These results strongly indicate that  $A_{corr}(\zeta)$  for  $O^{2-}$  depends on its environment.

The excellent agreement (fourth line, table 14) between experiment and the most sophisticated of the present calculations, namely those using the  $A_{corr}(\zeta)$  of table 8, depends on the significant difference between the MgO and CaO  $A_{corr}(\zeta)$  values of 1.436 and 1.987. The MgO results are very similar to those derived using the free  $F^-$  ion  $A_{corr}(\zeta)$  because this hardly differs from 1.436. The OEMFS anion electron densities  $\rho_{TS}(\mathbf{r})$  in MgO and CaO at their respective equilibrium geometries are very similar, that in CaO being slightly more compressed as shown by 2p orbital mean radii and mean-square radii (table 3) smaller by 2% and 4%, respectively. This

similarity explains why the prediction of  $-164 \text{ kJ mol}^{-1}$  for  $E_{\text{re}}^{\text{corr}}(R_e)$  in CaO of is only 3% greater in magnitude than that of  $-159 \text{ kJ mol}^{-1}$  in MgO if both  $A_{\text{corr}}(\zeta)$  are taken to be unity in (4.6). The much greater magnitude of the final prediction of  $-326 \text{ kJ mol}^{-1}$  for  $E_{\text{re}}^{\text{corr}}(R_e)$  in CaO compared with that of  $-228 \text{ kJ mol}^{-1}$  in MgO arises from the significantly larger value (table 8) of  $A_{\text{corr}}(\zeta)$  in CaO. Anion correlation energies would be expected to be more environmentally sensitive than  $\rho_{\text{TS}}(\mathbf{r})$  because the perturbation description of the former contains excitation energies. The smaller binding energy, as reflected in the orbital eigenvalue ( $\varepsilon_{2\text{p}}$ , see table 3), of an  $\text{O}^{2-}$  2p electron in CaO compared with MgO suggests that the excitation energies are much less in the former which would cause  $|E_{\text{A}}^{\text{corr}}(R_e)|$  and, hence,  $|E_{\text{re}}^{\text{corr}}(R_e)|$  to be greater in CaO. Such reduced excitation energies are supported by the significantly greater anion polarizability  $\alpha_{\text{A}}$  in CaO (table 8). Thus, the approximation (Vinti 1932) of introducing an average excitation energy  $\Delta_{\text{E}}$  into the standard perturbation-theory expression for  $\alpha_{\text{A}}$  and then neglecting certain terms involving the coordinates of two electrons (Salem 1960) yields  $\alpha_{\text{A}}$  as  $2\langle r^2 \rangle / (3\Delta_{\text{E}})$ . The  $\text{O}^{2-}$  2p electrons, the largest contributors to  $\alpha_{\text{A}}$ , have very similar values of  $\langle r^2 \rangle$  in MgO and CaO, which shows that the enhancement of  $\alpha_{\text{A}}$  in CaO arises almost entirely from reduction of  $\Delta_{\text{E}}$ .

## 6. Conclusion

This paper presented the three refinements needed for a fully satisfactory description of a solid oxide within the fully ionic model. The cohesive properties thereby predicted for MgO and CaO agree well with experiment. There is no evidence for covalent contributions to the cohesion.

The first refinement was the introduction of the optimized hyperbolic secant Madelung Fermi smoothed (OHSMFS), optimized with density Madelung Fermi smoothed (ODMFS) and optimized with eigenvalues Madelung Fermi smoothed (OEMFS) models for the interaction of an anion electron with its surroundings. These showed that the spherically symmetric part  $F_{\text{env}}^{(0)}(r_{\text{a}}; R)$  of this interaction, which is constant for small  $r_{\text{a}}$ , where the electron density of other ions is negligible, increases rapidly and exponentially at larger  $r_{\text{a}}$  and may become positive for  $r_{\text{a}}$  values close to the cation–anion separation  $R$ , corresponding to the core regions of neighbouring cations. Although, for MgO at its equilibrium geometry ( $R = R_e$ ),  $F_{\text{env}}^{(0)}(r_{\text{a}}; R)$  is everywhere negative, it is strongly positive for  $r_{\text{a}}$  values in the vicinity of  $R$  both for MgO at smaller  $R$  and for CaO at  $R = R_e$ . This shows the inadequacy of models such as the optimized Abarenkov & Antonova (3.7) function and the optimized Fermi function model (3.8), which can never become positive. The Watson, Watson–Madelung (WM), radius variable Madelung Watson (RVMW) and optimized radius variable Madelung Watson (ORVMW) models, which are also negative everywhere, are even less adequate because they vary as  $r_{\text{a}}^{-1}$  on increasing from their constant values at small  $r_{\text{a}}$  in contrast with exponential increases in the OHSMFS, ODMFS and OEMFS descriptions. Despite a long history, models such as the Watson, WM, RVMW and ORVMW, in which  $F_{\text{env}}^{(0)}(r_{\text{a}}; R)$  has the form of the potential generated by a spherical shell of charge, are insufficiently realistic to describe accurately the cohesion of MgO or CaO and are thus unsuitable for high-precision studies of oxides. The only insight given from such models that  $F_{\text{env}}^{(0)}(r_{\text{a}}; R)$  is constant and negative for small  $r_{\text{a}}$  while increasing at larger  $r_{\text{a}}$  is more clearly revealed by the ODMFS and OEMFS approaches.



The second refinement of calculations of crystal cohesion was to consider the variation with crystal geometry of the contribution of electron correlation to the oxide-ion rearrangement energy. It was not only shown that this variation must be taken into account if the cohesion of MgO and CaO are to be accurately described, but evidence has also been presented which indicates that this contribution to the lattice energy is significantly greater in magnitude for CaO than for MgO.

The third refinement was necessitated by using more realistic environmental models in which  $F_{\text{env}}^{(0)}(r_a; R)$  does not have the form of the potential generated by a shell of charge. In these more realistic models,  $F_{\text{env}}^{(0)}(r_a; R)$  does not vary as  $r_a^{-1}$  in any spatial regions where there is any appreciable probability of finding an anion electron. It would therefore be wrong to derive from the  $\text{O}^{2-}$  2p orbital eigenvalues the anion dispersion damping parameter needed to calculate the functions damping the dispersive attractions involving the anions. The derivation of these damping parameters from the decay of the  $\text{O}^{2-}$  2p orbitals provides the necessary refinement.

The refinements needed for a good description of MgO and CaO are valuable because the previous methods (Pyper 1986) would also be expected to fail for  $\text{ThO}_2$  and  $\text{UO}_2$ . This failure, and its rectification using the methods described in this paper, will be reported elsewhere (Harding *et al.* 1994). Since relativistic effects are important for ions of high nuclear charge,  $\text{ThO}_2$  and  $\text{UO}_2$  could only be studied because the relativistic integrals program (RIP) (Wood & Pyper 1981*b, c*, 1986) was available for computing the inter-ionic potentials both exactly and fully relativistically.

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## ERRATA

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### Relativistic ab-initio calculations of the properties of ionic solids

By N. C. PYPER

Section 2c(iii), on the calculation of the functions  $\chi_n^{ab}(r)$  damping the inter-ionic dispersive attractions, needs three types of correction, two being of notation.

(1) In all the formulae (2.27)–(2.39), the distance  $R$  is that between the pair of interacting ions and should thus be  $x_{ab}R$ .

(2) Equation (2.34c) contained the two errors that  $\tilde{P}_5(x)$  on the right-hand side should be  $\tilde{P}_6(x)$  and that the denominator in the last term should be 691 200 and not 69120, so that (2.34c) should read

$$P_9(x) = \tilde{P}_6(x) + \frac{1}{5120}x^7 + \frac{1}{46080}x^8 + \frac{1}{691\,200}x^9.$$

Equation (2.35) needs to be corrected by replacing both occurrences of  $\exp(-d_{a2}R)$

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