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# The cohesion of solid cubic calcium fluoride

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**Abstract.** The cohesion of cubic solid calcium fluoride is studied theoretically within the framework of the fully ionic model by a non-empirical approach in which the major portion of the cohesion, namely that not originating from electron correlation effects, is computed *ab initio* using the relativistic integrals program. Electron correlation is incorporated by adding the short-range contributions calculated using density functional theory to the inter-ionic dispersive attractions evaluated with the inclusion of their damping caused by the overlap of the ion wavefunctions. The interaction of the fluoride ion with its environment in crystal significantly modifies the computed inter-ionic potentials and two different methods for describing these modifications are compared. The more sophisticated and realistic of the two methods predicts values for the lattice energy, equilibrium closest cation–anion separation and bulk modulus in excellent agreement with experiment.

## 1. Introduction

Calcium fluoride is not only technologically important as a super-ionic conductor [1,2] but is also one of the simplest metal dihalides. These materials have recently become the subject of renewed interest on two accounts [3–5]. Firstly, it has been a long-established goal to understand the structures adopted by these materials in the solid state, including those of crystals whose low symmetries were previously considered to be evidence for partial covalency. The most recent study [3] reversed the earlier belief in partial covalency by demonstrating that the structures of all these materials can be understood on a fully ionic basis provided that the electric dipole polarization of ions in sites of low symmetry is considered. Secondly, the dynamical structures of melts of these dihalides have been investigated [4,5] particularly with regard to elucidating the role of anion polarization in determining the short- and intermediate-range order. All these theoretical studies [1–5] required information concerning the inter-ionic interactions which were taken to be effective two-body potentials having a semi-empirically determined Born–Mayer form.

Despite the success of the above investigations there are many factors [6–8] which motivate the theoretical study of polar solids by using non-empirical techniques. Since it would be inappropriate to detail these again here, it suffices to point out that it has been shown [9] that a cation–anion inter-ionic potential determined semi-empirically from data on one polymorph will not be fully transferable to a second polymorph having a different coordination number. Indeed it was shown [9] that one could not predict that caesium chloride adopts its experimentally observed eight fold coordinated structure without considering this non-transferability of the conventional effective two-body cation–anion potential. An overall approach for calculating, non-empirically, the electronic structures and hence inter-ionic potentials of binary solids within the assumption of a suitably defined fully ionic model has been presented and found to give a good account of the cohesive

properties of all five halides studied, as well as performing not unreasonably for MgO [7]. This approach was recently refined [10] in order to meet the more severe tests of both accounting for the cohesion of other binary oxides [10, 11] and correctly predicting the crystal structure of caesium chloride [9]. The present paper has two objectives, the first being to further test this fully ionic model by studying solid calcium fluoride in its ground state fluorite structure. A major part of this investigation lies in determining whether the earlier method [7] for generating in-crystal anion wavefunctions can account for the important in-crystal modifications of the properties of the fluoride ion or whether, as is the case for oxides, subsequent refinements [10] are needed for a fully satisfactory description. The second objective of this paper, attained as a by-product of achieving the first, is to present information, such as two-body potentials, concerning the cohesive energetics which could form the basis for future studies of either crystal defects or the high-pressure polymorph having the  $\text{PbCl}_2$  structure [12] or the liquid melt.

## 2. Theory and computational methods

### 2.1. Basic theory

*2.1.1. Fundamental assumptions.* The fundamental assumption of the present study is that  $\text{CaF}_2$  is fully ionic. Although the discussion [13] might suggest that this concept is not uniquely defined, the arguments of [8] justify the following definition of full ionicity used in all the previous studies of polar solids [7, 9–11, 14] performed with the relativistic integrals program [14, 15]. Here a solid is taken as fully ionic provided that, with the neglect of inter-ionic electron correlation, the total electronic wavefunction of the entire crystal can be written as an anti-symmetrized product of wavefunctions for the individual ions, each of which contains an integral number of electrons and is spherically symmetric with respect to its nucleus. Here the derivation [7, 8, 10] of the expression for the cohesive energy that results from this ionicity assumption and the computational methods [7, 8, 10, 14] need only be outlined, and a full description presented of just those refinements unique to the present study.

The wavefunction and properties of the  $\text{Ca}^{++}$  ion were taken to be those of the free ion because there is abundant evidence [16–19] that cations having  $1s^2$  or  $np^6$  outermost electronic configuration are essentially unaffected by their in-crystal environments. However, such environments greatly modify many anion properties such as the electronic charge distribution [7, 8, 10, 17, 18], polarizabilities [16–19] and inter-ionic dispersion coefficients [20, 21]. The earlier [7] and later more refined [10] methods for generating anion wavefunctions adapted to their in-crystal environments are described in section 2.2. The total crystal energy is written as the sum of the major and uncorrelated part plus corrections arising from the affects of electron correlation.

For uniform expansions or contractions of a cubic crystal from its equilibrium structure, the nuclear geometry is defined by the closest cation–anion separation, to be denoted  $R$ . For a bound crystal with this geometry, the negative binding energy  $U_L(R)$  is defined as the difference between the total crystal energy and the sum of the energies of free isolated  $\text{F}^-$  and  $\text{Ca}^{++}$  ions. The equilibrium closest cation–anion separation, denoted  $R_e$ , is the value of  $R$  for which  $U_L(R)$  is minimized. The lattice energy  $D_e$ , defined as the energy required to convert the crystal at its equilibrium geometry into free  $\text{F}^-$  and  $\text{Ca}^{++}$  ions, then equals  $-U_L(R_e)$ . Nuclear zero-point motion causes  $R_e$  to differ very slightly from the equilibrium  $R$  value measured at 0 K as well as making a small contribution to the lattice energy. These

effects are sufficiently small that they can be disregarded here. The bulk modulus, denoted  $B$  and defined by the relation (1a) with  $V$  the volume occupied by one formula unit, can be predicted from  $U_L(R)$  through

$$B = (V d^2 U_L(R) / dV^2)_{R=R_c} \quad (1a)$$

$$B = (1/9k_v)(d^2 U_L(R) / dR^2)_{R=R_c} \quad (1b)$$

where  $k_v$  (equal to  $16/(3\sqrt{3})$ ) is the constant relating  $V$  to  $R$  as  $k_v R^3$ .

**2.1.2. Formulation exclusive of electron correlation.** In the approximation, denoted by a zero superscript, in which all effects of electron correlation are neglected, the electronic wavefunction for the entire crystal reduces to a single anti-symmetrized product of individual ion wavefunctions each of which is a single anti-symmetrized product of one electron orbital. An expression for the total crystal energy resulting from this approximation has been derived [22] by taking the expectation value of the usual electronic Hamiltonian. After neglecting the resulting explicitly three-body and higher-order multi-body terms, expected to be small [8], and subtracting the Hartree-Fock, or in the relativistic approach the Dirac-Fock, energies of the free  $F^-$  and  $Ca^{++}$  ions, the crystal binding energy  $U_L^0(R)$  predicted for one mole of formula unit  $CaF_2$  in this uncorrelated approximation is found [7, 8] to be

$$U_L^0(R) = N_f \left\{ 2E_{re}^0(R) - 5.03878488/R + 8V_{sCA}^0(R) + 6 \left[ V_{sAA}^0(2/\sqrt{3}R) + V_{sCC}^0(2\sqrt{(2/3)R}) \right] \right\}. \quad (2)$$

Here all the terms inside the curly brackets are expressed in atomic units on a scale in which 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  $E_{re}^0(R)$  in (2) is the rearrangement energy required to convert one free fluoride ion of Dirac-Fock energy  $E_{Af}^0$  into the fluoride ion having the wavefunction considered optimal for the crystal having closest cation-anion separation  $R$  so that

$$E_{re}^0(R) = E_A^0(R) - E_{Af}^0. \quad (3)$$

Here  $E_A^0(R)$  is the energy that a fluoride ion with a wavefunction considered optimal for the crystal would have when isolated, if it were then to retain its in-crystal wavefunction. Thus  $E_A^0(R)$  is computed by taking the expectation value of the free-ion Hamiltonian using the wavefunction for the in-crystal  $F^-$  ion. The in-crystal  $F^-$  wavefunctions were computed using a version of the Oxford Dirac-Fock program [23] modified by adding a term  $F_{env}^{(0)}(r_a; R)$  to the potential energy acting on an anion electron, to describe its interaction with the crystalline environment. This term, whose explicit representations are discussed in section 2.2, depends on  $R$  and hence the energy  $E_A^0(R)$  and rearrangement energy  $E_{re}^0(R)$  depend on this variable. Both the energy  $E_{Af}^0$  and the  $Ca^{++}$  ion wavefunction were computed in a standard run of the Dirac-Fock program.

In the absence of an 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 on ion  $a$  and  $x_{ab}$  is a purely geometrical constant which yields the separation of the pair of ions as  $x_{ab} R$ . The sum of all such purely Coulombic interactions enters (2) as the Madelung term  $-5.03878488/R$ . If the overlap between the wavefunctions

of the 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

$$V_{sab}^0(x_{ab}R) = V_{ab}^0(x_{ab}R) - q_a q_b / (x_{ab}R). \quad (4)$$

For the pair of ions  $a$  and  $b$  separated by a distance  $x_{ab}R$ ,  $V_{ab}^0(x_{ab}R)$  is their total interaction energy 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 whilst not interacting ( $E_a^0(R)$  for a  $\text{Ca}^{++}$  ion is just the energy of the isolated ion). For  $\text{CaF}_2$ , the only non-negligible short-range interactions are: those ( $V_{sCA}^0(R)$ ) between a cation and its eight closest anion neighbours; those  $V_{sAA}^0(2/\sqrt{3}R)$  between one anion and its six nearest anion neighbours at a distance  $2/(\sqrt{3})R$ ; and the interaction  $V_{sCC}^0(2\sqrt{(2/3)}R)$  between one cation and its 12 closest cation neighbours at a distance  $2\sqrt{(2/3)}R$ . The terms  $V_{sab}^0(x_{ab}R)$  were evaluated by using the RIP program to compute, from the free  $\text{Ca}^{++}$  and in-crystal  $\text{F}^-$  Dirac–Fock wavefunctions, the total interaction energies  $V_{ab}^0(x_{ab}R)$ . The RIP program results for  $V_{sab}^0(x_{ab}R)$  are exact once the wavefunctions of the interacting ions have been specified. The use of the RIP program thus avoids the uncertainties, discussed elsewhere [7, 24, 25], which would arise were the  $V_{sab}^0(x_{ab}R)$  to be computed using density functional theory. Although relativistic effects would be expected to be very small for  $\text{CaF}_2$ , the Dirac–Fock and RIP computations took 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 Dirac–Fock and RIP programs differ from their relativistic counterparts solely by using an artificially large value for the velocity of light. Thus there would be no computational economies in using non-relativistic theory.

**2.1.3. Total crystal cohesion including electron correlation.** Electron correlation contributes to both the fluoride ion rearrangement energy and to the interaction energy of every pair of ions. These contributions were evaluated from the Dirac–Fock wavefunctions for the individual free  $\text{Ca}^{++}$  and in-crystal  $\text{F}^-$  ions and then added to  $U_L^0(R)$  to produce the complete prediction for the cohesive energy function  $U_L(R)$ . This approach neglects the explicitly three-body and higher-order multi-body contributions to the crystal correlation energy which are expected to be small for the reasons presented elsewhere [8].

The total fluoride ion rearrangement energy  $E_{re}(R)$  is given by adding to  $E_{re}^0(R)$  the electron correlation contribution  $E_{re}^{corr}(R)$ , so that

$$E_{re}(R) = E_{re}^0(R) + E_{re}^{corr}(R). \quad (5)$$

The term  $E_{re}^{corr}(R)$  is defined as the total correlation energy of the in-crystal  $\text{F}^-$  ion minus the correlation energy of a free fluoride ion, and is computed using the method described in section 2.3.

The contribution of electron correlation to the interaction of the pair of ions  $a$  and  $b$  separated by the distance  $x_{ab}R$  can be decomposed into a sum of a long-range term, usually called the dispersive or van der Waals attraction, plus a short-range term [26]. The summation over all pairs of ions of the dispersive attractions within each pair yields the total dispersion contribution ( $U_{disp}(R)$ ) to the crystal cohesion which is calculated by the methods described in section 2.4. The short-range contribution ( $V_{sab}^{corr}(x_{ab}R)$ ) of the electron correlation to the energy of interaction between the ions  $a$  and  $b$  originates explicitly from the overlap of their wavefunctions and therefore vanishes for separations  $x_{ab}R$  which are sufficiently large that this overlap has become negligible. Consequently,

the only non-negligible such terms are those for ion pairs for which the uncorrelated short-range interactions are not negligible. It is therefore useful to regard the term  $V_{sab}^{corr}(x_{ab}R)$  as the correlation correction to the uncorrelated short-range interaction and to define the total short-range interaction,  $V_{sab}(x_{ab}R)$ , between ion  $a$  and  $b$  through

$$V_{sab}(x_{ab}R) = V_{sab}^0(x_{ab}R) + V_{sab}^{corr}(x_{ab}R). \quad (6)$$

The density functional theory of electronic structure provides the only currently practical method for evaluating the  $V_{sab}^{corr}(x_{ab}R)$  for a pair of in-crystal ions. Here these terms were evaluated using the original method of Gordon and Kim [27] in which the required correlation energy functional is taken to be that for a non-relativistic electron gas of uniform density and infinite extent. This functional is presented in section 2.3 as equation (13). The reason why the predicted correlation energies would remain essentially unaffected even if the theoretical inconsistency of using a non-relativistic functional with relativistic wavefunctions were to be removed has been explained [8].

The addition to  $U_L^0(R)$  of the dispersive attractions, as well as the contributions of electron correlation to both the anion rearrangement energy and short-range two-body interactions, yields the result (7) for the cohesive energy function  $U_L(R)$

$$U_L(R) = N_f \{ 2E_{rc}(R) - 5.03878488/R + 8V_{sCA}(R) + 6[V_{sAA}(2/\sqrt{3}R) + V_{sCC}(2\sqrt{(2/3)R})] \} + U_{disp}(R). \quad (7)$$

There is evidence [8, 28] that the dispersive attractions remain essentially distinct from the correlation contributions to the short-range-overlap dependent two-body interactions in (6), even when the latter are evaluated using (13). Hence there will be only minimal double counting of the two-body correlation contributions when this functional enters (7) through its use in (6).

## 2.2. Description of the in-crystal modifications of the fluoride ion

An anion in a cubic crystal with closest cation-anion separation  $R$  differs from the isolated ion because an electron at a position  $r_a$  relative to the anion nucleus experiences a potential energy  $F_{env}(r_a; R)$ , called the environmental potential, which is generated by the nuclei and electrons of all the other ions. When the anion nucleus is taken as origin  $F_{env}(r_a; R)$  can be expanded into a series where spherical harmonics describe its angular dependence. In the conventional description of the electronic structure of a closed-shell ion in which all the orbitals have their standard central field form [29] and are either completely filled with electrons or entirely empty, the only portion of  $F_{env}(r_a; R)$  that needs to be considered is the spherically symmetric part  $F_{env}^{(0)}(r_a; R)$  which, for a given  $R$ , depends on just the distance  $r_a$  of the electron from the anion nucleus [7].

It is useful to consider that  $F_{env}(r_a; R)$  and hence  $F_{env}^{(0)}(r_a; R)$  is composed of two contributions [7, 8, 30], the first being that which would be generated if all the other ions  $b$  ( $\neq a$ ) were replaced by point charges of size  $q_b$ . The second contribution is the sum of all the additional effects generated by both the finite spatial extensions of the electronic charge distributions of these other ions, and by purely quantum mechanical effects originating from the Pauli principle. Since, firstly, all the ions are spherically symmetric and, secondly, the quantum mechanical effects originate from the overlap of orbitals belonging to different ions, the second contribution to  $F_{env}(r_a; R)$  and hence  $F_{env}^{(0)}(r_a; R)$  is zero in those spatial regions where the electron density of all ions  $b$  ( $\neq a$ ) is negligible. The point lattice

contribution to  $F_{env}^{(0)}(r_a; R)$  is a constant and stabilizing potential equal to  $-\phi_{env}/R$  from  $r_a = 0$  to  $r_a = R$ , after which it rises towards zero for larger  $r_a$  and then passes through several smaller oscillations associated with other distances between the anion  $a$  and other ions. For a  $\text{CaF}_2$  crystal the positive constant  $\phi_{env}$  equals 1.762 67 [31], the Madelung constant of the CsCl lattice. Thus the point lattice contribution to  $F_{env}^{(0)}(r_a; R)$  is a stabilizing well acting to contract the anion and reduce its polarizability [7, 8, 16–18, 30]. The second contribution to  $F_{env}^{(0)}(r_a; R)$  constitutes a repulsion in spatial regions where other ions have non-negligible electron densities, and therefore acts to reinforce the contractions and polarizability reductions generated by the point-lattice term. There are many models for  $F_{env}^{(0)}(r_a; R)$ ; both the earlier, reviewed in [8], and the later refinements have been extensively tested [10]. Any physically reasonable model for  $F_{env}^{(0)}(r_a; R)$  must both reduce to that generated by a point-charge lattice where the electron density of other ions is negligible and include, in regions of non-negligible electron density from other ions, a repulsion dependent on both the cation and crystal geometry.

The simplest model for  $F_{env}^{(0)}(r_a; R)$ , that is physically reasonable in the sense just outlined, is the radius variable Madelung Watson (RVMW) function [7] ( $F_{RVMW}(r_a; R)$ ), defined as

$$F_{RVMW}(r_a; R) = -k_{env}/R_W \quad \text{for } r_a \leq R_W \quad (8a)$$

$$F_{RVMW}(r_a; R) = -k_{env}/r_a \quad \text{for } r_a \geq R_W \quad (8b)$$

with

$$k_{env}/R_W = \phi_{env}/R. \quad (9)$$

The definition (9) for  $k_{env}$  causes  $F_{RVMW}(r_a; R)$  to correctly reduce, for  $r_a \leq R_W$ , to the spherically symmetric part of the potential generated by the point lattice with closest cation–anion separation  $R$ . Thus the parameter  $R_W$  is to be interpreted as the largest distance  $r_a$  from the anion nucleus at which the electron density arising from the first shell of cation neighbours is still negligible. The form (8b) is introduced for  $r_a \geq R_W$ , because, in spatial regions of non-negligible cation electron density, an anion electron will experience a repulsive potential acting to reduce the constant stabilization arising from the point lattice. In the RVMW model,  $R_W$  is taken to be  $R - R_C$  where the constant  $R_C$  is either the cation radius or some closely related combination of cation properties [7]. Here  $R_C$  will be taken to equal the ionic radius (0.99 Å) of  $\text{Ca}^{++}$  [32], thus having the value of 1.87 au used previously in RVMW model computations for CaO. The RVMW model satisfactorily described the five halides examined [7], as well as performing not unreasonably for MgO, but was subsequently shown to be inadequate for CaO [10]. Any inadequacies of the model must arise from the particular mathematical form assumed for the repulsive potential arising in spatial regions of non-negligible cation electron density. There is no evidence for the correctness of the form assumed in the RVMW model which also does not allow for the possibility that the full function  $F_{env}^{(0)}(r_a; R)$  might become positive in regions of high cation electron density.

The ‘optimized with eigenvalues Madelung Fermi smoothed’ (OEMFS) and ‘optimized with density Madelung Fermi smoothed’ (ODMFS) models for  $F_{env}^{(0)}(r_a; R)$  were the two most satisfactory descriptions that emerged from a thorough examination [10] of ways for representing the repulsive contributions to the environmental potential arising in regions of non-negligible cation electron density. For the two oxides studied, MgO and CaO, these two models were found to yield essentially identical predictions. It is straightforward to

construct the point lattice contribution to  $F_{env}^{(0)}(r_a; R)$  exactly, even though the gradient of this function with respect to  $r_a$  is discontinuous at  $r_a$ -values corresponding to the positions of other ions. However, it was found [10] that these discontinuities introduced numerical difficulties into the computation of the in-crystal anion wavefunctions. This result coupled with the observation that the total  $F_{env}^{(0)}(r_a; R)$  will have large overlap contributions at those  $r_a$  values where the gradient of the point lattice term is discontinuous shows that it is unnecessary to model these discontinuities. In both the OEMFS and ODMFS models the point lattice contribution to  $F_{env}^{(0)}(r_a; R)$  is therefore represented by the Madelung Fermi smoothed function  $F_{MFS}(r_a; R)$ , defined by

$$F_{MFS}(r_a; R) = -(\phi_{env}/R)\{1 + \exp[g(r_a - r_0)]\}^{-1}. \quad (10)$$

The parameter  $r_0$  is chosen such that (10) exactly reproduces the point lattice potential where the latter equals  $-\phi_{env}/(2R)$  whilst  $g$  is fixed by requiring that (10) reproduces the point lattice result half-way between  $R$  and  $r_0$ , that is at  $r_a = R + (r_0 - R)/2$ . For the fluorite lattice, the resulting values of  $r_0 = 1.23806R$  and  $g = 16.51508/R$  ensure that (10) accurately reproduces the point lattice result  $(-\phi_{env}/R)$  at small  $r_a$  where cation electron density is negligible. The ODMFS model [10] results from adding to  $F_{env}^{(0)}(r_a; R)$  the representation that consideration of the density functional theory of electronic structure suggested for the overlap contribution to  $F_{MFS}(r_a; R)$ . Thus the ODMFS environmental potential  $F_{ODMFS}(r_a; R)$  has the form

$$F_{ODMFS}(r_a; R) = F_{MFS}(r_a; R) + A \sum_b \{[\rho_{Tb}(r_b)]^k\}^{(0)} \quad (11)$$

where the sum over  $b$  is over the eight cations adjacent to anion  $a$  and  $\rho_{Tb}(r_b)$  is the total electron density of ion  $b$ , the position  $r_b$  being measured relative to the  $b$  nucleus. The superscript (0) denotes the spherically symmetric term in the series which results when  $[\rho_{Tb}(r_b)]^k$  is expanded about the nucleus of anion  $a$  into a series in which the angular dependence about the  $a$  nucleus is described using spherical harmonics centred on this nucleus. The density  $\rho_{Tb}(r_b)$  of cation  $b$  is spherically symmetric with respect to the  $b$  nucleus and was evaluated using the Dirac-Fock wavefunction for a free  $\text{Ca}^{++}$  ion. The constants  $A$  and  $k$  in (11) would have the values 4.785 and  $2/3$  respectively, if the density functional theory arguments used to suggest (11) were exact. In practice these constants are determined at each  $R$  through the variational criterion of maximizing the magnitude ( $|U_L^0(R)|$ ) of the crystal cohesion (2) predicted with the neglect of electron correlation. Although  $A$  and  $k$  could, in principle, be determined by maximizing the cohesion predicted with the inclusion of the electron correlation contributions, this procedure is highly dubious if these are not calculated exactly from a trial wavefunction but are evaluated approximately using density functional theory. The representation of the overlap contribution in (11) clearly vanishes where the cation electron density is negligible and suggests that  $F_{env}^{(0)}(r_a; R)$  rises much more rapidly from  $-\phi_{env}/R$  than the RVMW function (8) as  $r_a$  increases from the small values where only the point lattice term is appreciable. The ODMFS model also encompasses the possibility that  $F_{env}^{(0)}(r_a; R)$  becomes positive in regions of high cation electron density because a value greater than zero will result if the variational optimization of  $A$  and  $k$  produces a sufficiently large value for  $A$ .

This paper investigates the ability of the RVMW and ODMFS models to describe the in-crystal modifications of the fluoride ion in  $\text{CaF}_2$ . Although there are many other models for  $F_{env}^{(0)}(r_a; R)$ , these have not been investigated in detail for  $\text{CaF}_2$  because the results and discussion presented in [10] show that either they have serious theoretical deficiencies or that the results are not expected to be significantly different from those of either the RVMW or ODMFS approaches.



### 2.3. The electron correlation contribution to the fluoride ion rearrangement energy

Density functional theory would appear to provide the only currently feasible method for computing the correlation energy of an anion in a crystal. A comparison [10] of the ability of the many different variants of density functional theory to predict the contributions of electron correlation to both total atom energies and ionization potentials showed that no one variant was clearly preferable and that the performance of all of them was no better than mediocre. There is thus no reason for preferring technically more complex approaches over the commonly used local density approximation in which the spatial variation of the electron density is considered to be sufficiently slow that the correlation energy functional  $F^{corr}[\rho(\mathbf{r})]$  at position  $\mathbf{r}$  can be taken to equal that of a non-relativistic infinite electron gas having a uniform density equal to that of the system at position  $\mathbf{r}$ .

Standard application of the local density approximation incorrectly predicts a one-electron atom to have a non-zero correlation energy and similarly introduces spurious self-correlation terms into the calculation of the correlation energy of any multi-electron system. This objectionable feature was circumvented here by using the Cowan modification [33] which yields a prediction  $E_a^{Ccorr}$  for the total correlation energy of ion  $a$  gas

$$E_a^{Ccorr} = \sum_i \int \rho_i(\mathbf{r}) F^{corr}[\rho_{Ta}(\mathbf{r}) - \rho_i(\mathbf{r})] d\mathbf{r}. \quad (12)$$

The total electron density  $\rho_{Ta}(\mathbf{r})$  of ion  $a$  is evaluated in the Dirac-Fock approximation as a sum of contributions  $\rho_i(\mathbf{r})$  from the individual orbitals with the sum over  $i$  being over all the occupied orbitals each containing one electron. The local density functional used was that introduced by Gordon and Kim [27] and given by

$$F^{corr}[\rho(\mathbf{r})] = -0.438\beta^{-1} + 1.325\beta^{-3/2} - 1.47\beta^{-2} - 0.4\beta^{-5/2} \quad \beta \geq 0 \quad (13a)$$

$$F^{corr}[\rho(\mathbf{r})] = -0.06156 + 0.01898 \ln \beta \quad 0.7 \leq \beta \leq 10 \quad (13b)$$

$$F^{corr}[\rho(\mathbf{r})] = 0.0311 \ln \beta - 0.048 + 0.009\beta \ln \beta - 0.01\beta \quad \beta \leq 0.7 \quad (13c)$$

with

$$\beta = \{3/[4\pi\rho(\mathbf{r})]\}^{1/3}. \quad (14)$$

The prediction derived using (12)–(14) for the total correlation energy of an atom or ion is invariably too large by a factor of roughly two [10]. The required contribution  $E_{re}^{corr}(R)$  of electron correlation to the fluoride ion rearrangement energy was therefore evaluated by introducing a correction factor  $B_{corr}$  into the prediction derived from (12) so that one has

$$E_{re}^{corr}(R) = B_{corr} \left[ E_A^{Ccorr}(R) - E_{Af}^{Ccorr} \right]. \quad (15)$$

Here  $E_A^{Ccorr}(R)$  is for the fluoride ion in the crystal with closest cation-anion separation  $R$  the prediction derived for the correlation energy by using in (12) the in-crystal Dirac-Fock wavefunction computed with the inclusion of the environmental potential  $F_{env}^{(0)}(r_a; R)$  for the considered  $R$  value. The quantity  $E_{Af}^{Ccorr}$  in (15) is the prediction of (12) for the correlation energy of a free  $F^-$  ion. The correction factor  $B_{corr}$  is derived as the exact correlation energy of the free fluoride ion divided by the prediction  $E_{Af}^{Ccorr}$  of this energy afforded by (12). Thus  $B_{corr}$  is the factor by which the prediction of (12) must be multiplied if the true result is to be reproduced. Since the exact correlation energy of a free fluoride ion is

$-0.398$  au [34] compared with the corresponding  $E_{Af}^{C_{corr}}$  result of  $-0.69093$  au,  $B_{corr}$  has the value 0.576.

This method of deriving  $B_{corr}$  is less complex than that used [10] to obtain the corresponding correction factors for in-crystal  $O^{2-}$  ions. For a doubly charged anion the rearrangement energy, being defined as the energy required to convert a free electron and a free singly charged anion into the in-crystal doubly charged anion, is both much larger and more strongly dependent on the crystal geometry than  $E_{re}(R)$  defined for a halide ion by (3) and (5). Consequently, it had to be recognized that it would have been inappropriate to derive the correction factor from data relating entirely to the free ion and that so far as this correction factor was concerned the behaviour of this in-crystal anion resembled that of an isoelectronic species having a greater nuclear charge. Such complications do not need to be considered for a halide ion for which the rearrangement process just involves a compression of the ion relative to its free state corresponding to a much smaller energy change.

## 2.4. The dispersion energy

**2.4.1. Basic formalism.** The dispersive attraction between an ion  $a$  and a second ion  $b$  is that part of the inter-ionic correlation energy that does not involve exchange of electrons between the ions [26]. This attraction does not therefore originate from the overlap of the ion wavefunctions and is non-zero even for inter-ionic separations  $x_{ab}R$  which are sufficiently large that this overlap is negligible. For these large distances, the dispersive attraction can be expanded into the familiar multipole series whose first two terms are the instantaneous dipole-induced dipole interaction  $-C_6(ab)(x_{ab}R)^{-6}$  and the instantaneous dipole-induced quadrupole interaction  $-C_8(ab)(x_{ab}R)^{-8}$  [35, 36]. For inter-ionic separations sufficiently small that the overlap between the ion wavefunctions is not negligible each term  $-C_n(ab)(x_{ab}R)^{-n}$  in the multipole series has to be multiplied by a damping function  $\chi_n^{ab}(x_{ab}R)$  which reduces the magnitude of the undamped interaction [26, 35, 37, 38]. For distances  $x_{ab}R$  for which this overlap is appreciable, dispersion terms having high  $n$  values are very small because the  $\chi_n^{ab}(x_{ab}R)$  decrease rapidly with increasing  $n$ . Since such terms are also unimportant at large  $x_{ab}R$  due to their  $(x_{ab}R)^{-n}$  dependence, even though the damping functions are then close to unity, only the dipole-dipole and dipole-quadrupole dispersive attractions need to be retained in the evaluation of the total crystal dispersion energy  $U_{disp}(R)$ . After retaining only these terms and noting that the only damping functions significantly less than unity are those for the closest cation-anion, anion-anion and cation-cation pairs,  $U_{disp}(R)$  reduces to expression (2.22) of [7]. Hence the evaluation of this energy requires knowledge of only the damping functions and dipole-dipole  $C_6(ab)$  and dipole-quadrupole  $C_8(ab)$  dispersion coefficients.

The function  $\chi_n^{aa}(x_{aa}R)$  damping that portion varying as  $(x_{aa}R)^{-n}$  of the dispersive attraction between two like species depends, in addition to the inter-nuclear separation, on just a single dispersion damping parameter  $d_a$  for the species  $a$ . For two unlike species, the damping function  $\chi_n^{ab}(x_{ab}R)$  depends on the same two parameters  $d_a$  and  $d_b$  that control the damping of the interactions between the two like species. The function  $\chi_6^{aa}(x_{aa}R)$  damping the dipole-dipole dispersive attraction between two like species has been derived by Jacobi and Csanak [38] whose general formalism was used subsequently ([7] and erratum [39]) to derive both the function  $\chi_6^{ab}(x_{ab}R)$  damping the corresponding attraction between two unlike species as well as the functions  $\chi_8^{aa}(x_{aa}R)$  and  $\chi_8^{ab}(x_{ab}R)$  damping the dipole-quadrupole dispersive attractions. Although in general  $d_a$  and  $d_b$  depend on  $n$ , it has been shown [7] that for the interaction of systems having  $p^6$  outermost electronic configurations, the damping parameters are the same for both the  $n = 6$  and  $n = 8$  terms. The damping

parameter  $d_a$  is the sum of a contribution from the electronic ground state of species  $a$  plus one from the lowest-energy excited state having the correct symmetry to contribute to the sum over states perturbation theory description of the corresponding dispersion energy [40,41]. For an ion in which the potential energy experienced by an electron varies as  $r_a^{-1}$  at both intermediate and large distances  $r_a$  from the nucleus,  $d_a$  is evaluated from the eigenvalues of the most loosely bound orbitals in the ground and relevant lowest excited state [40,41]. Since an electron both in a free ion and in the RVMW description of an anion experiences such a potential energy, the  $\text{Ca}^{++}$  damping parameter  $d_C$  as well as that  $d_A$  for the  $\text{F}^-$  ion in the RVMW model were derived from the orbital eigenvalues as detailed elsewhere [7,10]. The  $d_C$  value reported in table 1 has already been derived [10] whilst  $d_A$  in the RVMW model is found to be 1.616. Since an anion electron in the ODMFS model does not experience a potential energy varying as  $r_a^{-1}$  except at distances  $r_a$  from the nucleus at which the anion electron density is negligible,  $d_A$  in the ODMFS model cannot be deduced from the orbital eigenvalues. Consequently the ODMFS anion  $d_A$  value reported in table 1 had to be deduced [41] from the decay of the outermost orbitals at intermediate distances from the nucleus using the method described elsewhere [10].

**Table 1.** The dipole-dipole dispersion coefficients, dispersion damping parameters and ancillary data for  $\text{CaF}_2$  (au)<sup>(1)</sup>.

$\alpha_C$	$\alpha_A$	$P_C$	$P_A$	$C_6(CC)$	$C_6(AA)$	$C_b(CA)$	$d_C$	$d_A$
3.193	6.843	6.106	4.455	10.574	28.337	16.700	3.240	2.755

<sup>(1)</sup> For species  $a$  (=cation  $C$  or anion  $A$ ), best polarizability ( $\alpha_a$ ), electron number ( $P_a$ ), dipole-dipole dispersion coefficient  $C_6(ab)$  derived from (16) using tabulated  $\alpha_a$  and  $P_a$  and dispersion damping parameter  $d_a$  derived from free cation and ODMFS anion wavefunctions as described in text.

It is now well established [7,20] that  $C_6(ab)$  coefficients for in-crystal ions are most reliably evaluated from the dipole polarizabilities  $\alpha_a$  and  $\alpha_b$  of the ions by using the Slater-Kirkwood formula [42]

$$C_6(ab) = (3/2)\alpha_a\alpha_b / [(\alpha_a/P_a)^{1/2} + (\alpha_b/P_b)^{1/2}] \quad (16)$$

provided that the electron number  $P_a$  for each ion  $a$  is chosen such that (16) exactly reproduces the  $C_6(ii)$  coefficient for the inert gas  $i$  isoelectronic with ion  $a$  from the exact polarizability  $\alpha_i$  of that gas. The electron numbers required for  $\text{Ca}^{++}$  and  $\text{F}^-$  have already been derived [7] and are presented in table 1. The  $\text{Ca}^{++}$  polarizability ( $\alpha_C$ ) presented in table 1 is the prediction [18] of an accurate *ab initio* quantum chemistry computation which included the effects arising from electron correlation. The total molar polarizability of  $\text{CaF}_2$  is deduced to be 16.879 au by substituting the experimental value (2.038 66 [43]) of the high-frequency dielectric constant and molar volume deduced from the room-temperature cell side of 5.462 Å into the Clausius-Mossotti relation [12]. The fluoride ion polarizability ( $\alpha_A$ ) presented in table 1 was derived by subtracting  $\alpha_C$  from the molar polarizability equal to  $\alpha_C + 2\alpha_A$ . The  $C_6(ab)$  coefficients calculated from these polarizabilities and electron numbers using (16) and assembled in table 1 are expected to be in error by 5% at most [7,20]. The use of both the experimental molar polarizability and cation polarizability predicted with the inclusion of electron correlation ensures that the correlation contributions are included in the  $C_6(ab)$  values of table 1.

2.4.2. *The dipole–quadrupole dispersion coefficients.* The dipole–quadrupole dispersion coefficient  $C_8(ab)$  is given by the sum

$$C_8(ab) = C_8^{DQ}(ab) + C_8^{QD}(ab) \quad (17)$$

where the contribution  $C_8^{DQ}(ab)$  originates from the quadrupole induced on ion  $b$  by a dipole instantaneously present on ion  $a$ . The quantity  $C_8^{QD}(ab)$  similarly governs the attraction resulting from the interaction between a quadrupole induced by ion  $a$  by a dipole instantaneously present on ion  $b$ . It has been shown [7, 21] that, in the absence of *ab initio* quantum chemistry computations, the currently most reliable method of deriving  $C_8(ab)$  coefficients is to use the Starkschall–Gordon formula [44].

The Starkschall–Gordon formula, an approximation derived by making a clever choice for the average energy in the sum over perturbation theory expression for the dispersion energy, relates  $C_8^{QD}(ab)$  to the corresponding dipole–dipole dispersion coefficient  $C_6(ab)$  through

$$C_8^{DQ}(ab) = (3/2)C_6(ab)\langle r^4 \rangle_b / \langle r^2 \rangle_b \quad (18a)$$

$$C_8^{QD}(ab) = (3/2)C_6(ab)\langle r^4 \rangle_a / \langle r^2 \rangle_a. \quad (18b)$$

Here  $\langle r^n \rangle_a$  is, for all the electrons belonging to ion  $a$ , the expectation value of the  $n$ th power of their distance from the nucleus of ion  $a$  with  $\langle r^n \rangle_b$  being the corresponding quantity for ion  $b$ . This presentation implies that all the electrons belonging to a given ion should be included in the evaluation of  $\langle r^4 \rangle_a$  and  $\langle r^2 \rangle_a$ . However since the interactions responsible for the dispersive attractions have only negligible contributions from the inner electrons, it would be illogical to include their contribution in the evaluation of the expectation values in (18). For both pairs of inert gases and pairs of isoelectronic cations and halide ions in ionic solids it was shown [7, 21] that the inclusion of all the electrons in the evaluation of the  $\langle r^n \rangle_b$  significantly degraded the quality of the predictions and that consideration of only the six outermost p electrons yielded significantly more accurate results. Hence, only these six outermost electrons will be considered in the present applications of (18).

Despite the demonstrated utility of the Starkschall–Gordon formula in contrast to those of Margenau [45] and Narayan [46] which often yield predictions in error by several hundred per cent [7], there is good evidence [21, 47] that (18) usually underestimates dipole–quadrupole dispersion coefficients for pairs of species each of which has a  $p^6$  outermost electronic configuration by at least 10–15%. This underestimation frequently exceeds 20%, as is the case for the ion pairs in MgO where the smallest error is some 23% [47], but has not so far been known to be greater than the 30% underestimation found [21] for  $C_8(\text{Na}^+ \dots \text{Na}^+)$ . It has been pointed out [8, 47] that, if the in-crystal environment caused the same fractional modification in the  $C_8(AA)$  coefficient as that which it induces in the  $C_6(AA)$  coefficient, then a better estimate  $C_8^{MA}(AA)$  of  $C_8(AA)$  in the salt with cation M could be deduced by using

$$C_8^{MA}(AA) = C_8^{NA}(AA) \left[ C_6^{MA}(AA) / C_6^{NA}(AA) \right] \quad (19)$$

if an accurate value ( $C_8^{NA}(AA)$ ) was known in the salt with cation N. The present attraction of this relation is that a value for  $C_8(\text{F}^- \dots \text{F}^-)$  in LiF has been computed *ab initio* [21] using coupled Hartree–Fock (CHF) theory. However, the suggestion (19) has been shown to be too superficial by the fact that it predicts unreasonably large values for  $C_8(\text{O}^{2-} \dots \text{O}^{2-})$

in CaO, ThO<sub>2</sub> and UO<sub>2</sub> [47] from the accurately known value of  $C_8(O^{-2}..O^{-2})$  in MgO. Although the Starkschall–Gordon formula supports the idea that an environmentally induced increase of  $C_6(AA)$  will also enhance  $C_8(AA)$ , this relation suggests that there are also other factors, which, in the Starkschall–Gordon approximation, are manifested through the ratio of the ground state expectation values. This shows that one way of rectifying (19) would be to introduce on the right-hand side the additional factor  $\langle r^4 \rangle_{MA} \langle r^2 \rangle_{NA} / (\langle r^4 \rangle_{NA} \langle r^2 \rangle_{MA})$ . However, such a procedure is equivalent to introducing scaling factors  $K^{DQ}(ab)$  and  $K^{QD}(ab)$  into the Starkschall–Gordon formula to produce the relations

$$C_8^{DQ}(ab) = K^{DQ}(ab)(3/2)C_6(ab)\langle r^4 \rangle_b / \langle r^2 \rangle_b \quad (20a)$$

$$C_8^{QD}(ab) = K^{QD}(ab)(3/2)C_6(ab)\langle r^4 \rangle_a / \langle r^2 \rangle_a \quad (20b)$$

The relations (20) will only be useful, yielding predictions more accurate than those of the unscaled relations (18), if the scaling factors  $K^{DQ}(ab)$  and  $K^{QD}(ab)$  are suitably determined from trustworthy data for closely related systems.

Table 2. Ancillary data for the derivation of Starkschall–Gordon predictions of dipole–quadrupole dispersion coefficient (au)<sup>(1)</sup>.

	$\langle r^2 \rangle_C$	$\langle r^4 \rangle_C$	$\langle r^2 \rangle_A$	$\langle r^4 \rangle_A$	$C_6^{CHF}(CC)$	$C_6^{CHF}(AA)$	$C_6^{CHF}(CA)$
LiF	0.890	1.052	11.613	57.119	0.077	19.14	1.066
NaCl	4.893	9.462	27.766	243.986	1.514	159.5	12.43

<sup>(1)</sup> Radial expectation values computed using free cation and OEMFS anion Dirac–Fock wavefunctions computed (this work) for  $R = 3.7965$  au (LiF) and for  $R = 5.239$  au (NaCl) the experimental  $R_e$  values used in [20] and [21]; coupled Hartree–Fock predictions  $C_6^{CHF}(ab)$  of dipole–dipole dispersion coefficients from [21].

Table 3. Comparison of coupled Hartree–Fock predictions for dipole–quadrupole dispersion coefficients with corresponding results from the Starkschall–Gordon formula (au)<sup>(1)</sup>.

	$C_8(CC)$		$C_8(AA)$		$C_8^{DQ}(CA)$		$C_8^{QD}(CA)$	
	CHF	SG	CHF	SG	CHF	SG	CHF	SG
LiF	0.251	0.273	352.8	282.423	9.749	7.865	1.665	1.890
NaCl	12.32	8.78	5404.0	4204.7	221.579	163.838	50.252	36.055

<sup>(1)</sup> Starkschall–Gordon (SG) predictions calculated (this work) using in (18) the radial expectation values and (CHF)  $C_6(ab)$  coefficients of table 2; CHF predictions for dipole–quadrupole dispersion coefficients from [21].

Data suitable for determining the scaling factors in (20) are provided by the *ab initio* CHF computations of  $C_8(ab)$  coefficients for the ion pairs in LiF, NaCl [21] and MgO [47] along with the CHF results for the corresponding  $C_6(ab)$  coefficients. The CHF results [21] for the  $C_6(ab)$  coefficients in LiF and NaCl are presented in table 2 along with the expectation values computed from free cation and in-crystal anion OEMFS Dirac–Fock wavefunctions, calculated here for the same equilibrium  $R$  values as used in the *ab initio* computations (see note to table 2). The  $C_8(ab)$  coefficients predicted from this data by using the Starkschall–Gordon formula (18) without scaling factors are reported in table 3 along with the corresponding *ab initio* CHF  $C_8(ab)$  values. Division of each CHF result by the corresponding Starkschall–Gordon prediction yields the scaling factor

$K^{DQ}(ab)$  or  $K^{QD}(ab)$  for the considered ion pair. The  $C_6(ab)$  and  $C_8(ab)$  coefficients used to determine the scaling factors should be fully comparable, as is the case if the CHF predictions are used for both coefficients. The subsequent use of these scaling factors to derive  $C_8(ab)$  coefficients, using the most accurate values currently available for the  $C_6(ab)$  coefficients as input to (20), carries the implicit assumption that electron correlation makes the same fractional contribution to all the quantities entering (20). However, since for in-crystal ions the contributions of electron correlation to these dispersion coefficients are expected to be not greater than some 10–15%, it is unlikely that any significant errors will be introduced by using this currently unavoidable assumption. Both the data in table 3 and the corresponding results for MgO reported in table 1 of [47] show that for the interaction of two ions each having a  $p^6$  outermost electronic configuration, the Starkschall–Gordon formula underestimates  $C_8(ab)$  which corresponds to scaling factors greater than unity. For LiF, the factor  $K^{DQ}(ab)$  corresponding to the attraction involving an instantaneous quadrupole on the fluoride, is also greater than unity. This scaling factor is only less than unity, corresponding to overestimation of  $C_8(ab)$  by the Starkschall–Gordon formula, for interactions in which the instantaneous quadrupole is present on the species of  $s^2$  electronic configuration.

It is clear that the scaling factor of 1.249 for the  $F^-F^-$  interaction in LiF should be used to calculate  $C_8(AA)$  in  $CaF_2$ . This factor is greater than that of 1.097 which would be deduced if the *ab initio* CHF  $C_8(AA)$  were to be compared with the prediction of 321.5 derived [21] from the Starkschall–Gordon formula with the expectation values calculated using in-crystal fluoride ion wavefunctions computed using the RVMW model for the crystalline environment. The OEMFS  $F^-$  wavefunction is considerably more compressed than its RVMW counterpart. This causes the former model to predict a smaller ratio  $\langle r^4 \rangle_A / \langle r^2 \rangle_A$  because a more repulsive environmental potential will produce a greater fractional reduction in  $\langle r^4 \rangle_A$  than in  $\langle r^2 \rangle_A$  since the former expectation value will have larger contributions from the environmentally sensitive outer spatial regions. For  $CaF_2$ ,  $K^{DQ}(CA)$  is taken to have the value of 1.240 equal to that (table 3) for LiF because both these interactions involve an instantaneous dipole on a cation interacting with an instantaneous quadrupole on a fluoride ion. For  $K^{QD}(CA)$  for  $CaF_2$ , NaCl provides a much better model system than LiF because in this latter the instantaneous quadrupole is carried by a species of  $s^2$  and not  $p^6$  outermost electronic configuration. Hence the required  $K^{QD}(CA)$  is taken to be 1.394. The scaling factor used to determine  $C_8(Ca^{++}..Ca^{++})$  will be taken to have the value of 1.418 deduced by comparing the CHF prediction of 3.153 au for  $C_8(Mg^{++}..Mg^{++})$  with its Starkschall–Gordon counterpart of 2.223 au [47]. This value for the scaling factor is very similar to that of 1.403 deduced for  $C_8(Na^+..Na^+)$  from the results in table 3 of [21].

**Table 4.** Dipole–quadrupole dispersion coefficients and radial expectation values for  $CaF_2$  (au) predicted using the OEMFS description for the in-crystal fluoride ion<sup>(1)</sup>.

$\langle r^2 \rangle_C$	$\langle r^4 \rangle_C$	$\langle r^2 \rangle_A$	$\langle r^4 \rangle_A$	$C_8(CC)$	$C_8(AA)$	$C_8^{DQ}(CA)$	$C_8^{QD}(CA)$
11.201	35.850	11.255	50.657	144.005	477.894	139.805	111.764

<sup>(1)</sup> Dipole–quadrupole dispersion coefficients calculated from (20) using the expectation values of this table and dipole–dipole dispersion coefficients of table 1. i.e. scaling the predictions of the Starkschall–Gordon formula (18) with the scaling factors of 1.418 ( $C_8(CC)$ ), 1.249 ( $C_8(AA)$ ), 1.240 ( $C_8^{DQ}(CA)$ ) and 1.394 ( $C_8^{QD}(CA)$ ) derived as described in the text.

The expectation values needed to calculate the dipole–quadrupole dispersion coefficients for  $CaF_2$  through (20) are presented in table 4. For the  $Ca^{++}$  ion, these expectation values

were evaluated from the same free-ion Dirac-Fock wavefunction as used to compute the short-range two-body interactions. The corresponding expectation values for the in-crystal anion were evaluated from the fluoride ion ODMFS wavefunction found to be optimal for  $R = 4.5$  au, very close to the experimental value of  $R_e$ . Since the expectation values predicted from the RVMW and ODMFS fluoride wavefunctions are different, these two models yield different predictions for those  $C_8(ab)$  coefficients involving the anion. The  $C_8(ab)$  coefficients resulting from the use in (20) of these expectation values, the scaling factors just presented and the currently most accurate values (table 1) for the  $C_6(ab)$  coefficients are also presented in table 4.

### 3. Results and discussion

For the closest cation-anion separations  $R$  listed in table 5, the cohesive energy function  $U_L(R)$  has been computed for  $\text{CaF}_2$  by using both the RVMW and the ODMFS models for describing the in-crystal modifications of the fluoride ion. The fluoride ion rearrangement energy and non-negligible short-range two-body interactions predicted by the ODMFS method both without and with the inclusion of the contributions from electron correlation are reported in this table. Numerical values for the correlation contributions can be obtained by merely subtracting the uncorrelated predictions in this table for the corresponding total results.

Table 5. The ODMFS model rearrangement energies and short-range two-body interactions (au).

$R$	$A$	$q$	$E_{re}^0(R)$	$E_{re}(R)$	$V_{sCA}^0(R)$	$V_{sCA}(R)$	$V_{sAA}^0(R')$	$V_{sAA}(R')$
3.5	4.83	1.59	0.151 671	0.142 901	0.092 233	0.089 214	0.014 733	0.013 575
3.75	5.70	1.50	0.098 051	0.091 058	0.056 601	0.054 300	0.009 048	0.008 079
4.0	6.40	1.36	0.061 255	0.055 688	0.035 842	0.034 080	0.005 746	0.004 923
4.25	6.16	1.17	0.034 552	0.030 236	0.023 554	0.022 182	0.003 785	0.003 054
4.5	5.60	1.06	0.019 855	0.016 570	0.015 894	0.014 822	0.002 360	0.001 715
4.75	5.20	0.988	0.011 899	0.009 388	0.010 548	0.009 714	0.001 420	0.000 864
5.0	4.94	0.968	0.007 405	0.005 505	0.007 003	0.006 356	0.000 826	0.000 354
5.5	4.60	1.01	0.003 042	0.001 988	0.003 087	0.002 699	0.000 258	-0.000 073
6.0	3.90	1.20	0.001 381	0.000 819	0.001 405	0.001 175	0.000 072	-0.000 153

$$R' = [2/(\sqrt{3})]R$$

$R$	$V_{sCC}^0(R'')$	$V_{sCC}(R'')$	$R$	$V_{sCC}^0(R'')$	$V_{sCC}(R'')$
3.5	0.000 300	0.000 214	4.5	0.000 011	0.000 009
3.75	0.000 093	0.000 053	4.75	0.000 009	0.000 008
4.0	0.000 033	0.000 015	5.0	0.000 005	0.000 005
4.25	0.000 015	0.000 008			

$R'' = 2\sqrt{(2/3)}R$ , all  $V_{sCC}^0(R'')$  and  $V_{sCC}^{corr}(R'')$  for  $R \geq 5.5$  are less than  $10^{-7}$ .

The anion orbital properties, rearrangement energies and crystal cohesions predicted using the RVMW and ODMFS methods without the inclusion of electron correlation are compared in table 6 both for an  $R$  (4.5 au) close to the experimental  $R_e$  value of 4.448 au [48] and for a significantly smaller  $R$  value. The ODMFS method predicts the in-crystal fluoride ion to be considerably more contracted than does the RVMW model as shown by the smaller mean radius ( $\langle r \rangle_{2p}$ ) and mean square radius ( $\langle r^2 \rangle_{2p}$ ) of the anion 2p orbital yielded by the former approach. Comparison of these expectation values with those of

Table 6. The influence of the environmental model on the fluoride ion properties and crystal binding<sup>(1)</sup>.

	$R = 4.5$				$R = 4.0$			
	$\langle r \rangle_{2p}$	$\langle r^2 \rangle_{2p}$	$E_{re}^0(R)$	$U_L^0(R)$	$\langle r \rangle_{2p}$	$\langle r^2 \rangle_{2p}$	$E_{re}^0(R)$	$U_L^0(R)$
RVMW	1.223	2.030	9.5	-2431	1.204	1.944	23.4	-2038
ODMFS	1.193	1.876	52.1	-2464	1.157	1.722	160.8	-2142

<sup>(1)</sup> Mean radius  $\langle r \rangle_{2p}$  and mean square radius  $\langle r^2 \rangle_{2p}$  in au are averages with weights of 1/3 and 2/3 over those for the relativistic orbitals  $2p_{1/2}$  and  $2p_{3/2}$  having  $j = 1/2$  and  $j = 3/2$  respectively. Energies  $E_{re}^0(R)$  and  $U_L^0(R)$  in kJ mol<sup>-1</sup>.

1.256 ( $\langle r \rangle_{2p}$ ) and 2.211 ( $\langle r^2 \rangle_{2p}$ ) for a free fluoride ion shows that the ODMFS method predicts reductions in these orbital properties which are roughly double those resulting from the RVMW computations. The rearrangement energies needed to generate the greater compressions in the ODMFS model are five times larger than the corresponding RVMW predictions. However, the reduced overlap of the cation orbitals with the former more compressed anion wavefunctions causes the ODMFS values of 41.7 kJ mol<sup>-1</sup> and 94.1 kJ mol<sup>-1</sup> for the short-range repulsions  $V_{sCA}^0(4.5)$  and  $V_{sCA}^0(4.0)$  to be significantly less than the corresponding RVMW results of 57.0 kJ mol<sup>-1</sup> and 138.6 kJ mol<sup>-1</sup>. The reduction of these repulsions in the ODMFS method, when compared with those of the RVMW model, more than offsets the greater  $E_{re}^0(R)$  values in the former approach with the consequence that the ODMFS method predicts greater crystal cohesions as manifested by more negative values of  $U_L^0(R)$ . The variational energy criterion thus shows that the ODMFS method is preferable to the RVMW model with the former providing a more realistic description of the in-crystal anion.

For the near-equilibrium  $R$  value of 4.5 au, the increase of some 33 kJ mol<sup>-1</sup> in the crystal cohesion predicted on passing from the RVMW to the ODMFS model is identical to that found [10] for MgO at  $R = 3.981$  au, near  $R_e$ , although less than that of 97 kJ mol<sup>-1</sup> at 4.544 au for CaO near its equilibrium  $R$  value. The experimental lattice energy of CaF<sub>2</sub> of 2630 kJ mol<sup>-1</sup> [49] is slightly less than that of 3038 kJ mol<sup>-1</sup> [50] for MgO, so that the fractional increase in the predicted cohesion is slightly greater for CaF<sub>2</sub>. Comparison of the CaF<sub>2</sub> RVMW and ODMFS potentials  $F_{env}^{(0)}(r_a; R)$  shows that the latter is much more sharply peaked for  $r_a$  in the vicinity of  $R$ . Thus for example at  $R = 4.5$ , the essentially constant portion of  $F_{env}^{(0)}(r_a; 4.5)$ , where the contribution from overlap with neighbouring cations is negligible, extends from zero  $r_a$  up to an  $r_a$  value of about 3.1 au in the ODMFS method, whilst in the RVMW model this constant portion ends at  $r_a = 2.629$  au. Furthermore, the ODMFS function  $F_{env}^{(0)}(r_a; 4.5)$  becomes positive for  $r_a = 4.0$  au and reaches its maximum of 1.85 au at  $r_a = 4.5$  au. This maximum should be compared with the value of -0.3917 au for  $F_{env}^{(0)}(r_a; 4.5)$  in its constant region at small  $r_a$ . With the occurrence of a positive region, this ODMFS environmental potential resembles the ODMFS and OEMFS potentials found for CaO for  $R = 4.5$  au, whereas these potentials are nowhere positive for MgO at  $R = 3.981$  au. It is only at smaller  $R$  for MgO that these environmental potentials have positive regions. The lattice energy, closest equilibrium cation-anion separation and bulk modulus predicted for CaF<sub>2</sub> by the RVMW and ODMFS methods but without consideration of electron correlation are compared in table 7 with the experimental values measured at temperatures close to 0 K. Although the ODMFS method predicts a greater cohesion as manifested by a larger  $D_e$  and smaller  $R_e$  values, even these ODMFS results show significant discrepancies with experiment, thus demonstrating the importance of electron correlation effects.



Table 7. The crystal cohesion predicted without inclusion of an electron correlation<sup>(1,2)</sup>.

	RVMW	ODMFS	expt
$D_e$	2458	2479	2630
$R_e$	4.731	4.698	4.448
$B$	7.141	5.915	8.825

<sup>(1)</sup> Lattice energy  $D_e$  in  $\text{kJ mol}^{-1}$ , equilibrium closest cation-anion separation  $R_e$  in au and bulk modulus  $B$  in  $10^{10} \text{ N m}^{-2}$ . Experimental  $D_e$  from [49],  $R_e$  at 6.4 K from [48] and  $B$  calculated as  $(C_{11} + 2C_{12})/3$  from the experimental 4.2 K measurements [51]  $C_{11} = 17.12 \times 10^{10} \text{ N m}^{-2}$  and  $C_{12} = 4.675 \times 10^{10} \text{ N m}^{-2}$ .

<sup>(2)</sup> All results derived from cohesive energy function (2).

Table 8. The crystal cohesion predicted with the inclusion of electron correlation<sup>(1,2)</sup>.

		no disp	no $E_{re}^{corr}(R)$	full $U_L(R)$ <sup>(3)</sup>	expt
RVMW	$D_e$	2500	2553	2560	2630
	$R_e$	4.681	4.625	4.616	4.448
	$B$	7.701	8.382	8.491	8.825
ODMFS	$D_e$	2522	2613	2631	2630
	$R_e$	4.640	4.478	4.457	4.448
	$B$	6.085	8.346	8.899	8.825

<sup>(1)</sup> See note 1 to table 7.

<sup>(2)</sup> All calculations include short-range two-body correlation terms  $V_{sCA}^{corr}(R)$ ,  $V_{sAA}^{corr}([2/\sqrt{3}]R)$  and  $V_{sCC}^{corr}([2\sqrt{2/3}]R)$ . The column headed no disp excludes dispersion energy  $U_{disp}(R)$  but includes  $E_{re}^{corr}(R)$ , that headed no  $E_{re}^{corr}(R)$  uses full  $U_L(R)$  function (7) but with correlation contribution (15) to rearrangement energy excluded.

<sup>(3)</sup> Computed using full  $U_L(R)$  function (7).

The crystal cohesions predicted by both the RVMW and ODMFS methods on successively introducing the different contributions from electron correlation are compared with experiment in table 8. Even with the inclusion of all the correlation contributions to  $U_L(R)$ , namely the short-range two-body terms  $V_{sub}^{corr}(x_{ab}R)$ , the correlation contribution  $E_{re}^{corr}(R)$  to the rearrangement energy and the dispersive attractions  $U_{disp}(R)$ , the predictions of the RVMW model do not show good agreement with experiment. Thus this model underestimates the lattice energy by  $70 \text{ kJ mol}^{-1}$  whilst overestimating  $R_e$  by 0.168 au. However, the introduction of all these correlation corrections into the ODMFS predictions yields results in excellent agreement with experiment. This shows that the behaviour of  $\text{CaF}_2$  parallels both that of  $\text{MgO}$  and  $\text{CaO}$  [10] in that, whilst the RVMW model is not fully adequate, the ODMFS method provides a realistic description of the environmental potential, yielding rearrangement energies and two-body potentials sufficiently accurate to generate excellent predictions for the crystal cohesion.

Comparison of the second and third columns of results shows that, in the ODMFS method, the contribution of electron correlation to the rearrangement energy is small but nevertheless of crucial importance in obtaining agreement between theory and experiment. It should be pointed out that this excellent agreement does not depend on using the data for free fluoride ion to determine the correction factor  $B_{corr}$  in (15). Thus if one were to adopt the arguments presented [10] for in-crystal  $\text{O}^{2-}$  ions and conclude that the behaviour of the electron correlation for a fluoride ion in-crystal is more similar to that of neon than that of a free fluoride ion,  $B_{corr}$  would be derived by dividing the exact correlation energy of  $-0.393 \text{ au}$  [34] for neon by the density functional (12) prediction [10] of  $-0.7397 \text{ au}$ . The use of  $E_{re}^{corr}(R)$  values derived from the resulting correction factor of 0.531 yields

predictions of  $2630 \text{ kJ mol}^{-1}$ ,  $4.459 \text{ au}$  and  $8.853 \times 10^{10} \text{ N m}^{-2}$  for  $D_e$ ,  $R_e$  and  $B$  respectively which are essentially unchanged from those of table 8. The greater contractions of the anion wavefunctions predicted by the ODMFS method compared with their RVMW counterparts cause the former approach to predict more negative values for  $E_{re}^{corr}(R)$ . For example at  $R = 4.5 \text{ au}$  with  $B_{corr}$  taken to have the value of  $0.576$  derived from the data for a free fluoride ion, the RVMW prediction for  $E_{re}^{corr}(4.5)$  of  $-4.2 \text{ kJ mol}^{-1}$  is about half of that of  $-8.6 \text{ kJ mol}^{-1}$  computed from the ODMFS anion wavefunction. The two methods predict  $E_{re}^{corr}(R)$  values differing by this factor of about two over the entire range of  $R$  considered. The quantities  $E_{re}^{corr}(R)$  were neglected in the earlier RVMW computations for halides on the grounds that the smallness of the uncorrelated terms  $E_{re}^0(R)$  indicated that these correlation contributions would be insignificant. For the RVMW model the absolute magnitude of  $E_{re}^{corr}(R)$  constitutes a much greater fraction of the uncorrelated prediction  $E_{re}^0(R)$  than is the case with the ODMFS method. This has the consequence that the total rearrangement energies  $E_{re}(R)$  predicted with the RVMW model are far too small especially at intermediate and larger  $R$  values, a conclusion demonstrated by comparison with their ODMFS counterparts. Thus for  $R = 4.5$ , the addition of the  $E_{re}^{corr}(4.5)$  values just reported to the uncorrelated values in table 6 yields an RVMW prediction of only  $5.3 \text{ kJ mol}^{-1}$  for the total rearrangement energy  $E_{re}(4.5)$  compared with the ODMFS result of  $43.5 \text{ kJ mol}^{-1}$ .

The importance of the inter-ionic dispersive attractions in the cohesion of  $\text{CaF}_2$  is shown by comparing the predictions derived with their neglect and reported in the first numerical column of table 8 with those computed using the full  $U_L(R)$ . It should be noted that, unless the dispersion is included, the ODMFS method predicts values for the bulk modulus which are too small by at least 25%. The dispersion energies predicted for the ODMFS calculations have magnitudes  $|U_{disp}(R)|$  considerably greater than those derived from the RVMW model because the significantly more compressed ODMFS anion  $2p$  orbitals produce a value (2.755) for the fluoride ion dispersion damping parameter  $d_A$  which is considerably larger than that of 1.616 resulting from the RVMW model. For a given inter-ionic separation a larger dispersion damping parameter increases the value of the dispersion damping function  $\chi_n^{ab}(x_{ab}R)$  with the result that the magnitude of the dispersion energy is less reduced by the damping. Thus, the predicted lattice energy increase of  $60 \text{ kJ mol}^{-1}$  on the introduction of dispersion into the RVMW model is only about half of that of  $109 \text{ kJ mol}^{-1}$  resulting from introducing dispersion into the ODMFS calculations. The behaviour of  $\text{CaF}_2$  has therefore been shown to exactly parallel that found for  $\text{MgO}$  and  $\text{CaO}$  [10] where it is the interplay between the dispersion and the improvement of the description of the environmental potential provided by the ODMFS method which together are responsible for the much better description of the crystal cohesion by the ODMFS method.

#### 4. Conclusions

The cohesion of cubic  $\text{CaF}_2$  has been studied within the framework of a suitably defined fully ionic model in which it is assumed that the total electronic wavefunction of the crystal can be written as an anti-symmetrized product of individual ion wavefunctions each of which is spherically symmetric and contains a fixed integral number of electrons. The radius variable Madelung–Watson (RVMW) [7] and later optimized on density Madelung–Fermi smoothed (ODMFS) models [10] for describing the environmental potential acting on an anion electron and hence for generating fluoride ion wavefunctions adapted to their inter-crystal environments were compared. The use of these wavefunctions to compute with the

relativistic integrals program that portion of the crystal cohesion not arising from electron correlation showed the ODMFS method to be preferable to the RVMW model.

The evaluation of the contributions made by electron correlation to the crystal cohesion necessitated refining the method for deriving the dipole–quadrupole dispersion coefficients using the Starkschall–Gordon formula as well as developing a new way for computing the contribution of electron correlation to the fluoride ion rearrangement energy. The RVMW model has been shown to be not fully adequate for  $\text{CaF}_2$  as its predictions for the crystal cohesion show significant discrepancies with experiment even after introducing all the contributions from electron correlation. The introduction of all these contributions to the ODMFS calculations generated predictions for the lattice energy, closest equilibrium cation–anion separation and bulk modulus agreeing excellently with experiment. The behaviour of  $\text{CaF}_2$  is thus similar to that of  $\text{MgO}$  and  $\text{CaO}$  for which it has already been shown [10] that, whilst the RVMW model is not fully adequate, the ODMFS method provides an excellent description.

It has been shown that the ODMFS approach realistically describes the in-crystal modifications of the anion wavefunction in  $\text{CaF}_2$ . It can therefore be concluded that the rearrangement energies and two-body inter-ionic potentials predicted from the ODMFS method and reported in table 5 are sufficiently accurate to provide a trustworthy springboard for future investigations of other properties of this material.

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