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RELATIVISTIC *AB INITIO* CALCULATIONS OF THE PROPERTIES OF IONIC SOLIDS

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CONTENTS

Relativistic *ab initio* calculations of inter-ionic potential energies are used to develop a reliable non-empirical method for predicting the properties of ionic solids containing the heaviest ions. A physically realistic method for describing the non-negligible differences between free and in-crystal ion wavefunctions is described. Functions are presented for describing the partial quenching, arising from ion wavefunction overlap, of the standard long-range form of the inter-ionic dispersive attractions. These attractions are shown to be distinct from the contributions to the inter-ionic potentials that arise from that portion of the electron correlation energy which is non-zero solely because of overlap of the ion wavefunctions. The results presented for NaCl, MgO and the fluorides of Li, Na, Ag and Pb show that these modifications overcome the deficiencies of previous calculations.

Ab initio predictions of the closest cation–cation and anion–anion short-range interactions, which are not available from semi-empirical fits to experimental data, are presented. The non-point coulombic interactions between pairs of anions, derived by adding the dispersive attractions to the short-range interactions, are compared with previous semi-empirical and approximate *ab initio* results.

The uncorrelated short-range inter-ionic potentials computed exactly are compared with those predicted from electron-gas theory. The use of the electron-gas approximation to describe any of these potentials degrades the quality of the predicted crystal properties.

1. INTRODUCTION

Knowledge of the forces and potentials acting between ions in ionic solids is required to predict and understand the behaviour of both pure crystalline materials (Tosi 1964) and those containing defects (Lidiard & Norgett 1972).

The most widely used theories so far for studying ionic crystals describe the interactions between pairs of ions by empirical potentials of the Born–Mayer type. Each such potential is a simple analytic function of the relevant inter-nuclear distance and contains some unknown parameters which are determined by demanding that the appropriate number of experimentally known properties of the crystal are reproduced. Although such calculations have undoubtedly played, and will continue to play, a useful role in elucidating the behaviour of ionic crystals (Tosi 1964; Sangster & Dixon 1976; Catlow *et al.* 1977; Sangster *et al.* 1978; Catlow & Mackrodt 1982), there are four different reasons why one should wish to progress to more fundamental and rigorous *ab initio* approaches. First, at a fundamental level, it can be questioned whether empirical theories explain any features of inter-ionic potentials. Such theories merely correlate those crystal properties used to determine the adjustable parameters of the ionic potentials with other properties of the crystal that were not included in the fitting procedure. Second, it is common for there to be insufficient experimental data to determine uniquely all the inter-ionic potentials. For example, the repulsive parts of the halide–halide interaction in the alkali halides (Catlow *et al.* 1977) and of the oxide–oxide interaction in UO_2 (Catlow 1977) cannot be determined by empirical fitting. This is because such fits merely yield parameters simulating the attractive anion–anion dispersion interactions which are greater than the short-range anion–anion repulsions for these crystals near their equilibrium geometries. Consequently, it was decided to attempt to calculate these short-range anion–anion potentials by non-empirical methods (Catlow & Hayns 1972; Catlow *et al.* 1977; Catlow 1977; Kendrick & Mackrodt 1983). Furthermore, as any properties predicted for the pure alkali halides will be invariant with respect to the interchange of the cation–cation and anion–anion potentials, further ambiguities arise if attempts are made to determine both these short-range potentials by empirical fittings (Sangster *et al.* 1978). The need to introduce into empirical schemes arbitrary assumptions about these interactions, such as that the anion–anion and cation–cation interactions have the same Born–Mayer hardness parameter (Sangster *et al.* 1978), must provide strong motivation for developing *ab initio* methods. The third reason for developing *ab initio* calculations is that empirical potentials, derived by fitting data that are determined by points on the potential curves corresponding to near equilibrium crystal configurations, may be unreliable for points corresponding to configurations far from equilibrium. Knowledge of such regions of the potentials is required to investigate both crystal defects involving interstitial ions (Lidiard & Norgett 1972; Mackrodt & Stewart 1979) and the behaviour of perfect crystals under very high pressures such as those arising in the mantle of the earth (Cohen & Gordon 1976). The fourth motive for developing *ab initio* calculations is that it is clearly impossible to use semi-empirical methods to investigate the properties of hitherto unknown materials and of materials which can be prepared only in quantities too small for many experiments. Compounds of transactinide elements such as Ru or Ha provide examples of the latter type of material, while those of superheavy elements having nuclear charges of 112–124 lying within the predicted island of nuclear stability provide an interesting example of the former (Lodhi 1978).

One non-empirical approach that has been widely applied to study ionic crystals is the electron-gas method (Gordon & Kim 1972; Kim & Gordon 1974; for a review see Clugston 1978). Although this method has achieved some success in describing both pure (Cohen & Gordon 1976; Muhlhausen & Gordon 1981*a*, *b*) and defect (Mackrodt & Stewart 1979) materials, its theoretical status is uncertain. Thus the method cannot be completely trusted because it is unclear why such a simple method should work well, and because there are some ambiguities in its implementation (Rae 1974, 1975; Lloyd & Pugh 1977; Clugston & Pyper 1979; Waldman & Gordon 1979; Wood & Pyper 1981) which have generated a large number of variants. Indeed fully *ab initio* calculations are required to distinguish between some of these variants (Wood & Pyper 1981). Furthermore, there is evidence that for some systems, such as AgF discussed in this paper, currently developed electron-gas calculations can fail quite badly (Wood & Pyper 1981).

The conclusions that one should progress beyond empirical theories and that the electron-gas method is not completely trustworthy, strongly motivate the development of fundamental *ab initio* approaches. A fundamental *ab initio* description of ionic crystals is developed by expressing the wavefunction of the entire crystal as an anti-symmetrized product of the wavefunctions of the individual ions (Löwdin 1950, 1956; Abarenkov & Antonova 1970). From this an expression for the cohesive energy is derived by calculating the expectation value of the hamiltonian. Both the Löwdin and Abarenkov & Antonova approaches use this starting point to show that the cohesive energy can be expressed as a sum of two-body and many-body potentials that can be reduced to readily computable sums of integrals if each ion wavefunction is approximated by a single Slater determinant. Although the fundamental formalisms

(Löwdin 1950, 1956; Abarenkov & Antonova 1970) are undoubtedly correct mathematically, the results of previous calculations, with three very recent exceptions (Andzelm & Piela 1977, 1978; Wood & Pyper 1986), have been either misleading or disappointing. The deficiencies of previous calculations have arisen from one or more of the following:

(i) the use of the approximation in which all integrals involving charge densities constructed as products of different orbitals on the same centre are neglected;

(ii) the use of wavefunctions of isolated ions or the use of inappropriate methods for describing the modifications to the wavefunctions caused by the crystalline environment;

(iii) inappropriate treatment of the inter-ionic dispersion energy.

Approximation (i), which is extraneous to the basic theory (Löwdin 1950, 1956; Abarenkov & Antonova 1970), is so poor that the results of calculations that use it are quite misleading. Although early calculations (Löwdin 1950, 1956; Fröman & Löwdin 1962; Mansikka & Bystrand 1966; Yamashita & Asano 1970; Calais *et al.* 1971; Hayns & Calais 1973) which included only the Madelung and nearest-neighbour short-range repulsive terms yielded results in good agreement with experiment, it has been shown subsequently (Abarenkov & Antonova 1970; Andzelm & Piela 1977, 1978; Wood & Pyper 1986; see also §5*c*) that this agreement with experiment disappears when approximation (i) is avoided. Furthermore, use of approximation (i) predicts unreasonably large short-range anion–anion repulsive energies which completely destroy the previous (spurious) agreement with experiment (Petterson *et al.* 1967, 1968; Vallin *et al.* 1967; Calais *et al.* 1971). The most extreme example of this phenomenon is provided by the case of MgO where the short-range $O^{2-}\ldots O^{2-}$ interaction is predicted to be two to three times as important as the short-range part of the Mg^{2+}–O^2 interaction (Calais *et al.* 1971).

Those few calculations (Abarenkov & Antonova 1970; Andzelm & Piela 1977, 1978; Wood & Pyper 1986) that have avoided approximation (i) have shown that use of free ion wavefunctions predicts insufficient binding. This is manifested by too small lattice energies and too large equilibrium inter-nuclear distances. Hitherto, three methods have been used to generate wavefunctions adapted to the crystalline environment, none of which is completely satisfactory. The first method (Fröman & Löwdin 1962), based on the virial theorem, merely introduces a single overall scale factor into the wavefunctions of all the free ions. This method can never fully describe the distortion of these wavefunctions caused by the crystalline environment because the innermost core orbitals are scaled by the same factor as the outer orbitals. Consequently, the optional scale factor determined by minimizing the crystal energy is close to unity because the total energy is dominated by that of the innermost core orbitals. In any realistic description of the environmentally induced modifications, the outermost orbitals will be most affected, while the innermost ones will remain essentially unchanged from their free ion forms (see §2*b*). The scaling of just the outermost orbital is thus more reasonable (Mansikka & Bystrand 1966), although the use of the same scaling factor for both the inner and outer spatial regions is still not completely realistic. In the second approach (Andzelm & Piela 1977, 1978), the wavefunction of each ion is computed from a hamiltonian which includes the purely electrostatic potential generated either by a point charge description of the neighbouring ions (the approach labelled DP by Andzelm & Piela) or by the Hartree–Fock charge density of the neighbours (the approached labelled DC, Andzelm & Piela). Even though the predicted properties of both LiF and NaF agreed well with experiment it is shown in §2 that use of either of these two electrostatic potentials alone is theoretically questionable. The third method of computing crystal adapted wavefunctions approximates the environment of an ion by the potential generated by a 'Watson shell' (Watson 1958; Pachalis & Weiss 1969) which is a shell of total charge equal to minus the charge of the ion, and radius equal to the ionic radius. Although it was shown in the previous paper (Wood & Pyper 1986) that this method yields ion wavefunctions which well describe the systems LiF, NaF, NaCl, it was also found that PbF_2 was unsatisfactorily described. It will be shown here that the failure of the method to produce wavefunctions which correctly describe PbF_2 arises from theoretical inadequacies that are especially marked for cations.

All previous calculations of ionic crystals have failed to treat the attractive inter-ionic dispersion energy in a way even remotely satisfactory. Thus the basic formalisms (Löwdin 1950, 1956; Abarenkov & Antonova 1970) do not incorporate dispersion which has also been neglected in all but the most recent calculations (Andzelm & Piela 1977, 1978; Wood & Pyper 1986). These calculations incorporate the dispersion energy in its undamped expanded multipole form (Kreek & Meath 1969) in which the attraction between a pair of ions a and b is written as $C_6(\mathrm{ab})/r_{\mathrm{ab}}^6 + C_8(\mathrm{ab})/r_{\mathrm{ab}}^8$. However, this form is only correct when the distance r_{ab} between the ions is sufficiently large that the overlap of the ion wavefunctions is negligible (Kreek & Meath 1969; Jacobi & Csanak 1975). As the short-range repulsive forces, which prevent an ionic crystal from collapsing under the coulomb attraction of the ions, arise from the overlap of the ion wavefunctions, overlap must be important for inter-ionic distances near equilibrium, thus showing that it is theoretically incorrect to use the undamped expanded dispersion series. This undamped series predicts too great an attraction when wavefunctions overlap significantly, a theoretical fault that cannot be ignored. Wood & Pyper (1986) showed for PbF_2 and also, in particular, for AgF, that use of the dipole–dipole (C_6) and dipole–quadrupole (C_8) terms of the undamped expanded dispersion series does indeed yield spuriously large lattice energies and equilibrium inter-nuclear distances that are far too short. As this difficulty is masked in systems such as LiF and NaF, where the dispersion energy is much smaller than for AgF and PbF_2, the quality of the numerical results obtained was not significantly degraded (Andzelm & Piela 1977, 1978). However, the AgF and PbF_2 results show that one should use a theory (Jacobi & Csanak 1975; Koide 1976) in which each term of the expanded dispersion series is multiplied by a theoretically well defined and, in principle, calculable damping factor.

The object of this paper is to describe *ab initio* calculations which not only contain all the essential features needed to rectify the deficiencies of previous calculations but which, unlike previous calculations by other groups, incorporate all the major one-electron relativistic effects. It has been shown not only that relativity significantly modifies the behaviour of even the valence electrons in a heavy element (Grant *et al.* 1976; Rose *et al.* 1978; Malli 1983) but also that this cannot be adequately treated by first-order perturbation treatments of relativity (Pyper & Marketos 1981). Hence, a computational method capable of handling ionic solids containing the heaviest ions should use the four-component wavefunctions that arise in the fully relativistic description provided by the Dirac equation (Dirac 1958). This paper presents results of calculations for halides of metals ranging from the lightest, Li, where relativity and dispersion are unimportant, to the heavy, Pb, where it is essential to consider both these phenomena. A useful by-product of this research is the *ab initio* determination of halide–halide short-range potentials which cannot be readily derived by semi-empirical methods for the reasons discussed above. Although relativity will be quite unimportant for MgO, the results of the MgO calculations presented here are of interest for three reasons. First it is shown that an *ab initio* (not electron-gas) calculation can provide a realistic description of MgO and hence that the previous unacceptable results (Calais *et al.* 1971) arose solely from use of approximation (i) already discussed. Second, comparison of experimental results with the theoretical results computed assuming full ionicity, probes the validity of a fully ionic description of this oxide. Third, this investigation yields a short-range oxide–oxide potential whose *ab initio* determination is of interest for the reason discussed in the first paragraph of this introduction.

2. Theory

(*a*) *Basic method*

The precise mathematical meaning of the assumption that the crystal is composed of N_{ion} ions must be that the wavefunction $|\Psi_{\text{cr}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{\text{cr}}})\rangle$ for the N_{cr} electrons in the crystal is able to be factorized into an antisymmetrized product of N_{ion} wavefunctions $|\Phi_{\text{a}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N\text{a}})\rangle$ of the individual ion a:

$$|\Psi_{\text{cr}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{\text{cr}}})\rangle = S_{\text{cr}}\mathscr{A}'\left\{\prod_{\text{a}=1}^{N_{\text{ion}}} |\Phi_{\text{a}}(\boldsymbol{r}_{N_{\text{as}}}, \ldots, \boldsymbol{r}_{N_{\text{as}}+N_{\text{a}-1}})\rangle\right\}. \tag{2.1}$$

Here N_{a} is the number of electrons of ion a and N_{as} is the label of the electron appearing first in the wavefunction of ion a in (2.1) so that $N_{\text{as}} = 1+\sum_{b=1}^{\text{a}-1} N_b$, where the sum over b is over all ions preceding a in the wavefunction (2.1). The overlap of the wavefunction of any ion with those of the other ions causes the normalization constant S_{cr} to be less than unity for all finite separations of the ions. The quantity $\mathscr{A}'$ is the partial antisymmetrizer containing, besides the identity, only permutations that interchange coordinates of electrons belonging to different ions. The ionic model is defined by specifying the number N_{a} of electrons on each ion; it is not necessary in principle either to be restricted to a Hartree–Fock description of the individual antisymmetric ion wavefunctions $|\Phi_{\text{a}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{\text{a}}})\rangle$ or to assume that these wavefunctions are the same as those of the isolated ions, an assumption which would neglect the modifications of the wavefunctions caused by the crystalline environment.

It would appear in the current state of theory and computational machinery that the development of a program which not only is fully relativistic but can also handle the heaviest ions is a sufficiently new and major undertaking without attempting the further new step of using correlated ion wavefunctions. Hence, the wavefunction of each of the ions a will be approximated by a single determinant of Dirac–Fock atomic orbitals expressed in the standard central field form (Grant 1970, eq. 2–13, Pyper 1982, eq. 2–24)

$$|\Phi_{\text{a}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{\text{a}}})\rangle = \mathscr{A}\left(\prod_{i=1}^{N_{\text{a}}} |\phi_{i_{\text{a}}}(\boldsymbol{r}_{\text{a},i})\rangle\right), \tag{2.2}$$

where $\boldsymbol{r}_{\text{a},i}$ is the vector describing the position of electron i with respect to the nucleus of ion a and $\mathscr{A}$ is the antisymmetrizer. It should be stressed that the crystalline environment will cause the orbitals $|\phi_{i_{\text{a}}}(\boldsymbol{r}_{\text{a},i})\rangle$ to differ from those $|\phi_{\text{a}}^{\text{F}}(\boldsymbol{r}_{\text{a},i})\rangle$ obtained from a Dirac–Fock calculation for the isolated ion. The total relativistic electronic hamiltonian $\mathscr{H}_{\text{cr}}(R)$ for the crystal having nuclear positions defined by the closest cation–anion inter-nuclear separation R will be taken to be

$$\mathscr{H}_{\text{cr}}(R) = \sum_{\text{a}=1}^{N_{\text{ion}}} \mathscr{H}_{T\text{a}} + \sum_{\text{a}} \sum_{\text{b}<\text{a}} (\mathscr{H}_{T\text{ab}}(x_{\text{ab}}R) - \mathscr{H}_{T\text{a}} - \mathscr{H}_{T\text{b}}), \tag{2.3}$$

where x_{ab} is a purely geometrical constant relating R to the separation $x_{ab}R$ between the nuclei of the ions a and b. The hamiltonian $\mathscr{H}_{Tab}(x_{ab}R)$ for the pair of ions a and b having nuclear charges Z_a and Z_b is

$$\mathscr{H}_{Tab}(x_{ab}R) = \mathscr{H}_{Ta} + \mathscr{H}_{Tb} - \sum_{i=N_{as}}^{N_{as}+N_a-1} Z_b r_{b,i}^{-1} - \sum_{i=N_{bs}}^{N_{bs}+N_b-1} Z_a r_{a,i}^{-1} + \sum_{i=N_{as}}^{N_{as}+N_a-1} \sum_{j=N_{bs}}^{N_{bs}+N_b-1} r_{ij}^{-1} + Z_a Z_b/(x_{ab}R), \qquad (2.4)$$

with the hamiltonian $\mathscr{H}_{Ta}$ for an isolated ion a given by

$$\mathscr{H}_{Ta} = \sum_{i=N_{as}}^{N_{as}+N_a-1} \{c\boldsymbol{\alpha}(i)\cdot\hat{\boldsymbol{p}}(i) + c^2[\beta(i)-1] - Z_a r_{a,i}^{-1}\} + \sum_{i=N_{as}}^{N_{as}+N_a-2} \sum_{j=i+1}^{N_{as}+N_a-1} r_{ij}^{-1}, \qquad (2.5)$$

where $\boldsymbol{\alpha}(i)$ and $\beta(i)$ are Dirac matrices and c is the velocity of light. Under the approximation (2.2) for the individual ion wavefunctions, the crystal wavefunction (2.1) becomes a single Slater determinant whose energy $E_{cr}(R)$ calculated as the expectation value of the hamiltonian (2.3) can be written (Abarenkov & Antonova 1970) as a sum of 2-body, 3-body, up to N_{cr}-body terms

$$\begin{aligned} E_{cr}(R) &= \langle \Psi_{cr}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{cr}}) | \mathscr{H}_{cr}(R) | \Psi_{cr}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_{cr}}) \rangle \\ &= \sum_{a=1}^{N_{cr}} E_a(R) + \sum_{a=1}^{N_{cr}-1} \sum_{b=a+1}^{N_{cr}} V_{ab}^0(x_{ab}R) + \tfrac{1}{6} \sum_{a \neq b \neq c} + \ldots . \qquad (2.6) \end{aligned}$$

Here $E_a(R)$ is the energy that single ion a would have if it had the wavefunction (2.2) optimal for the crystal with separation R, so that

$$E_a(R) = \langle \Phi_a(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_a}) | \mathscr{H}_{Ta} | \Phi_a(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_a}) \rangle, \quad \text{with } N_{as} = 1. \qquad (2.7)$$

The quantity $V_{ab}^0(x_{ab}R)$ is the energy of interaction of a pair of ions a and b separated by a distance $x_{ab}R$ described by wavefunctions (2.2) optimal for the crystal. It can therefore be calculated as

$$\begin{aligned} V_{ab}^0(x_{ab}R) = &\langle \Psi_{ab}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_a+N_b}) | \mathscr{H}_{Tab}(x_{ab}R) | \Psi_{ab}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_a+N_b}) \rangle \\ &- E_a(R) - E_b(R), \quad \text{with } N_{as} = 1,\ N_{bs} = N_a + 1, \qquad (2.8) \end{aligned}$$

where $$|\Psi_{ab}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_a+N_b})\rangle = S_{ab}\mathscr{A}'\{|\Phi_a(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_a})\rangle |\Phi_b(\boldsymbol{r}_{N_a+1}, \ldots, \boldsymbol{r}_{N_a+N_b})\rangle\}. \qquad (2.9)$$

The result (2.6) is exact (Abarenkov & Antonova 1970), unlike the corresponding result of Löwdin (1950, 1956) derived by truncating an expansion in powers of the orbital overlap. Although (2.3) is unsatisfactory (Brown & Ravenhall 1951; Mittelman 1971, 1972) as a general relativistic hamiltonian because it does not correctly yield the energies of wavefunctions describing the presence of a positron, it can be used in (2.6) because all the orbitals entering the crystal wavefunction (2.1) are solutions of a Dirac–Fock equation describing an electron in the crystal.

The expansion (2.6) of the crystal energy as a sum of n-body terms is expected to converge rapidly (Abarenkov & Antonova 1970); thus three-body energies are known to be much smaller than two-body terms (Abarenkov & Antonova 1970; Andzelm & Piela 1977, 1978). Although the deviation from the equality of the elastic constants C_{12} and C_{44} predicted for a static lattice subject only to pairwise inter-ionic interactions (Zener 1947) can be naturally explained by the three-body terms (Löwdin 1950, 1956), it has been suggested that the experimentally observed deviations can also be explained otherwise (Ree & Holt 1973), at least for the alkali halides. This observation coupled with the smallness of the three-body compared with the two-body terms indicates that attention should be focused initially on the two-body interactions, knowledge of which is still rather limited. In the two-body approximation, the binding energy $U^0_{\mathrm{L}}(R)$ of the crystal with respect to its component free gaseous ions is found from (2.6) to be

$$U^0_{\mathrm{L}}(R) = \sum_{\mathrm{a}=1} \sum_{\mathrm{b}<\mathrm{a}} V^0_{\mathrm{ab}}(x_{\mathrm{ab}} R) + \sum_{\mathrm{a}} E^{\mathrm{a}}_{\mathrm{re}}(R). \tag{2.10}$$

Here $E^{\mathrm{a}}_{\mathrm{re}}(R)$ is the 'rearrangement energy' required to convert a free gaseous ion, a, of energy E_{a} (2.12) to the non-stationary state described by the wavefunction (2.2) optimal for the crystalline environment with closest cation–anion separation R

$$E^{\mathrm{a}}_{\mathrm{re}}(R) = E_{\mathrm{a}}(R) - E_{\mathrm{a}}, \tag{2.11}$$

$$E_{\mathrm{a}} = \langle \Phi^{\mathrm{F}}_{\mathrm{a}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\mathrm{a}}}) | \mathscr{H}_{T\mathrm{a}} | \Phi^{\mathrm{F}}_{\mathrm{a}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\mathrm{a}}}) \rangle, \quad N_{\mathrm{as}} = 1, \tag{2.12}$$

with

$$|\Phi^{\mathrm{F}}_{\mathrm{a}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\mathrm{a}}})\rangle = \hat{\mathscr{A}} \left(\prod_{i=1}^{N_{\mathrm{a}}} |\phi^{\mathrm{F}}_{i_{\mathrm{a}}}(\boldsymbol{r}_{\mathrm{a},i})\rangle \right), \tag{2.13}$$

so that $|\Phi^{\mathrm{F}}_{\mathrm{a}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_{N_{\mathrm{a}}})\rangle$ is the Dirac–Fock wavefunction for the free ion a. It is convenient to separate $V^0_{\mathrm{ab}}(x_{\mathrm{ab}} R)$ into the point coulombic value ($q_{\mathrm{a}} q_{\mathrm{b}}/x_{\mathrm{ab}} R$, where $q_{\mathrm{a}} = Z_{\mathrm{a}} - N_{\mathrm{a}}$ is the charge of the ion a) it would have if the ion wavefunctions did not overlap, and the remainder $V^0_{\mathrm{sab}}(x_{\mathrm{ab}} R)$ arising from wavefunction overlap. This separation is useful because the point coulomb terms in (2.10) which decrease very slowly with increasing x_{ab} constitute a known Madelung sum while the remaining short-range potentials $V^0_{\mathrm{sab}}(x_{\mathrm{ab}} R)$ decrease rapidly with increasing x_{ab}. It is, therefore, only necessary to consider a few near neighbour short-range terms $V^0_{\mathrm{sab}}(x_{\mathrm{ab}} R)$. If only the nearest cation–anion, anion–anion and cation–cation short-range interactions are considered, (2.10) with definition (2.14) shows the binding energy $U^0_{\mathrm{L}}(R)$ per formula unit of compounds CA_m to be expressible through

$$V^0_{\mathrm{ab}}(x_{\mathrm{ab}} R) = V^0_{\mathrm{sab}}(x_{\mathrm{ab}} R) + q_{\mathrm{a}} q_{\mathrm{b}}/(x_{\mathrm{ab}} R), \tag{2.14}$$

$$U^0_{\mathrm{L}}(R) = -M/R + n_{\mathrm{CA}} V^0_{\mathrm{sCA}}(R) + \tfrac{1}{2}\{n_{\mathrm{CC}} V^0_{\mathrm{sCC}}(x_{\mathrm{CC}} R) + m n_{\mathrm{AA}} V^0_{\mathrm{sAA}}(x_{\mathrm{AA}} R)\} + E^{\mathrm{C}}_{\mathrm{re}}(R) + m E^{\mathrm{A}}_{\mathrm{re}}(R), \tag{2.15}$$

where n_{ab} is the number of nearest b ions around each a ion and M is the Madelung constant. The closest cation–anion separation at the equilibrium minimum energy geometry of the crystal R_{e}, the lattice energy $-U^0_{\mathrm{L}}(R_{\mathrm{e}})$ and bulk compressibility can be predicted from the function $U^0_{\mathrm{L}}(R)$. This function can be evaluated because the short-range interactions are known from (2.14) after computing the total interactions $V^0_{\mathrm{ab}}(x_{\mathrm{ab}} R)$ from (2.8) by using the Relativistic Integrals Program RIP described in the preceding paper (Wood & Pyper 1986), while the rearrangement energies (2.11) are readily computed from the expectation values (2.7) and (2.12) of the free ion hamiltonians (2.5).

The expression (2.15) for the crystal binding energy entirely neglects electron correlation. The intra-ionic correlation is neglected by invoking the Dirac–Fock form (2.2) for the ion wavefunctions, while the form (2.1) for the crystal wavefunction implicitly neglects inter-ionic correlation thereby omitting the dispersion interactions between the ions. Although there is no evidence that the intra-ionic correlation contributes significantly to the crystal binding energy,

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the inter-ionic correlation, and also, more significantly, the dispersion, is far from negligible, particularly for heavy ions. At large ionic separations for which ion wavefunction overlap is negligible, the dispersion series describes the inter-ionic correlation almost entirely because the only terms omitted arise from third- and higher-order perturbation theory treatments of the inter-ionic interaction hamiltonian (the last four terms of (2.4)). However, at smaller separations where ion wavefunction overlap is appreciable, the dispersion series, even in its unexpanded form valid in the presence of overlap (Kreek & Meath 1969), does not describe the entire inter-ionic correlation. As the additional terms depend explicitly on overlap, these decrease rapidly with inter-ionic distance so that only the nearest cation–anion, anion–anion and cation–cation contributions need be considered.

As no rigorous theory of the correlation energy of a solid exists, these overlap dependent terms are estimated by using the density functional theory based on the uniform electron-gas (Gordon & Kim 1972). The total inter-ionic correlation energy is then calculated as the sum of the electron-gas overlap contribution plus the dispersion energy since there is evidence (Clugston & Pyper 1979; Wood & Pyper 1981 (and in Appendix 4)) that these two terms are distinct. The crystal binding energy then becomes

$$\begin{aligned} U_{\mathrm{L}}(R) &= U_{\mathrm{L}}^{0}(R) + n_{\mathrm{CA}}\, V_{\mathrm{sCA}}^{\mathrm{corr}}(R) + \tfrac{1}{2}\{n_{\mathrm{CC}}\, V_{\mathrm{sCA}}^{\mathrm{corr}}(x_{\mathrm{CC}}\, R) + m n_{\mathrm{AA}}\, V_{\mathrm{sAA}}^{\mathrm{corr}}(x_{\mathrm{AA}}\, R)\} + U_{\mathrm{disp}}(R) \\ &= -M/R + n_{\mathrm{CA}}\, V_{\mathrm{sCA}}^{\mathrm{T}}(R) + \tfrac{1}{2}\{n_{\mathrm{CC}}\, V_{\mathrm{sCC}}^{\mathrm{T}}(x_{\mathrm{CC}}\, R) + m n_{\mathrm{AA}}\, V_{\mathrm{sAA}}^{\mathrm{T}}(x_{\mathrm{AA}}\, R)\} \\ &\qquad + E_{\mathrm{re}}^{\mathrm{C}}(R) + m E_{\mathrm{re}}^{\mathrm{A}}(R) + U_{\mathrm{disp}}(R), \end{aligned} \tag{2.16a}$$

with

$$V_{\mathrm{sab}}^{\mathrm{T}}(x_{\mathrm{ab}}\, R) = V_{\mathrm{sab}}^{0}(x_{\mathrm{ab}}\, R) + V_{\mathrm{sab}}^{\mathrm{corr}}(x_{\mathrm{ab}}\, R), \tag{2.16b}$$

so that $V_{\mathrm{sab}}^{\mathrm{T}}(x_{\mathrm{ab}}\, R)$ can be regarded as a short-range potential corrected for short-range explicitly overlap dependent correlation. In (2.16) $U_{\mathrm{disp}}(R)$ is the total dispersion energy whose calculation is described in §2*c*. As the inter-ionic dispersion interactions decrease relatively slowly with distance, the leading term varying as R^{-6}, the interactions between all the ions must be considered, unlike the short-range overlap correlation $V_{\mathrm{sab}}^{\mathrm{corr}}(x_{\mathrm{ab}}\, R)$. For all the ions studied except oxide O^{2-} the rearrangement energies $E_{\mathrm{re}}^{\mathrm{a}}(R)$ are small so that the correlation contribution to these energies will be even smaller and can therefore be neglected.

The free doubly charged oxide ion O^{2-} is unknown because it is unstable with respect to decay into a single charged oxide ion O^{-} and a free electron. Hence for oxides, the experimentally observable quantity is the energy of the lattice relative to free cations, free O^{-} ions and free electrons (Cohen & Gordon 1976). This observable crystal binding energy is still given by (2.16) provided the definition (2.11) of the rearrangement energy is replaced by

$$E_{\mathrm{re}}^{\mathrm{O}^{2-}}(R) = E_{\mathrm{O}^{2-}}(R) - E_{\mathrm{O}^{-}} + E_{\mathrm{re}}^{\mathrm{corr}}, \tag{2.17}$$

where the energy $E_{\mathrm{O}^{-}}$ of the O^{-} ion is evaluated as (2.12) with $|\varPhi_{\mathrm{O}^{-}}^{\mathrm{F}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_9)\rangle$ the single determinant Dirac–Fock O^{-} ion wavefunction. The correlation contribution $E_{\mathrm{re}}^{\mathrm{corr}}$, which is taken to be independent of R, is derived by subtracting the correlation energy of O^{2-}, estimated by extrapolating along the neon iso-electronic sequence (Clementi & McLean 1964), from the known correlation energy of O^{-} (Clementi & McLean 1964). The rearrangement correlation contribution $E_{\mathrm{re}}^{\mathrm{corr}}$ is then found to be -0.083 a.u.† (Cohen & Gordon 1976).

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† 1 a.u. (atomic unit) = 1 hartree ≈ 4.359828 aJ.

(*b*) *Description of the crystalline environment*

(i) *Basic physics*

The inter-ionic pair potentials (2.8) can only be calculated after orbitals suitably adapted to the crystalline environment have been computed. A fundamental theory of the effect of the environment on the ion wavefunctions would be developed by assuming that the crystal wavefunction (2.1) can be written as a product of ion wavefunctions (2.2) each of which is constructed from orbitals having a central field form with respect to the ion and then demanding, subject to appropriate orthonormality constraints, that the total crystal energy $E_{\mathrm{cr}}(R)$ be stationary with respect to variation of the radial parts of each of the central field orbitals. Such a theory could then be cast into a form yielding the orbitals of any ion as eigenfunctions of a Fock-like operator which contains, besides purely intra-ionic terms, additional operators originating from the environment. These additional operators can be divided into two classes: first, those constituting the purely coulombic potential generated by the nuclei and electrons of the surrounding ions, and second, those originating from the overlap of the occupied orbitals of one ion with the occupied orbitals of neighbouring ions.

The operators originating from the environment, whether local or non-local, can be expanded in spherical tensors defined with the nucleus of the relevant ion as origin. It is shown in Appendix 1 for closed shell ions that only the spherically symmetric (rank zero tensor) part of this expansion contributes to the energy if for every sub-shell A the radial parts of all the $2j_{\mathrm{A}}+1$ orbitals belonging to that sub-shell are taken to be identical. It should be stressed that this result is a purely mathematical consequence of the assumption that the radial parts of the orbitals belonging to a sub-shell are identical and that it is not assumed that the environment can be replaced by its spherical average.

(ii) *Potential for anion electrons*

For an anion whose nucleus is taken as the origin, the negative of the spherically symmetric part of the electrostatic potential generated by a cubic lattice of ions each described as a point charge is constant and negative from the origin out to a distance equal to closest cation–anion separation R. This function then increases rapidly for large separations and tends to zero at large distance (see figures 1 and 3 of Mahan 1980) after small oscillations associated with non-nearest neighbour separations. The addition of this function, which describes the influence of a point charge lattice on an anion electron, to the free ion Dirac–Fock hamiltonian causes the outermost orbitals of an anion to contract relative to those of the free ion. These contractions are illustrated by the orbital mean radii for the fluoride ion in sodium fluoride at $R = 4.5$ reported in column 3 of table 1. The much smaller expansion of the 2s orbital is a secondary effect caused by the contraction of the 2p orbitals. The decrease of the short range $\mathrm{Na^+}$–$\mathrm{F^-}$ repulsion $V^0_{\mathrm{sCA}}(R)$ (2.14) caused by the contraction of the fluoride ion more than offsets the rearrangement energy (2.11) thus causing the binding energy U^0_{L} (4.5) to be slightly more negative than that calculated by using free ion wavefunctions. The binding energy calculations reported in this subsection include only the Madelung, rearrangement and uncorrelated short-range $\mathrm{Na^+}$–$\mathrm{F^-}$ repulsion terms. The essential conclusions of this section do not require consideration of the remaining terms.

In contrast to the anion orbital contractions induced by a point charge lattice, these orbitals are predicted to expand if the electrostatic potential generated by the nearest cations is

Table 1. Ion wavefunction influence on the crystal binding energy of sodium fluoride at $R = 4.5$ kJ mol^{-1}

	Description of potential from environment used to compute wavefunctions$^{(1)}$						
	(1) free	(2) exact DC	(3) point charge	(4)	(5) Watson shell	(6) (2.18)	(7) full Watson shell
$\langle r \rangle$/a.u.							
1s	0.1752	0.1752	0.1752	0.1752	0.1752	0.1752	0.1752
2s	1.0340	1.0324	1.0350	1.0344	1.0361	1.0361	1.0361
$2\bar{p}$	1.2525	1.2692	1.2403	1.2467	1.2175	1.2207	1.2175
2p	1.2574	1.2746	1.2450	1.2512	1.2211	1.2243	1.2211
ϵ/Ryd							
1s	51.7178	52.5502	52.4702	52.4837	52.4078	52.4016	52.4078
2s	2.1560	2.9695	2.9150	2.9247	2.8822	2.8710	2.8822
$2\bar{p}$	0.3652	1.1762	1.1263	1.1349	1.0952	1.0840	1.0952
2p	0.3593	1.1701	1.1207	1.1292	1.0897	1.0785	1.0897
$E_{\mathrm{re}}^{\mathrm{tot}(2)}$	0.0	9.2	2.8	0.6	11.5	9.7	13.9
V_{sCA}^{0} (4.5)	23.5	26.2	20.6	22.1	17.1	17.5	16.8
$V_{\mathrm{int}}{}^{(3)}$	878.6	862.6	896.0	886.9	917.0	914.7	918.6
$-U_{\mathrm{L}}^{0}$ (4.5)$^{(4)}$	878.6	853.4	893.2	886.3	905.5	905.0	904.7

(1) Free Na$^+$ wavefunctions used for columns (1)–(6), hence $E_{\mathrm{re}}^{\mathrm{C}}$ (4.5) = 0.

(2) $E_{\mathrm{re}}^{\mathrm{tot}} = E_{\mathrm{re}}^{\mathrm{C}}(4.5) + E_{\mathrm{re}}^{\mathrm{A}}(4.5)$.

(3) $V_{\mathrm{int}} = (M/4.5) - 6V_{\mathrm{sCA}}^{0}(4.5)$.

(4) $-U_{\mathrm{L}}^{0}(4.5) = V_{\mathrm{int}} - E_{\mathrm{re}}^{\mathrm{tot}}$ is crystal cohesive energy for $R = 4.5$ a.u.

(1) Free F$^-$ wavefunctions.

(2) F$^-$ wavefunctions computed in the direct electrostatic potential generated by the Dirac–Fock charge distribution of nearest cations plus the potential arising from a point charge description of all other ions.

(3) F$^-$ wavefunctions computed in the electrostatic potential generated by a lattice of point charges.

(4) F$^-$ wavefunctions computed in potential due to a shell of total charge equal to the Madelung constant and of radius 4.5 a.u. This potential equals that of (3) for $r_{\mathrm{A}} \leqslant 4.5$ a.u.

(5) F$^-$ wavefunctions computed in potential due to a shell of total charge of 1 having a radius equal to the F$^-$ ionic radius (2.513 a.u.; Johnson 1968).

(6) F$^-$ wavefunctions computed in potential (2.18).

(7) F$^-$ wavefunctions computed as in (5). Na$^+$ wavefunction computed in potential due to a shell of total charge -1 of radius equal to the Na$^+$ ionic radius (1.890 a.u.; Johnson 1968).

calculated from the full cation Dirac–Fock charge distribution rather than by approximating these ions as point charges. These expansions, illustrated by the sodium fluoride results in column 2 of table 1, arise because the attractive well generated by the full cation nuclear charge is much greater in magnitude than the purely electrostatic repulsion generated by the cation electrons. These orbital expansions increase the short-range cation–anion repulsion thus causing the binding energy U_{L}^{0} (4.5) to be less negative, even disregarding the positive contribution of the rearrangement energy (2.11). This approach (labelled DC by Andzelm & Piela 1977) of using the full Dirac–Fock nearest neighbour ion wavefunctions to generate the electrostatic potential added to the free anion Dirac–Fock hamiltonian is incorrect on both physical and mathematical grounds unless the further terms that arise from overlap of the anion wavefunctions with neighbouring cation wavefunctions are also included. These additional terms, whether represented by a local function or more exactly by some non-local operator, constitute an additional repulsive potential acting on an anion electron in spatial regions where the density of neighbouring cation electrons is appreciable. This repulsive potential arises from the increase in kinetic energy caused by the requirement that the anion orbitals must be orthogonal to the cation orbitals; the orthogonality requirement originates from the Pauli principle. This DC approach is incorrect physically because the overlap repulsion more than outweighs the attractive well arising from the nuclei of neighbouring cations. The DC approach also fails mathematically because the variation principle, which can be used to gauge the quality of wavefunctions describing states containing only electrons and no positrons, shows that the crystal wavefunction (2.1) constructed from free ion wavefunctions (2.13) is a better approximation than the function (2.1) built from the ion wavefunctions of the DC approach. Thus the DC approach predicts a less negative binding energy and hence a total crystal energy less negative than that calculated by using free ion wavefunctions (2.13).

The spherically symmetric component $\hat{F}^{(0)}_{\text{env}}(r_{\text{A}}; R)$ of the operator for the potential energy of an anion electron, arising from its interaction with the crystalline environment, is hard to construct exactly because the overlap contribution to $\hat{F}^{(0)}_{\text{env}}(r_{\text{A}}; R)$ will be non-local. However, the variation principle justifies the use of approximations to the potential because the greater the predicted lattice energy the more closely the potential approximates the true crystalline potential and the more closely the resulting ion wavefunction (2.2) approximates the true ion wavefunction. The potential function of r_{A}, the distance from the anion nucleus, which depends parametrically on the closest cation–anion separation R,

$$\left.\begin{aligned}\hat{F}^{(0)}_{\text{env}}(r_{\text{A}}; R) &= -k_{\text{env A}}/(R-R_0), \quad r_{\text{A}} \leqslant R-R_0\\ &= -k_{\text{env A}}/r_{\text{A}}, \quad r_{\text{A}} \geqslant R-R_0\end{aligned}\right\}, \tag{2.18}$$

with

$$k_{\text{env A}}/(R-R_0) = \phi_{\text{env A}}/R, \tag{2.19}$$

has the correct physical behaviour, qualitatively reproducing the exact $\hat{F}^{(0)}_{\text{env}}(r_{\text{A}}; R)$. The ratio $-\phi_{\text{env A}}/R$ reproduces exactly the electrostatic potential energy of an electron at the anion nucleus arising from a point charge lattice thus defining the constant $k_{\text{env A}}$. For the NaCl lattice $\phi_{\text{env A}}$ is the Madelung constant, while for the fluorite lattice $\phi_{\text{env A}}$ equals the Madelung constant of CsCl lattice (Benson & van Zeggeren 1957). The contribution to the exact potential energy operator $\hat{F}^{(0)}_{\text{env}}(r_{\text{A}}; R)$ arising from overlap with neighbouring ions is negligible at small distances r_{A} from the anion nucleus, where the amplitudes of the orbitals of neighbouring ions is minute. As examination of the exact $L = 0$ component of the electrostatic potential generated by the Dirac–Fock charge distributions of neighbouring ions showed this to approximate that generated by the corresponding lattice of point charges, being constant for those small r_{A} at which the electron density of neighbouring cations is negligible, the potential (2.18) has the correct physical behaviour at small r_{A}. A suitable choice for the parameter R_0 in (2.18) also ensures that the physical behaviour of (2.18) is correct at larger distances r_{A} for which the electron density of neighbouring ions is significant because this reproduces the increase of the potential caused by overlap with neighbouring ions. The choice of either the ionic radius of the neighbouring cation or of some parameter reproducing this ensures that (2.18) has the correct physical behaviour for all r (see figure 3 of Mahan 1980). The choice $1.85\sqrt{\epsilon_0}\langle r_0\rangle$ for R_0, where ϵ_0 and $\langle r_0\rangle$ are the eigenvalues and mean radius of the outermost cation orbital in atomic units reproduces the covalent radii of the groups IA and IB ions, while a similar expression reproduces the univalent radius of Pb^{2+} to which the normal ionic radius can be related (Pauling 1960).

The very close similarity (columns 3 and 4 of table 1) between the orbital radii and binding energies predicted by using the $L = 0$ component of the exact electrostatic potential generated by a point charge lattice and those predicted when this potential is replaced by $-\phi_{\mathrm{env\,A}}/R$ for $r_A \leqslant R$ and by $-\phi_{\mathrm{env\,A}}/r_A$ for $r_A \geqslant R$ shows that the details of the potential for $r_A > R$ are unimportant. Hence the use of (2.18) is in no way impaired by the absence of these details. Table 1 shows that the anion orbitals computed by adding the potential energy (2.18), which simulates the overlap repulsion, to the free ion Dirac–Fock operator are significantly contracted compared with both those of the free ion and those of the ion subject to the purely electrostatic potential of a point charge lattice. Furthermore, the short-range cation–anion repulsion $V^0_{\mathrm{sCA}}(R)$ is significantly reduced, thereby predicting a considerably more negative crystal binding energy.

Although the potential (2.18) is that due to a spherical shell of charge $k_{\mathrm{env\,A}}$ and radius $(R-R_0)$, it differs from the Watson shell model (Watson 1958; Schmidt *et al.* 1979) in which the potential is that due to a shell of radius equal to the anion radius carrying a total charge equal to minus the anion charge. Thus the potential (2.18), unlike that due to Watson shell which is independent of R, has the correct physical variation with cation–anion separation R, and tends to zero for large R. For NaF at $R = 4.5$ the anion orbitals and crystal binding energy (column 5 of table 1) predicted by using the Watson shell model differ very little from those predicted with (2.18) (column 6 of table 1) because the Watson shell potential is very similar to (2.18) for values of R close to the experimental R_e (4.38 a.u.).

(iii) *Potential for cation electrons*

For a cation whose nucleus is taken as the origin, the negative of the spherically symmetric part of the electrostatic potential generated by a point charge lattice is positive and constant for distances r_C from the cation nucleus less than the closest cation–anion separation R. This potential then decreases for larger r_C. The addition both of the correction arising from the spatial extension of the electron density of neighbouring anions and of the overlap repulsion causes the total potential energy to increase slightly at distances greater than the cation radius (see figure 3 in Mahan 1980). As this increase is not large, the spherically symmetric component of the operator for the environmentally generated potential energy of a cation electron will be taken to be

$$\left.\begin{aligned} \hat{F}^{(0)}_{\mathrm{env}}(r_C;R) &= \phi_{\mathrm{env\,C}}/R \quad & r_C \leqslant R \\ &= \phi_{\mathrm{env\,C}}/r_C \quad & r_C \geqslant R \end{aligned}\right\}. \tag{2.20}$$

The constant $\phi_{\mathrm{env\,C}}$ is chosen such that (2.20) exactly equals the potential energy of an electron at the cation nucleus generated by a point charge lattice. As this definition of $\phi_{\mathrm{env\,C}}$ ensures that (2.20) is correct at small r_C while the decrease for $r_C > R$ is also reproduced, (2.20) has the correct physical behaviour for all r_C. For the NaCl lattice $\phi_{\mathrm{env\,C}} = \phi_{\mathrm{env\,A}}$ and also equals the Madelung constant M_{NaCl} of the lattice, while for the fluorite lattice $\phi_{\mathrm{env\,C}} = \sqrt{\tfrac{3}{2}}M_{\mathrm{NaCl}} + M_{\mathrm{CsCl}}$, where M_{CsCl} is the Madelung constant for the CsCl lattice (Benson & van Zeggeren 1957). For all cation–anion separations R, other than those small R yielding repulsions $V^0_{\mathrm{sCA}}(R)$ so large as to render the crystal configuration energetically inaccessible, the cation orbitals have only minute amplitudes at distances $r_C > R$. Consequently, the cation wavefunctions computed with the addition of (2.20) to the free ion Dirac–Fock hamiltonian are virtually identical to those of the free cation.

The potential (2.20) is qualitatively different from that (figure 1 of Schmidt *et al.* 1979) generated by a Watson shell of radius equal to the cation radius and carrying a charge equal to minus the cation charge. This potential is physically incorrect because it decreases rapidly at distances greater than the cation radius rather than increasing slightly. The use of such a qualitatively incorrect environmental potential can cause the cation orbitals to be excessively expanded compared with those of the free ion. For NaF at $R = 4.5$ a.u. the binding energy (table 1, column 7) predicted by using the Watson shell model to generate both cation and anion wavefunctions is only slightly less negative than that predicted by using the potentials (2.20) for the cation and (2.18) for the anion. However, the results for other systems, particularly PbF_2 discussed later, clearly reveal the deficiencies of the Watson shell model for cations.

(iv) *Total environmental potential*

The operators (2.18) and (2.20), describing the environment of anion and cation orbitals respectively, provide an approximate representation of the exact potential but one which, nonetheless contains the essential physics.

The localized orbital formalism (Adams 1961, 1962; Gilbert 1964) might seem to be preferable for computing atomic orbitals adapted to the crystalline environment (Kunz 1973*a*, *b*); Pantelides *et al.* 1974) because this provides an equation for generating such orbitals that is formally exact even though it contains an arbitrary operator $\hat{A}$. However, although the choice of the localizing potential $\hat{A}$ is in principle arbitrary, the degree to which the exact solutions of any Adams–Gilbert equations are localized about just one centre must depend on the choice for $\hat{A}$. Thus for the valid choice $\hat{A} = 0$, the Adams–Gilbert equations reduce to the Hartree–Fock equations for the entire crystal whose solutions are delocalized orbitals. However, in this case the assumption that the orbitals are localized about only one centre reduces the Adams–Gilbert equations (equation 5 of Kunz 1973*a*) to the atomic Hartree–Fock equations incorporating the electrostatic environmental potential of the DC approach (Andzelm & Piela 1977) which has been shown to be unsatisfactory. This example shows that the orbitals computed through the Adams–Gilbert formalism depend on the arbitrary choice of the localizing potential $\hat{A}$ if the orbitals are forced to be centred on just one nucleus having the standard central field form with respect to that nucleus as origin. There is, therefore, no reason to prefer this formalism over the potentials (2.18) and (2.20) even if the Adams–Gilbert equations, which are greatly complicated by the presence of multi-centre integrals, could be solved for the heavy ions considered in this paper.

(*c*) *The dispersion energy*

(i) *Fundamental theory*

The total dispersion energy $U_{\mathrm{disp}}(R)$ of a crystal composed of closed shell ions can be written

$$U_{\mathrm{disp}}(R) = -\sum_{\mathrm{a}=1}^{N_{\mathrm{ion}}-1} \sum_{\mathrm{b}=\mathrm{a}+1}^{N_{\mathrm{ion}}} \sum_{n=6,8,\ldots} \chi_n^{\mathrm{ab}}(x_{\mathrm{ab}} R)\, C_n(\mathrm{ab})\, (x_{\mathrm{ab}} R)^{-n}. \tag{2.21}$$

Here $C_n(\mathrm{ab})$ is the dispersion coefficient yielding that part of the dispersive attraction $C_n(\mathrm{ab})\, r_{\mathrm{ab}}^{-n}$ between the ions a and b (r_{ab} is the a–b internuclear separation) which varies as r_{ab}^{-n} in the limit of negligible wavefunction overlap. The quantities $\chi_n^{\mathrm{ab}}(r)$ are damping parameters (Jacobi & Czanak 1975; Koide 1976) which are unity for distances r for which the overlaps of the wavefunctions of ion a with those of ion b are negligible, but which reduce the undamped energies $C_n(\mathrm{ab})\, r_{\mathrm{ab}}^{-n}$ when wavefunction overlap is not negligible. For inter-ionic distances where overlap is appreciable, the damping functions $\chi_n^{ab}(r)$ decrease rapidly with increasing n so that terms with high n in (2.21) are unimportant; the r^{-n} dependence also ensures that these terms are unimportant at large r.

The overlaps between all pairs of ions except the closest cation–anion, anion–anion and cation–cation pairs will be negligible so that the corresponding dispersion damping parameters can be replaced by unity. After invoking this simplification and retaining only the dominant C_6 (dipole–dipole) and C_8 (dipole–quadrupole) terms, the total dispersion energy (2.21) for a CA_m crystal becomes

$$U_{\text{disp}}(R) = U_{\text{disp}}^{\text{un}}(R) + U_{\text{disp}}^{\text{cd}}(R), \tag{2.22}$$

$$U_{\text{disp}}^{\text{un}}(R) = -\sum_{n=6,8} [S_n(\text{CA})\, C_n(\text{CA}) + \tfrac{1}{2}(S_n(\text{CC})\, C_n(\text{CC}) + mS_n(\text{AA})\, C_n(\text{AA}))]\, R^{-n}, \tag{2.23}$$

$$\begin{aligned} U_{\text{disp}}^{\text{cd}}(R) = -\sum_{n=6,8} \{ & n_{\text{CA}}(\chi_n^{\text{CA}}(R) - 1)\, C_n(\text{CA})\, R^{-n} + \tfrac{1}{2}[n_{\text{CC}}(\chi_n^{\text{CC}}(x_{\text{CC}} R) - 1)\, C_n(\text{CC})\, (x_{\text{CC}} R)^{-n} \\ & + m n_{\text{AA}}(\chi_n^{\text{AA}}(x_{\text{AA}} R) - 1)\, C_n(\text{AA})\, (x_{\text{AA}} R)^{-n}]\}. \end{aligned} \tag{2.24}$$

Here $U_{\text{disp}}^{\text{un}}(R)$ is the 'undamped' dispersion energy predicted if all the dispersion damping parameters are unity, while $U_{\text{disp}}^{\text{cd}}(R)$ is the correction which replaces the undamped by the damped dispersion interaction for the closest cation–anion, anion–anion and cation–cation pairs. The constant $S_n(\text{XY})$ is a purely geometrical factor which yields the undamped R^{-n} dispersion interaction of one ion of type X with all other ions of type Y as $S_n(\text{XY})\, C_n(\text{XY})\, R^{-n}$.

For four common lattice types the values of the lattice dispersion sum constants $S_n(\text{XY})$ computed by direct summation in real space are reported in table 2. These results agree with those derived (Tosi 1964) from the lattice sum constants for close-packed homonuclear lattices calculated by Ewald summation techniques (Lennard-Jones & Ingham 1925). The derivation (Tosi 1964) of these constants from the homonuclear results was also found to be correct in an independent check made in the present work. This check coupled with the agreement between the two sets of results provides strong evidence that the values reported in table 2 are correct and that the two different sets of results (Morris 1957; Reitz *et al.* 1961) for the fluorite structure and the slightly different results (Mayer 1933; Waddington 1959) for $S_8(\text{AC})$ and $S_8(\text{AA})$ in the CsCl structure are in error. The results of table 2, unlike those (Morris 1957; Reitz *et al.* 1961; Mayer 1933; Waddington 1959) believed to be in error, satisfy the relations $S_n(\text{CA})(\text{CaF}_2) = S_n(\text{CA})(\text{CsCl}) = 2S_n(\text{CA})(\text{ZnS})$ and $S_n(\text{AA})(\text{CaF}_2) = S_n(\text{AA})(\text{CsCl})$ where the bracketed chemical formulae denote the crystal structure with ZnS being the zinc blende structure.

TABLE 2. LATTICE DISPERSION SUM CONSTANTS†

Lattice type	$S_6(\text{CA})$	$S_6(\text{CC})$	$S_8(\text{CA})$	$S_8(\text{CC})$
NaCl	6.5952	1.8067	6.1457	0.8001
CsCl	8.7090	3.5445	8.1575	2.1977
ZnS	4.3544	0.7622	4.0787	0.2532
CaF_2	8.7090	0.7622	8.1575	0.2532

† For NaCl, CsCl and ZnS (zinc blende) structure $S_n(\text{AA}) = S_n(\text{CC})$. For CaF_2 $S_6(\text{AA}) = 3.5445$, $S_8(\text{AA}) = 2.1977$.

In principle the crystal dispersion energy can be calculated *ab initio* from (2.21) to (2.24) because the dipole–dipole C_6(ab) and dipole–quadrupole C_8(ab) dispersion coefficients can be computed (Dalgarno & Davison 1966; Buckingham 1967; Doran 1974) as integrals over the appropriate frequency-dependent ion polarizabilities which can be computed *ab initio*. The damping functions could also be computed *ab initio* as integrals over certain generalized polarizabilities (Koide 1976). However, the *ab initio* computation of both the dispersion coefficients and damping functions for ions in crystals, although possible in principle, constitutes a major task which has not yet been done. The difficulties would be especially severe for the heavier ions such as Pb^{2+}, where relativistic effects would need to be considered. Hence in the present work these important parameters must be estimated by using less rigorous methods. It is shown in the next section that the dispersion coefficients can be estimated reliably by a semi-empirical approach, while a non-empirical method for calculating the dispersion damping parameters is presented in §2 (*c*) (iii).

(ii) *Dispersion coefficients*

The dipole–dipole C_6 coefficient. The dipole–dipole dispersion coefficient $C_6(Li^+ Li^+)$ for the interaction of two gaseous Li^+ ions is known exactly from *ab initio* calculation (Glover & Weinhold 1977). The C_6 coefficients can, in principle, be derived also from experiment by integration of the optical spectra of crystals (Mayer 1933; Lynch 1967). However, this method, although providing a useful check on the semi-empirical calculation described below (see Appendix 2), has only been applied to a very small number of systems. Its applicability is also limited by the requirement that the experimental spectrum can be clearly separated into individual cation and anion contributions. However, since the C_6 coefficients, excepting $C_6(Li^+ Li^+)$, required here are not known from either *ab initio* calculation or experiment, semi-empirical methods of evaluation have to be used.

An approximate variational calculation (Slater & Kirkwood 1931) predicts the C_6 coefficient for the interaction between two species a and b to be

$$C_6(\mathrm{ab}) = \tfrac{3}{2}\alpha_\mathrm{a}\,\alpha_\mathrm{b}/[(\alpha_\mathrm{a}/P_\mathrm{a})^{\frac{1}{2}} + (\alpha_\mathrm{b}/P_\mathrm{b})^{\frac{1}{2}}], \tag{2.25a}$$

hence

$$C_6(\mathrm{aa}) = \tfrac{3}{4}\alpha_\mathrm{a}^{\frac{3}{2}}P_\mathrm{a}^{\frac{1}{2}}. \tag{2.25b}$$

Here α_a is the static dipole polarizability of a, and P_a, the electron number, is the effective number of electrons contributing to the polarizability. It is shown in Appendix 2 that the Slater–Kirkwood formula with P_a taken as the number of electrons in the outermost shell of a predicts the accurately known C_6 coefficients for the inert gases, alkali and alkaline earth metals and Hg much more reliably than either the London formula (Eyring *et al.* 1944; Salem 1960) or than the ground state expectation values of Fraga *et al.* (1976). The results show that the London formula is not reliable because the C_6 coefficients involving alkali and alkaline earth metals are overestimated by factors as great as three, while $C_6(K^+ K^+)$ is overestimated by a factor of two. The ground state expectation values (Fraga *et al.* 1976) also seriously overestimate the C_6 coefficients of the heavier inert gases and alkali metals and of all the alkaline earths. The Slater–Kirkwood approximation, however, does not suffer from these deficiencies with even the C_6 coefficients of some molecules being reliably predicted.

The Slater–Kirkwood approximation does least well for the inert gases Ne to Xe, where there is an ambiguity in the choice of the electron number which might plausibly assume any value between 6 and 8. In Appendix 2 it is shown that the Slater–Kirkwood formula with the electron number P_a chosen to reproduce exactly the coefficient $C_6(aa)$ for the interaction of two species a accurately reproduces the C_6 coefficients for pairs of unlike atoms. This method has the advantage of avoiding inaccuracies that might arise through ambiguities in the choice of P_a. The C_6 coefficients required in the present work are therefore calculated through (2.25) by using electron numbers that reproduce exactly known $C_6(aa)$ coefficients for systems iso-electronic with those of interest. For the alkali and alkaline earth cations and halide ions, P_a is chosen to reproduce the $C_6(aa)$ coefficient for the iso-electronic inert gas, while the electron number of Pb^{2+} is taken from Hg. As there is no system iso-electronic with Ag^+ whose $C_6(aa)$ coefficient is known from either experiment or accurate *ab initio* calculation, P_{Ag^+} is calculated from the values of α_{Ag^+} and $C_6(Ag^+\ Ag^+)$ computed (Mahan 1982) by using an approximate density functional description of exchange and correlation.

The in-crystal polarizabilities for Li^+, Na^+ and Mg^{2+} needed in (2.25) are taken to equal those of the gaseous ions because there is strong evidence that the polarizabilities of small cations remain essentially unchanged on passing from the gas to the crystal (Fowler & Madden 1983, 1984). These polarizabilities are known accurately from large basis set *ab initio* calculations in which the Hartree–Fock prediction is augmented by using second-order Moller–Plesset perturbation theory to compute the contribution originating from electron correlation (Fowler & Madden 1983, 1984, 1985). The polarizabilities of the anions in the crystals LiF, NaF, NaCl, and MgO are calculated by subtracting the known cation values from the molar crystal polarizabilities derived from experimental refractive index data extrapolated to infinite wavelength (Fowler & Pyper 1985). For AgF and PbF_2, the fluoride ion polarizability is derived from a function describing the dependence of α_{F^-} on the closest cation–anion separation (Fowler & Pyper 1985). The cation polarizabilities are then obtained by subtracting α_{F^-} from the molar crystal polarizability. The polarizability of Ag^+ is probably less firmly established than those of the other cations because there is evidence that α_{Ag^+} is substantially increased from the free ion value of 8.6 a.u. to 11.8 a.u. upon entering the AgF crystal (Fowler & Pyper 1985). However, the use of the free ion electron number to calculate the in-crystal C_6 coefficients is still fully consistent with the approach of deriving P_a from iso-electronic model systems. It should be pointed out that the computed crystal properties of AgF are surprisingly insensitive to the exact value used for α_{Ag^+} provided a value for α_{F^-} is used which yields the experimental molar polarizability (equal to $\alpha_{Ag^+}+\alpha_{F^-}$). The polarizabilities and electron numbers used are presented in table 3, while the C_6 coefficients calculated therefrom are reported in table 4.

TABLE 3. ION POLARIZABILITIES, ELECTRON NUMBERS AND DISPERSION DAMPING PARAMETERS$^{(1)}$

		cation			anion	
crystal	α_a	P_a	$d_{a1}{}^{(2)}$	α_a	P_a	$d_{a1}{}^{(2)}$
LiF	0.192	1.430	3.386	5.983	4.455	1.718
NaF	1.002	4.455	2.918	6.947	4.455	1.606
NaCl	1.002	4.455	2.918	21.153	6.106	1.528
AgF	11.825	5.863	1.514	7.435	4.455	1.567
PbF_2	17.924	2.605	2.744	7.783	4.455	1.551
MgO	0.486	4.455	3.860	11.345	4.455	1.820

(1) Polarizabilities α_a and dispersion damping parameters d_{a1} in atomic units.
(2) $d_{a2} = d_{a1}$ for all ions except Ag^+; $d_{Ag+2} = 2.336$ a.u.

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TABLE 4. INTER-IONIC DISPERSION COEFFICIENTS (IN ATOMIC UNITS)

crystal	C_6(CA)	C_6(CC)	C_6(AA)	C_8(CA)	C_8(CC)	C_8(AA)
LiF	1.130	0.078	23.167	10.587	0.278	351.968
NaF	6.061	1.588	28.986	62.655	8.558	443.071
NaCl	13.615	1.588	180.301	209.707	8.558	4582.659
AgF	47.973	71.970	32.093	624.058	762.761	494.832
PbF_2	53.045	91.858	34.372	711.042	1022.752	538.779
MgO	4.292	0.536	60.491	58.450	2.013	1420.423

The dipole–quadrupole C_8 coefficients. The coefficients $C_8(\mathrm{ab})$ yielding the dipole–quadrupole dispersion interaction $C_8(\mathrm{ab})\, r_{\mathrm{ab}}^{-8}$ were computed from the $C_6(\mathrm{ab})$ coefficients by using the formula of Starkschall & Gordon (1972)

$$C_8(\mathrm{ab}) = \tfrac{3}{2}C_6(\mathrm{ab})\,[(\langle r^4\rangle_{\mathrm{a}}/\langle r^2\rangle_{\mathrm{a}}) + (\langle r^4\rangle_{\mathrm{b}}/\langle r^2\rangle_{\mathrm{b}})]. \tag{2.26}$$

The ground-state expectation values $\langle r^n\rangle_{\mathrm{a}}$ were computed from the ion wavefunctions which had to be calculated as input to the relativistic program used to determine the short range V^0_{sab} ion–ion repulsions. It is shown in Appendix 3 that (2.26) reproduces the $C_8(\mathrm{ab})$ coefficients known more accurately from other sources.

It is also shown in Appendix 3 that both the approximate expression of Margenau (1939) and the more recent one of Narayan (1977) are quite unreliable. Thus the Margenau expression underestimates $C_8(\mathrm{ab})$ for the inert gases by factors which can be as great as five to eight while overestimating those of the alkali atoms by factors of two or three. The Narayan formula, however, always seems to underestimate $C_8(\mathrm{ab})$ by factors of four or more.

The $C_8(\mathrm{ab})$ coefficients used in this work which were computed from (2.26) and the C_6 coefficients of table 4 are also reported in table 4.

(iii) *The dispersion damping functions*

An exact expression, valid in the presence of non-negligible wavefunction overlap, for the total energy of interaction $U^{\mathrm{ab}}_{\mathrm{disp}}(r)$, between the pair of ions a and b, arising from dispersion has been presented by Jacobi & Csanak (1975). Their expression is

$$\begin{aligned} U^{\mathrm{ab}}_{\mathrm{disp}}(R) = {} & -\frac{2}{\pi^4}\frac{1}{4\pi}\sum_{L L' l}\begin{pmatrix} L & L' & l \\ 0 & 0 & 0 \end{pmatrix}^2 [L]\,[L']\,[l] \\ & \times \int_0^\infty \mathrm{d}q \int_0^\infty \mathrm{d}q'\, j_l(qR)\, j_l(q'R) \sum_{\bar{e}_{\mathrm{a}}\bar{e}_{\mathrm{b}}} \int_0^\infty \mathrm{d}u \\ & \times [X_{\bar{e}_{\mathrm{a}} L}(q)\, X_{\bar{e}_{\mathrm{a}} L}(q')\, (E_{\bar{e}_{\mathrm{a}} L} - E_{0,\mathrm{a}})\, ((E_{\bar{e}_{\mathrm{a}} L} - E_{0,\mathrm{a}})^2 + u^2)^{-1}] \\ & \times [X_{\bar{e}_{\mathrm{b}} L'}(q)\, X_{\bar{e}_{\mathrm{b}} L'}(q')\, (E_{\bar{e}_{\mathrm{b}} L} - E_{0,\mathrm{b}})\, ((E_{\bar{e}_{\mathrm{b}} L'} - E_{0,\mathrm{b}})^2 + u^2)^{-1}], \end{aligned} \tag{2.27}$$

where $j_l(x)$ is a spherical Bessel function (Rose 1961), $[L] = 2L+1$ and $E_{0,\mathrm{a}}$ is the ground state energy of ion a. The quantities $X_{\bar{e}_{\mathrm{x}} L}$ are defined through

$$X_{\bar{e}_{\mathrm{x}} L M}(\boldsymbol{q}) = X_{\bar{e}_{\mathrm{x}} L}(q)\, Y_{LM}(\hat{q}), \tag{2.28}$$

where

$$X_{\bar{e}_{\mathrm{x}} L M}(\boldsymbol{q}) \equiv X_{e_{\mathrm{x}}}(\boldsymbol{q}) = \int \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})\, X_{e_{\mathrm{x}}}(rr)\,\mathrm{d}r. \tag{2.29}$$

Here $X_{e_x}(rr)$ is the one-electron transition density matrix element between the ground state and excited state e_x of ion x. The symmetry of atomic systems enables the excited states to be classified by the quantum number L and M so that the triple label $\bar{e}_x LM$ can serve as an alternative to e_x. The quantity $E_{\bar{e}_x L}$ is the energy of the excited state $\bar{e}_x LM$ of atom x. It should be stressed that the transition density matrix element $X_{e_x}(rr)$ is by definition a one-electron function even when derived from exact correlated wavefunctions for the ground and excited state so that its Fourier transform also has this property. Symmetry dictates that the transform can be factorized according to (2.28).

The term in (2.27) with $L = L' = 1$ yields the dipole–dipole dispersion energy, while the sum of that having $L = 1$ and $L' = 2$ and the one with $L = 2$ and $L' = 1$ yields the dipole–quadrupole dispersion energy. The quantities $X_{\bar{e}_x 1}q)$ and $X_{\bar{e}_x 2}(q)$ can be expressed (Csanak & Taylor 1972) as

$$X_{\bar{e}_x 1}(q) = D_{e_x}\, d_{x1}^6\, q(q^2+d_{x1}^2)^{-3}, \tag{2.30}$$

$$X_{\bar{e}_x 2}(q) = \tfrac{1}{2} Q_{e_x}\, d_{x2}^8\; q^2(q^2+d_{x2}^2)^{-4}, \tag{2.31}$$

where D_{e_x} and Q_{e_x} are the dipole and quadrupole transition matrix elements which are independent of q. The quantities d_{x1} and d_{x2} which are related to the ionization potentials in the ground and excited state can be taken to a high degree of approximation to be independent of the particular excited state e_x (Lassettre 1965; Csanak & Taylor 1972). This approximation separates the q and q' integrations from the summation over excited states. For $L = L' = 1$, this later summation yields the C_6 coefficient, while the terms $L = 1$, $L' = 2$ and $L = 2$, $L' = 1$ yield two contributions to the C_8 coefficient (Buckingham 1967). Hence the dispersion damping parameters $\chi_n^{ab}(r)$ required to calculate the dispersion energy via (2.24) can be derived by substituting (2.30) and (2.31) into (2.27) and calculating the resulting integrals over q and q' by contour integration. As the resulting algebra is very tedious it was done by using the algebraic manipulation program REDUCE on the University computer. The resulting damping functions are

$$\chi_6^{aa}(R) = [1-e^{-d_{a1}R}\, P_7(d_{a1}R)]^2 + \tfrac{2}{9}(d_{a1}R)^6\, [e^{-d_{a1}R}\, P_4(d_{a1}R)]^2; \tag{2.32}$$

$$\chi_8^{aa}(R) = [1-e^{-d_{a2}R}\, P_9(d_{a2}R)]^2 + \tfrac{1}{12150}(d_{a2}R)^{10}\, [e^{-d_{a2}R}\, P_4(d_{a2}R)]^2; \tag{2.33}$$

where

$$P_4(x) = \tfrac{1}{512}(7+7x+3x^2+\tfrac{2}{3}x^3+\tfrac{1}{15}x^4), \tag{2.34a}$$

$$P_7(x) = \tilde{P}_4(x) + \tfrac{31}{3840}x^5 + \tfrac{13}{11520}x^6 + \tfrac{1}{11520}x^7, \tag{2.34b}$$

$$P_9(x) = \tilde{P}_5(x) + \tfrac{1}{5120}x^7 + \tfrac{1}{46080}x^8 + \tfrac{1}{69120}x^9, \tag{2.34c}$$

$$\tilde{P}_n(x) = \sum_{m=0}^{n} x^m/m! \tag{2.34d}$$

$$\begin{aligned}\chi_6^{ab}(R) = {} & \left\{1 + d_{a1}\,d_{b1}\left(\frac{d_{a1}}{d_{b1}} - \frac{d_{b1}}{d_{a1}}\right)^{-5} [Q_1(d_{a1}, d_{b1}, R)\, e^{-d_{a1}R} - Q_1(d_{b1}, d_{a1}, R)\, e^{-d_{a2}R}]\right\}^2 \\ & + \tfrac{2}{9} d_{a1}^2\, d_{b1}^2\, R^4 \left(\frac{d_{a1}}{d_{b1}} - \frac{d_{b1}}{d_{a1}}\right)^{-10} [Q_2(d_{a1}, d_{b1}, R)\, e^{-d_{a1}R} - Q_2(d_{b1}, d_{a1}, R)\, e^{-d_{a2}R}]^2;\end{aligned} \tag{2.35}$$

$$Q_1(x, y, R) = [y^4x^{-6} - 5x^{-4}y^2 + 10x^{-2}]\, \tilde{P}_4(xR) - R^2[1 + xR + \tfrac{3}{8}(xR)^2 - \tfrac{1}{8}(yR)^2], \tag{2.36a}$$

$$Q_2(x, y, R) = -3 + (R/16)\,[14x^{-1}y^2 - 13x - x^{-3}y^4 + R(2y^2 - x^2 - x^{-2}y^4)]; \tag{2.36b}$$

$$\chi_8^{\mathrm{ab}}(R) = [C_8^{\mathrm{DQ}}(\mathrm{ab})\, \chi_8^{\mathrm{ab}}(R) + C_8^{\mathrm{QD}}(\mathrm{ab})\, \chi_8^{\mathrm{ba}}(R)]/C_8(\mathrm{ab}); \tag{2.37}$$

$$\begin{aligned}\chi_8^{\mathrm{ab}}(R) = {} & \left\{1+\left(\frac{d_{\mathrm{b}2}}{d_{\mathrm{a}2}}-\frac{d_{\mathrm{a}2}}{d_{\mathrm{b}2}}\right)^{-6}[Q_3(d_{\mathrm{a}2}, d_{\mathrm{b}2}, R)\,\mathrm{e}^{-d_{\mathrm{a}2}R}+Q_4(d_{\mathrm{a}2}, d_{\mathrm{b}2}, R)\,\mathrm{e}^{-d_{\mathrm{b}2}R}]\right\}^2 \\ & +\tfrac{8}{675}(d_{\mathrm{b}2}R)^4\left(\frac{d_{\mathrm{b}2}}{d_{\mathrm{a}2}}-\frac{d_{\mathrm{a}2}}{d_{\mathrm{b}2}}\right)^{-12}[Q_5(d_{\mathrm{a}1}, d_{\mathrm{b}1}, R)\,\mathrm{e}^{-d_{\mathrm{a}2}R}-Q_6(d_{\mathrm{a}1}, d_{\mathrm{b}1}, R)\,\mathrm{e}^{-d_{\mathrm{b}2}R}]^2;\end{aligned} \tag{2.38}$$

$$\begin{aligned}Q_3(x, y, R) = {} & [6x^{-4}y^4-x^{-6}y^6-15x^{-2}y^2]\,\tilde{P}_4(xR)+x^{-2}y^2[(xR)^2+(xR)^3] \\ & +\tfrac{1}{60}[27x^{-2}y^2-2x^{-4}y^4]\,(xR)^4-\tfrac{1}{120}x^{-4}y^4\left(\frac{y}{x}-\frac{x}{y}\right)^2(xR)^5,\end{aligned} \tag{2.39a}$$

$$\begin{aligned}Q_4(x, y, R) = {} & [20-15x^2y^{-2}+6x^4y^{-4}-x^6y^{-6}]\,\tilde{P}_5(yR)-(yR)^2-(yR)^3 \\ & +\tfrac{1}{60}(3x^2y^{-2}-28)\,(yR)^4+\tfrac{1}{60}(3x^2y^{-2}-8)\,(yR)^5+\tfrac{1}{720}x^3y^{-3}\left(\frac{y}{x}-\frac{x}{y}\right)^3(yR)^6,\end{aligned} \tag{2.39b}$$

$$Q_5(x, y, R) = 5+5xR-(y^2-x^2)\,R^2+\tfrac{1}{16}(y^2-x^2)^2\,x^{-1}\,R^3, \tag{2.39c}$$

$$Q_6(x, y, R) = 5+5yR+\tfrac{3}{2}(y^2-x^2)\,R^2+\tfrac{1}{96}(y^2-x^2)^2\,(19y^2-x^2)\,y^{-3}\,R^3+\tfrac{1}{96}(y^2-x^2)^3\,y^{-2}\,R^4. \tag{2.39d}$$

The dipole–quadrupole dispersion energy is the sum of two different terms, namely that ($L = 1$, $L' = 2$ in (2.27)) involving the dipole oscillator strength (2.30) on ion a with the quadrupole term (2.31) for ion b plus the $L = 2$, $L' = 1$ term which involves the quadrupole term for ion a plus the dipole term for ion b. As the damping factors for these two terms are different, the overall damping function (2.37) is a sum of two distinct terms where

$$C_8(\mathrm{ab}) = C_8^{\mathrm{DQ}}(\mathrm{ab})+C_8^{\mathrm{QD}}(\mathrm{ab}). \tag{2.40}$$

The quantities $C_8^{\mathrm{DQ}}(\mathrm{ab})$ and $C_8^{\mathrm{QD}}(\mathrm{ab})$ are calculated as the second and first terms in square brackets in (2.26) respectively. The result (2.32) for the damping function for the dipole–dipole interaction between identical ions agrees with that derived by Jacobi & Csanak (1975).

The dispersion damping parameters $d_{\mathrm{x}1}$ and $d_{\mathrm{x}2}$ are governed by the radius of convergence of power series (2.30) and (2.31) (Lassettre 1965, Csanak & Taylor 1972) which is determined by the asymptotic behaviour at large distance from the nucleus of the wavefunctions for the ground and first excited state contributing to the relevant oscillator strength (2.30) or (2.31). For a system where the potential experienced by an electron varies inversely with distance (i.e. is proportional to r^{-1}) at large distances r from the nucleus but where the electron density is not negligible, the dispersion damping parameter $d_{\mathrm{x}L}$ is given by

$$d_{\mathrm{x}L} = \surd(2\epsilon_{\mathrm{xog}})+\surd(2\epsilon_{\mathrm{xoe}}), \tag{2.41}$$

where ϵ_{xog} and ϵ_{xoe} are the eigenvalues (in atomic units) of the outermost orbitals of the ground and first relevant excited state of system x.

For the halide and oxide ions the outermost orbitals of both the ground $n\mathrm{p}^6$ and excited $n\mathrm{p}^5(n+1)\,\mathrm{s}$ states have appreciable amplitudes for distances $r_{\mathrm{A}} > R_0$ (2.18) for which the total potential experienced by an electron tends to zero as $-\mathrm{constant}/r_{\mathrm{A}}$. Hence the dispersion damping parameters reported in table 3 were calculated from (2.41) by using the eigenvalues, for the ion computed in the crystal potential (2.18), of the $n\mathrm{p}$ orbital in the ground $n\mathrm{p}^6$ state and of the $(n+1)\,\mathrm{s}$ orbital in the $n\mathrm{p}^5(n+1)\,\mathrm{s}$ excited state. As the $n\mathrm{p}^5(n+1)\,\mathrm{s}$ state is the lowest-energy excited state contributing to both the dipole–dipole and dipole–quadrupole dispersion energy, $d_{\mathrm{x}2}$ equals $d_{\mathrm{x}1}$.

For all the cations studied except Ag^{+}, the amplitudes of all the orbitals of both the ground and relevant excited states are negligible for distances $r_{\mathrm{C}} > R$ (2.20), thus showing that the crystal potential (2.20) is essentially a constant which merely shifts the eigenvalues of all orbitals by this constant ($\phi_{\mathrm{env\,C}}/R$). This interpretation is confirmed by the result that the eigenvalue of each orbital of the in-crystal ion is identical to the sum of the corresponding eigenvalue of the free ion plus $\phi_{\mathrm{env\,C}}/R$ and by the result that the expectation values $\langle r^{n}\rangle$ of the free and crystal orbitals are identical. Hence the parameters $d_{\mathrm{x}1}$ and $d_{\mathrm{x}2}$ for the alkali and alkaline earth cations except Li^{+} were derived from the free ion eigenvalues of the np orbitals of the ground $n\mathrm{p}^{6}$ state and of the $(n+1)$ s orbital in the $n\mathrm{p}^{5}(n+1)$ s excited state. For Li^{+} and Pb^{2+}, $d_{\mathrm{x}1}$ and $d_{\mathrm{x}2}$ were derived from the free ion eigenvalues of the 1s and 6s orbitals orbitals in the respective $1\mathrm{s}^{2}$ and $6\mathrm{s}^{2}$ ground states and of the 2p and 6p orbitals in the respective 1s2p and 6s6p excited states.

The free and in-crystal 5s orbitals of the Ag^{+} $4d^{9}5\mathrm{s}$ state, which is the lowest excited state contributing to C_{8} coefficients involving Ag^{+}, have identical $\langle r^{n}\rangle$, are negligible for $r_{\mathrm{c}} > R$ and have eigenvalues differing by $\phi_{\mathrm{env\ C}}/R$. The parameter $d_{\mathrm{Ag}^{+}2}$ was therefore calculated by using (2.41) from the free ion eigenvalues of the $4d$ orbital in the $4d^{10}$ ground state and of the 5s orbitals in the $4d^{9}5\mathrm{s}$ state. The $4d^{9}5\mathrm{s}$ state does not contribute to any C_{6} dispersion energy, the $4d^{9}5\mathrm{p}$ state being the lowest energy contributor to the Ag^{+} dipole oscillator strength. However, this state has $\langle r\rangle_{5\mathrm{p}} = 5.38$ a.u. in the crystal but $\langle r\rangle_{5\mathrm{p}} = 3.71$ a.u. in the free state showing that the 5p orbital does experience the spatial region in the crystal where the potential varies as $-\mathrm{constant}/r_{\mathrm{C}}$. The parameter $d_{\mathrm{Ag}^{+}1}$, was therefore calculated from the free ion eigenvalue of the $4d$ orbital in the $4d^{10}$ ground state and from the in-crystal eigenvalue of the 5p orbital in the $4d^{9}5\mathrm{p}$ state.

All the dispersion damping parameters used are reported in table 3. The reliability of the computed dispersion damping functions can be assessed from the results presented in Appendix 4.

3. Crystal property predictions

(*a*) *Comparison of wavefunctions*

In table 5 are shown the lattice energy, closest equilibrium inter-ionic separation R_{e} and compressibility for LiF, NaF, NaCl, AgF and PbF_{2} predicted from (2.16*a*) for three different descriptions of the ionic wavefunctions (2.2) both with and without the damped dispersion energy U_{disp} (see (2.22)). In all the calculations reported in this table the uncorrelated short-range cation–anion repulsions $V^{0}_{\mathrm{sCA}}(R)$ ((2.14) and (2.8)) were computed exactly by using the relativistic integrals program RIP, but the cation–cation and anion–anion uncorrelated short-range interactions were calculated from the Lloyd & Pugh exchange corrected electron-gas method (Lloyd & Pugh 1977; Wood & Pyper 1981). Each ion was taken to contribute eight electrons to the total number of valence electrons per ion pair needed to evaluate the Lloyd & Pugh exchange correction factor, except for Li^{+}, Ag^{+} and Pb^{2+}, which were taken to contribute two, ten and twelve electrons respectively (Wood & Pyper 1981). The electron-gas correlation contributions ($V^{\mathrm{corr}}_{\mathrm{sCA}}$, $V^{\mathrm{corr}}_{\mathrm{sCC}}$, $V^{\mathrm{corr}}_{\mathrm{sAA}}$) to the short-range potentials were included in all the calculations reported in table 5. The cation–anion short-range potentials and re-arrangement energies (2.11) are reported in Appendix 5.

Three main conclusions can be drawn from the results of table 5. First, the use of free ion wavefunctions, whether without (column 1) or with (column 4) the damped dispersion energy,

Table 5. Comparison of crystal properties predicted with different ion wavefunctions(1)

		without dispersion(2) wavefunction type(4)			computed with (2.16)(2) (3) wavefunction type(4)			
		free(5)	Watson(5)	(2.18) + (2.20)	free	Watson	(2.18) + (2.20)	experiment
LiF	D_e	944	991	992	957	1006	1007	1036(6)
	R_e	4.24	4.05	4.03	4.19	4.02	3.99	3.80(7)
	B	4.43	7.98	7.75	5.08	8.63	7.05	6.98(8) 7.2(9) 8.67(10) (11)
NaF	D_e	880	908	908	896	925	927	923(6) 931(12)
	R_e	4.62	4.48	4.46	4.57	4.44	4.41	4.38(7)
	B	4.58	5.43	5.05	4.85	5.78	5.50	5.14(13) 5.17(12)
NaCl	D_e	720	738	738	742	763	765	773(14) 786(6)
	R_e	5.72	5.57	5.55	5.61	5.47	5.43	5.33(15)
	B	2.08	2.54	2.33	2.33	2.87	2.67	2.66(12) 2.74(16)
AgF	D_e	870	877	874	930	940	934	942(15) 953(14)
	R_e	4.85	4.77	4.83	4.73	4.655	4.70	4.66(17)
	B	5.19	6.12	5.32	6.29	7.46	6.40	—
PbF_2	D_e	2248	2276	2311	2330	2385	2406	2491(14)
	R_e	5.17	4.86	5.03	5.05	4.77	4.90	4.86(17)
	B	4.49	7.89	5.34	5.37	9.39	6.26	6.08(18) 6.27(19)

(1) D_e lattice energy in kilojoules per mole; R_e in bohr, B in 10^{12} newtons per square metre extrapolated to low temperature except PbF_2.

(2) All calculations included $V^0_{\mathrm{sCA}}(R)$ computed with RIP; $V^0_{\mathrm{sCC}}(x_{\mathrm{CC}}R)$ and $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}R)$ computed with the Lloyd & Pugh exchange corrected electron-gas method, and short-range correlation terms $V^{\mathrm{corr}}_{\mathrm{sCA}}(R)$, $V^{\mathrm{corr}}_{\mathrm{sCC}}(x_{\mathrm{CC}}R)$ and $V^{\mathrm{corr}}_{\mathrm{sAA}}(x_{\mathrm{AA}}R)$.

(3) Includes damped dispersion energy (2.22).

(4) Free: free ion wavefunctions; Watson: cation and anion wavefunctions computed in potential due to the Watson shell of total charge equal to minus the ion charge and radius equal to the ionic radius; (2.18) + (2.20): cation wavefunctions with description (2.20) of the environment and anion wavefunctions computed with (2.18).

(5) From Wood & Pyper (1986).

(6) Weast (1979, C.R.C. handbook).

(7) Muhlhausen & Gordon (1981*a*).

(8) Briscoe & Squire (1957).

(9) Kittel (1966).

(10) Susse & Rech (1961).

(11) Cohen & Gordon (1975).

(12) Vallin *et al.* (1966).

(13) Lewis *et al.* (1967).

(14) Johnson (1968).

(15) Tosi (1964).

(16) Frigate & Scheule (1966).

(17) Landolt-Börnstein (1973*a*).

(18) Samara (1976).

(19) Rimai & Sladek (1980).

predicts insufficiently strong binding as manifested by calculated lattice energies and compressibilities that are too small and calculated R_e values that are too large. This shows that the environmentally induced modifications of the free ion wavefunctions cannot be ignored if the crystal properties are to be described accurately. The second main conclusion to be drawn from table 5 is that the predictions of calculations that use wavefunctions computed in the potential of a Watson shell are not trustworthy. For LiF, NaF and NaCl the use of such wavefunctions yields results very similar to those derived from wavefunctions computed with the environmental potentials (2.18) and (2.20).

These predictions are similar because the Li^+ and Na^+ wavefunctions are so tightly bound that the Watson shell potential, which incorrectly decreases for distances r_C greater than the cation radius R_C, fails to perturb significantly the free ion wavefunctions, while for anions at R values close to R_e, the Watson shell potential is similar to (2.18). For anions at $R = R_e$ the Watson shell radius, which is taken to equal the anion radius (Watson 1958; Schmidt *et al.* 1979), is virtually identical to that of (2.18) constructed as $R - R_C$ simply because R_e is approximately the sum of the cation and anion radii. However, for PbF_2 without dispersion, the use of wavefunctions computed in the Watson shell potential predicts a lattice energy which is too small but a compressibility which is too large (column 2 of table 5). The perfect agreement between observed and calculated R_e values is clearly fortuitous because any incorporation of dispersion must reduce the predicted R_e to a value less than the experimental one. Indeed the addition of the damped dispersion energy (column 5 of table 5) predicts too small an R_e value, increases even more the too large compressibility of column 2, while still predicting too small a lattice energy. This unphysical combination of discrepancies between theory and experiment shows that the theoretical shortcomings of the Watson shell potential discussed in §2*b* cannot be ignored and hence that the Watson shell model should be regarded as unsatisfactory. For Pb^{2+} the Watson shell potential fails not only because it incorrectly decreases for $r_C > R_C$ but also because it is too large (0.87 a.u.) for $r_C < R_C$, the potential (2.20) due to a point charge lattice being only 0.67 a.u. at $r_C < R$ for $R = R_e$. Both these failures cause the Pb^{2+} wavefunction to be too expanded ($(\langle r \rangle_{6s} = 2.60$ a.u. compared with $\langle r \rangle_{6s} = 2.23$ a.u. with the potential (2.20)) leading to an excessively high re-arrangement energy (2.11) of 187 kJ mol^{-1} compared with 0.2 kJ mol^{-1} at $R = R_e$ for the wavefunction computed with the crystalline potential (2.20).

The third main conclusion from table 5 is that the predictions derived by using wavefunctions calculated with the description (2.18) and (2.20) of the crystalline potential do not suffer from the deficiencies of those derived by using either free ion wavefunctions or wavefunctions calculated in the Watson potential. In particular, the predictions (column 6 of table 5) derived with the inclusion of the damped dispersion energy not only agree fairly well with experiment but also show a systematic and physically sensible trend in their discrepancies with experiment. This the predicted lattice energies are always slightly too small with predicted R_e values slightly too large; this suggests that the entire crystal cohesion is slightly underestimated.

(*b*) *Predictions with exact non-correlated short-range potentials*

The conclusions of the last section, that the potentials (2.18) and (2.20) satisfactorily describe the environmentally induced modifications of the ion wavefunctions but that the crystal cohesion is slightly underestimated, suggest that the calculations should be repeated computing exactly, with the RIP program, all the uncorrelated short-range interactions. The results of such calculations, both with and without the inclusion of correlation, dispersion and dispersion damping are reported in table 6.

It is known that the crystal properties derived from $U_L(R)$ values computed for a finite number of values of R can depend on the numerical method used if this is not carefully chosen. The lattice energies, R_e values and compressibilities were derived from the best calculations (column 6) by fitting a polynomial of the highest possible order in $(R-R_e)/R$ to the total crystal cohesive energies $U_L(R)$. It will be shown in detail elsewhere that the results of this procedure, recommended as numerically stable (Simons *et al.* 1973), remain essentially unchanged if either the order of the polynomial is changed or if the number of points used to define the potential $U_L(R)$ is reduced. It will also be shown that the results derived by fitting the highest-order polynomial in R to all the points are identical to those derived from the $(R-R_e)/R$ fits. That method was used to derive all the results presented in this paper except those in column 6 of table 6.

In all the calculations reported in table 6, the anion–anion and cation–cation uncorrelated

TABLE 6. CRYSTAL PROPERTIES PREDICTED BY USING THE RIP PROGRAM WITH ION WAVEFUNCTIONS COMPUTED WITH THE ENVIRONMENTAL DESCRIPTION OF §2*b*(1)

		(1)(2)	(2) undamped dispersion	(3) undamped dispersion + correlation	(4) correlation	(5) damped dispersion	(6) correlation + damped dispersion	experiment(3)
LiF	D_e	1002	1032	1054	1021	1018	1038	1036
	R_e	3.97	3.86	3.81	3.92	3.93	3.885	3.808
	B	7.13	7.88	8.60	7.75	7.66	8.16	6.98, 7.2, 8.67
NaF	D_e	901	935	953	916	919	938	923, 931
	R_e	4.48	4.33	4.28	4.43	4.42	4.377	4.378
	B	4.88	5.51	5.97	5.23	5.29	5.69	5.14, 5.17
NaCl	D_e	732	767	788	749	758	778	773, 786
	R_e	5.56	5.36	5.28	5.48	5.44	5.363	5.329
	B	2.29	2.77	3.10	2.57	2.70	2.99	2.66, 2.74
AgF	D_e	847	1023	1086	881	906	944	942, 953
	R_e	4.87	4.29	4.19	4.77	4.73	4.642	4.658
	B	4.57	8.62	10.99	5.21	5.58	6.37	—
PbF_2	D_e	2288	2464	2530	2336	2380	2433	2491
	R_e	5.06	4.72	4.64	4.99	4.93	4.866	4.861
	B	5.20	6.57	7.44	5.62	6.01	6.56	6.08, 6.27, 6.53(4)
MgO	D_e	2922	2997	3050	2972	2968	3020	3038
	R_e	4.17	4.06	4.03	4.14	4.12	4.09	3.979
	B	17.0	17.4	18.1	17.6	17.8	18.8	17.5

(1) See first note to table 5. $U^0_L(R)$ computed by using only the RIP program.

(2) Includes neither dispersion nor correlation, i.e. predictions from $U^0_L(R)$ (2.15).

(3) See notes to table 5 for references. MgO data as follows. D_e: Muhlhausen & Gordon (1980); R_e: Landolt-Börnstein (1973*b*); and average of these different results is reported by La & Barsch (1968).

(4) Estimated value at 0 K Samara (1976).

short-range interactions $V^0_{sAA}(x_{AA}R)$ and $V^0_{sCC}(x_{CC}R)$, as well as the uncorrelated short-range cation–anion interactions, were computed exactly with the RIP program with ion wavefunctions computed with the description (2.18) and (2.20) of the environment. Thus the electron-gas method is not used to calculate any uncorrelated short-range potential, this method being retained only to estimate the short-range correlation contributions $V^{corr}_{sab}(x_{ab}R)$. All the potentials computed are presented in detail in Appendix 5. As the uncorrelated short-range interactions are calculated exactly with wavefunctions well adapted to the crystalline environment, the results of this series of calculations can be used both to test the accuracy of the electron-gas predictions of the uncorrelated short-range interactions and to probe the role of the correlation, dispersion and dispersion damping. It should be pointed out that such tests have not been possible hitherto because a program such as RIP, which can calculate both relativistically and exactly the energy of interaction of two ions such as Pb^{2+}, a system containing 156 electrons, has not been previously available.

Six main conclusions can be drawn from the series of calculations reported in table 6. First, the use solely of the exact uncorrelated short-range potentials (column 1) always predicts insufficient crystal cohesion as manifested by lattice energies and compressibilities that are too small, R_e values that are too large. This shows that either correlation or dispersion plays a non-negligible role in determining crystal properties. Second, the results in column 4 computed by including also the estimate of correlation provided by the electron-gas method show that dispersion cannot be neglected because the lattice energies are still underestimated and the R_e values overestimated. This underestimation (column 4) of the crystal cohesion increases as the polarizability of the constituent ions increases and becomes particularly marked for AgF and PbF_2, the systems where dispersion might be expected to be most important. Third, it is not correct to introduce the dispersion series in its undamped form. The use of undamped dispersion (column 2), even without correlation, very seriously overestimates the cohesion of AgF while predicting for PbF_2 the undesirable combination of too small a lattice energy at too small R_e. The deficiency of omitting any form of dispersion damping is masked for the other systems studied because these have much smaller dispersion coefficients. The deficiencies of the undamped dispersion treatment are accentuated (column 3) if the correlation energy is also included, all the lattice energies being overestimated. Fourth, the second conclusion showed that the dispersion energy must be included while the third conclusion showed dispersion damping to be necessary, but the use of damped dispersion without correlation predicts insufficient cohesion (column 5) as manifested by too small lattice energies and too large predicted R_e values. This shows that use of the damped dispersion energy alone is not sufficient and that one must include also some estimate of that portion of the correlation energy which is non-zero solely by virtue of the overlap of the ion wavefunctions.

The fifth conclusion from table 6 is that the closest anion–anion ($V^0_{\mathrm{SAA}}(x_{\mathrm{AA}}\,R)$) and for AgF and PbF_2 the closest cation–cation ($V^0_{\mathrm{SCC}}(x_{\mathrm{CC}}\,R)$) uncorrelated short-range interactions are sufficiently important that significant errors arise if these are calculated, not exactly by using RIP, but by using the electron-gas approach. Thus comparison of either column 4 of table 6 with column 3 of table 5 or of columns 6 of tables 5 and 6 shows that use of the exchange corrected electron-gas method overestimates these short-range repulsions thus predicting insufficient crystal cohesion. This difficulty is especially marked for systems such as LiF and PbF_2 which have the smallest anion–anion separations $x_{\mathrm{AA}}\,R$. The electron-gas method overestimates both the short-range Ag^+–Ag^+ interaction and all the short-range anion–anion repulsions. (See Appendix 5.) The computations show that the short-range cation–cation interactions (2.16*b*) are negligible for Li^+, Na^+ and Mg^{2+} while showing that the uncorrelated short-range Pb^{2+}–Pb^{2+} interaction although underestimated by electron-gas theory is less important than that F^-–F^- uncorrelated short-range repulsion which the electron-gas approach overestimates.

The sixth conclusion to be drawn from table 6 is that the predictions of the highest level of theory (column 6), in which the uncorrelated short-range interactions computed exactly with RIP are augmented by both the correlation energy and damped dispersion series, agree well with experiment. Thus all the computed lattice energies lie within the experimental uncertainties except for the large PbF_2 value which is slightly underestimated. The closest cation–anion equilibrium separations R_e also agree well with experiment. The values of the C_6 coefficients and hence the C_8 coefficients for AgF are less firmly established than the other dispersion coefficients reported in table 4 because the individual Ag^+ and F^- polarizabilities in AgF are less well established, with only their sum, the molar crystal polarizability of AgF, being known accurately (Bottger & Geddes 1972; Fowler & Pyper 1985). However, use of the much lower free ion polarizability for Ag^+ of 8.3 predicted by an accurate *ab initio* SCF calculation (Fowler & Pyper 1985) with a new F^- polarizability chosen to reproduce the known molar polarizability, although substantially changing the dispersion coefficients calculated from (2.25) and (2.26), hardly changes the predicted crystal properties. Thus the predicted lattice energy remains unchanged from the result of column 6, while the calculated R_e and compressibility only change to 4.645 a.u. and 6.35×10^{12} N m^{-2}.

Unlike the other values reported in table 6, the experimental compressibility of PbF_2 was measured at room temperature and can therefore be expected to be smaller by approximately 10% than the 0 K value which is directly comparable with the calculations. Indeed a value of 6.53×10^{12} N m^{-2} has been estimated for PbF_2 (Samara 1976) by assuming the temperature dependence to be the same as that of the alkaline earth halides. As the second nearest neighbour F^-–F^- separation in PbF_2 is the same as the nearest Pb^{2+}–Pb^{2+} one, it is *a priori* inconsistent to include the latter while excluding the former. However, the inclusion of the second nearest neighbour F^-–F^- total short-range potential (2.16*b*) calculated as the sum of the exactly computed uncorrelated short-range interaction plus the electron-gas correlation energy did not change the predicted lattice energy and R_e from the values reported in column 6 while only changing the predicted compressibility to 6.53×10^{12} N m^{-2}. The total short-range potentials (2.16*b*) for the second nearest anion–anion interactions were only 10^{-6} a.u. and 6×10^{-5} a.u. for LiF at $R = 3.75$ and MgO at $R = 4.0$ respectively, thus showing that second nearest anion–anion short-range terms can be neglected in the present studies.

The MgO results presented in table 6 appear to be the first *ab initio* calculations including the oxide–oxide short-range interaction, not based entirely on the electron-gas method, to yield sensible predictions as discussed in §5. The discrepancies between theory and experiment are only insignificantly greater than for the other systems in that the predicted R_e is too large by 0.11 a.u. compared with a maximum discrepancy of 0.08 a.u. for the remaining crystals studied. Thus the three crystal properties examined do not provide any evidence for a significant covalent contribution to the cohesion of MgO.

The cation wavefunctions are only minimally affected by the environmental potential (2.20); consequently the Ag^+–Ag^+ and Pb^{2+}–Pb^{2+} potentials (Appendix 5) computed with the RIP program should be transferable to any crystal containing these cations. It has not so far been possible to extract these potentials from experimental data while the size and relativistic nature of these cations has hitherto precluded their computation *ab initio*.

4. Anion–anion potentials

(*a*) *Comparison of ab initio methods*

The *ab initio* computation of short-range anion–anion potentials is of current interest (Catlow *et al.* 1977; Catlow 1977; Kendrick & Mackrodt 1983) because it has not so far been possible to extract these from empirical fits to experimental crystal properties. For the anion wavefunctions generated with the environmental potential (2.18), the uncorrelated short-range anion–anion potentials computed exactly with the RIP program are compared in Appendix 5 with those predicted by the Lloyd & Pugh (1977) and Waldman–Gordon (1979) modifications of electron-gas theory.

The Waldman–Gordon modification of electron-gas theory scales both the kinetic and exchange contributions to the interaction energy predicted by the original electron-gas approach (Gordon & Kim 1972) by factors derived from a Hartree–Fock calculation for one atom having the same number of electrons as two anions. These factors are calculated as the ratio of the total kinetic or exchange energy computed from atomic Hartree–Fock theory to the corresponding total energy predicted by electron-gas theory with the same Hartree–Fock electron density. For the F^-–F^- and O^{2-}–O^{2-} interactions these correction factors were taken to be the same as those for the interaction of a pair of neon atoms (Waldman & Gordon 1979). However, as the derivation of correction factors from the total number of electrons is objectionable (Wood & Pyper 1981) because the core electrons do not contribute actively to the interaction energy (Clugston & Pyper 1979), the Waldman–Gordon correction factors for the Cl^-–Cl^- interactions were taken to be the same as those for the F^-–F^- and O^{2-}–O^{2-} interactions.

Ab initio calculations at both the Hartree–Fock molecular orbital and configuration interaction levels have been done for dimers A_2^{2q-} (Catlow & Hayns 1972; Kendrick & Mackrodt 1983) in attempts to calculate non-empirically the interaction potential for a pair of A^{q-} anions. However, the interaction energy calculated by subtracting the energy of two isolated A^{q-} ions from the *ab initio* energy of the dimer A_2^{2q-} does not yield the desired anion–anion potential because the nuclei in the dimer do not lie on a centre of symmetry so that the *ab initio* electron density for A_2^{2q-} is polarized along the A^{q-}–A^{q-} direction. Interaction energies calculated by this method will be too low because such polarization of the A^{q-} electron density is necessarily absent in the crystal where each A^{q-} ion does lie on a centre of symmetry. This shows that the energy associated with this polarization must be subtracted from the computed interaction energy if one is to obtain a potential relevant to the anions in the crystal. It has been suggested (Kendrick & Mackrodt 1983) that the polarization energy to be subtracted can be calculated by subtracting the energy of an isolated A^{q-} ion from the energy of one anion computed in the presence of a point charge of magnitude $-q$ located at the position of the second nucleus in the dimer. However, it is far from clear that this procedure will yield even a reasonable estimate of the polarization energy because in the A_2^{q-} dimer each A^{q-} ion is polarized by another A^{q-} ion whose spatial charge distribution is very different from that of a point charge. The approach adopted here of calculating the anion wavefunctions in the presence of a potential such as (2.18), whose symmetry is consistent with the anion site symmetry in the crystal, avoids these problems because no spurious polarization energies are introduced.

(*b*) *Halide–halide interactions*

(i) *Short-range potentials*

The halide–halide potentials $V_{\mathrm{SAA}}^{\mathrm{T}}(x_{\mathrm{AA}}R)$ (2.16) in different crystals containing the same halide ion are not identical because the halide wavefunctions are crystal dependent as a result of the anion contractions induced by overlap with neighbouring cation orbitals being dependent on the cation size. The magnitude of these variations, which may need to be considered in empirical fitting procedures assuming a single transferable halide–halide repulsion, can be gauged from the detailed potentials presented in Appendix 5. The Lloyd & Pugh (1977) variant of electron-gas theory overestimates the uncorrelated short-range halide–halide repulsions $V_{\mathrm{SAA}}^{0}(x_{\mathrm{AA}}R)$ (2.14) in all the crystals studied, while the Waldman–Gordon (1979) variant also overestimates these repulsions, at all but very large R in LiF, NaF and PbF_2 excepting $R = 3.0$ for NaF. The Waldman–Gordon approach, however, underestimates $V_{\mathrm{SAA}}^{0}(x_{\mathrm{AA}}R)$ in AgF and NaCl.

For fluorides having the NaCl structure, the dependence of $V_{\mathrm{SAA}}^{0}(x_{\mathrm{AA}}R)$ evaluated at constant $R\,(= 4.0\text{ a.u.})$ upon the size of the cation is shown by the results presented in table 7. The size of the fluoride ion decreases on passing from the free ion through that in LiF and

TABLE 7. COMPARISON OF UNCORRELATED SHORT-RANGE F^-–F^- INTERACTIONS $V^0_{SAA}(4\sqrt{2})$ FOR $R = 4.0$ a.u.

method(2)	free	F⁻ wavefunction type(1) in LiF	in NaF	in AgF
electron LP	0.00395	0.00272	0.00218	0.00199
gas WG	0.00228	0.00161	0.00128	0.00116
exact RIP	−0.00014	0.00095	0.00118	0.00127

(1) Computed by using the description (2.18) of the environment for last three columns.

(2) LP; Lloyd & Pugh exchange corrected electron-gas method; WG: electron gas method with Waldman–Gordon correction factors for kinetic and exchange energies.

NaF to the most compact in AgF as the size of the cation increases. Consequently, it is not surprising that both variants of electron-gas theory predict $V^0_{SAA}(x_{AA} R)$ to decrease along this series because the magnitudes of the kinetic and exchange components of the interaction energy depend solely on the overlap of the electron densities which clearly decreases as the anions become more compact. However, the actual uncorrelated short-range interactions $V^0_{SAA}(4\sqrt{2})$, computed exactly with the RIP program, increase along this series from attraction between the free ions to the greatest repulsion in AgF. The electron-gas method completely fails to reveal this subtle trend. Although this trend and the short-range attraction between the free anions were not expected and, in addition calculated with a new computer program, it is shown in §5*b* that the present results are completely trustworthy.

The practical importance of the differences between the electron-gas and the RIP predictions computed exactly of second nearest neighbour uncorrelated short-range interactions can be assessed from the results of table 8. In all these calculations that use wavefunctions computed from the potentials (2.18) and (2.20), the closest cation–anion interaction $V^0_{SCA}(R)$ was computed with the RIP program, the short-range electron-gas correlation and damped dispersion energies were both included so that the calculations differ only in the uncorrelated

TABLE 8. CRYSTAL PROPERTIES PREDICTED FROM DIFFERENT METHODS OF COMPUTING THE UNCORRELATED SHORT-RANGE CATION–CATION AND HALIDE–HALIDE INTERACTIONS(1)

	LiF electron-gas(2) LP	 WG	 RIP	NaF electron-gas(2) LP	 WG	 RIP	NaCl electron-gas(2) LP	 WG	 RIP
D_e	1007	1025	1038	927	935	938	765	781	778
R_e	3.99	3.94	3.88	4.41	4.38	4.38	5.43	5.35	5.36
B	7.06	7.63	8.16	5.50	5.71	5.69	2.67	2.82	2.99

	AgF electron-gas(2) LP	 WG	 RIP	PbF_2 electron-gas(2) LP	 WG	 RIP
D_e	934	944	944	2406	2425	2433
R_e	4.70	4.67	4.64	4.90	4.88	4.87
B	6.40	6.70	6.37	6.26	6.47	6.56

(1) See first note to table 5. In all calculations the wavefunctions are computed by using the descriptions (2.18) and (2.20) of the environment; $V^0_{SCA}(R)$ is computed with the RIP program and both correlation and damped dispersion are included.

(2) LP and WG (see second note to table 7) denote the different electron-gas methods to compute $V^0_{SCC}(x_{CC} R)$ and $V^0_{SAA}(x_{AA} R)$.

short-range cation–cation $V^0_{\mathrm{sCC}}(x_{\mathrm{CC}}\,R)$ and anion–anion $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ potentials. For LiF, NaF and NaCl the total short-range cation–cation interactions $V^{\mathrm{T}}_{\mathrm{sCC}}(x_{\mathrm{CC}}\,R)$ are negligible so that variations of the predicted crystal properties arise from differences in the uncorrelated short-range halide–halide interactions. The deficiency or excess of the crystal cohesion predicted by electron-gas theory compared with the RIP results is directly related to the over or underestimation of the uncorrelated short-range halide–halide potentials $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ shown by the results of table 7 and Appendix 5. For PbF_2, both electron-gas approaches erroneously predict (Appendix 5) the short-range Pb^{2+}–Pb^{2+} interaction to be almost negligible. However, the overestimation of the short-range F^-–F^- interaction by the electron-gas theory more than outweighs the underestimation of the Pb^{2+}–Pb^{2+} interaction so that both electron-gas approaches very slightly underestimate the crystal cohesion. The Lloyd and Pugh electron-gas method overestimates both the uncorrelated short-range F^-–F^- and Ag^+–Ag^+ interactions in AgF thus predicting insufficient crystal cohesion while in the Waldman–Gordon approach the underestimation of $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ partially cancels the overestimation of $V^0_{\mathrm{sCC}}(x_{\mathrm{CC}}\,R)$ to yield predictions similar to those computed with the RIP program.

(ii) *Critique of ab initio dimer calculations*

The short-range F^-–F^- interaction cannot be calculated meaningfully by minimal basis set Hartree–Fock molecular orbital calculations (Catlow & Hayns 1972) because this overestimates the repulsion by an order of magnitude over the entire range of relevant inter-nuclear separations as noted previously (Catlow *et al.* 1977; Kendrick & Mackrodt 1983). Larger basis set Hartree–Fock molecular orbital results (Kendrick & Mackrodt 1983) do not appear to yield reliable values for $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ even after correction for spurious polarization energies. Thus such calculations predict uncorrelated short range F^-–F^- repulsions of 0.0014, 0.0032 and 0.0055 a.u. for $R = 4.0$, 3.7 and 3.5 a.u. compared with $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ values of -0.00015 (this work), 0.000063 (Andzelm & Piela 1977) and 0.00037 a.u. (Abarenkov & Antonova 1970) computed from free ion wavefunctions. The Hartree–Fock molecular orbital results are taken from figure 2 of Kendrick & Mackrodt (1983). Thus the variation principle shows that the description of F_2^{2-} provided by an antisymmetrized product of two free fluoride ion wavefunctions is superior to that derived by correcting the molecular orbital result with the polarization induced by a point charge. The very similar configuration interaction results (Kendrick & Mackrodt 1983) have the same problems.

As the calculation (Kendrick & Mackrodt 1983) did not consider the influence of the environment including that of the cations, it is hard to see how the results can accurately provide the information of primary interest on the anion–anion potential in the crystal. It should be pointed out that any similarities between the Kendrick & Mackrodt (1983) results and the in-crystal $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ reported in Appendix 5 have little significance because, in the former, the energy of the two interacting ions is measured relative to that of two isolated free fluoride ions, while in the latter the energy is measured relative to that of two separate fluoride ions having wavefunctions (2.2) computed with the environmental potential (2.18) with the appropriate crystal spacing R. Thus the quantities directly comparable with the Kendrick & Mackrodt (1983) calculation are those obtained by adding twice the re-arrangement energy (2.11) of one ion to the $V^0_{\mathrm{sAA}}(x_{\mathrm{AA}}\,R)$ values of Appendix 5. There is no similarity between these two sets of results.

(iii) *Total non-point coulombic interaction*

The total interaction energy between a pair of anions excluding the point coulomb term $q^2_{\rm A}/(x_{\rm AA}\,R)$ but including the uncorrelated short-range term (2.14), the short-range correlation energy entering (2.16*b*) and the damped dispersion energy constitutes the total non-point coulombic interaction $V^{\rm npc}_{\rm AA}(x_{\rm AA}\,R)$ given by

$$V^{\rm npc}_{\rm AA}(x_{\rm AA}\,R) = V^0_{\rm SAA}(x_{\rm AA}\,R) + V^{\rm corr}_{\rm SAA}(x_{\rm AA}\,R) + \chi^{\rm AA}_6(x_{\rm AA}\,R)\,C_6({\rm AA})\,(x_{\rm AA}\,R)^{-6} + \chi^{\rm AA}_8(x_{\rm AA}\,R)\,C_8({\rm AA})\,(x_{\rm AA}\,R)^{-8}. \quad (4.1)$$

These quantities are of interest because it has been suggested (Catlow *et al.* 1977) on the basis of semi-empirical fits to experimentally determined properties of alkali halide crystals that the interactions (4.1) are attractive at halide–halide distances $\surd 2R$ for values of the closest cation–halide separation R near to equilibrium $R_{\rm e}$. However, this conclusion was not supported by the results of *ab initio* calculations at either the Hartree–Fock or configuration interaction levels (Kendrick & Mackrodt 1983).

The total non-point coulombic anion–anion interactions in NaF and NaCl are derived from the first of the two sets of potentials presented by Catlow *et al.* (1977) by adding a Born–Mayer type repulsion derived from electron-gas calculations to the attractive term $-2C_{--}(\surd 2R)^{-6}$ in which the constant C_{--} was impirically determined. The factor of two enters the attractive term because the total cation–cation and anion–anion dispersive attractions were arbitrarily divided equally between the cation–cation and anion–anion interactions, whereas the dispersive attraction between pairs of Na$^+$ ions is negligible for R in the vicinity of $R_{\rm e}$. For values of $R > 4.5$ in fluorides and $R > 5.25$ in NaCl each anion–anion potential in the second set (table 3 of Catlow *et al.* 1977) can be represented accurately by the semi-empirical dispersive term $-C_{--}(\surd 2R)^{-6}$, where C_{--} is not in general the same as that entering the first potential set. For R values near equilibrium in NaF, NaCl and AgF, the halide–halide attractions calculated from both the parameter sets reported by Catlow *et al.* (1977) are compared in table 9 with the present *ab initio* predictions for the quantities (4.1). All three sets of results are in qualitative agreement that the total non-point coulombic interaction (4.1) between a pair of halide ions is attractive at R near $R_{\rm e}$ in distinction to the repulsion derived from the *ab initio* calculations (Kendrick & Mackrodt 1983) believed to be less reliable (see previous section).

TABLE 9. COMPARISON OF SEMI-EMPIRICAL NON-POINT COULOMB HALIDE–HALIDE INTERACTIONS WITH PREDICTIONS OF THE RIP PROGRAM WITH HALIDE WAVEFUNCTION COMPUTED ACCORDING TO §2*b* (DATA IN ATOMIC UNITS)

		RIP computations			semi-empirical†	
crystal	R	$V^0_{\rm SAA}(\surd 2R)$	$V^{\rm T}_{\rm SAA}(\surd 2R)$	$V^{\rm npc}_{\rm AA}(\surd 2R)$	set 1	set 2
NaF	4.5	0.00028	−0.00003	−0.00042	−0.00039	−0.00067
AgF	4.5	0.00031	−0.00002	−0.00040	−0.00039	−0.00067
AgF	4.75	0.00016	−0.00040	−0.00038	−0.00032	−0.00049
NaCl	5.25	0.00092	+0.00019	−0.00101	−0.00029	−0.00165
NaCl	5.5	0.00049	−0.00009	−0.00103	−0.00031	−0.00125

† Catlow *et al.* (1977).

The strong empirical element of the total non-point coulombic halide–halide potentials for NaF and NaCl (Catlow *et al.* 1977) should ensure that these reflect at least partly the true interaction in the crystal. This coupled with the results presented in table 9 provides some indirect evidence for the accuracy of the present *ab initio* potentials. The re-arrangement energy (2.11) necessarily present in *ab initio* lattice energy calculations based on (2.15) or (2.16) is probably absorbed without explicit consideration into the semi-empirical cation–anion potential in the semi-empirical theory (Catlow *et al.* 1977). However, the semi-empirical C_{++} and C_{--} coefficients should be regarded with some caution. Thus from the parameter set 2 the coefficients C_{--} of 45 and 277 a.u. (Catlow *et al.* 1977) for the F^-–F^- and interactions appear to be too large as judged by the $C_6(AA)$ coefficients reported in table 4 for $C_{--}\ (\surd 2R)^{-6}$ to be equated to the dipole–dipole dispersion energy. This suspicion that $C_{--}(\surd 2R)^{-6}$ does not equal the dispersion energy but contains a substantial component correcting both for errors in the short-range potential and the lack of dispersion damping is confirmed by the semi-empirical value (Catlow *et al.* 1977) for C_{++} for the K^+–K^+ interaction of 87 a.u. This is over three times the accurate *ab initio* value for $C_6(K^+K^+)$ of 23 a.u. (see Appendix 2, Fowler *et al.* 1985).

It should be noted that for NaF at $R = 4.5$, NaCl and AgF the present prediction of non-point coulombic halide–halide attractions does not depend on the electron-gas correlation energy since the sum of $V^0_{\text{sAA}}(x_{\text{AA}}\,R)$ and the dispersion contribution in (4.1) alone is negative. An alternative view shows that at the larger halide–halide separations the total short-range interaction $V^{\text{T}}_{\text{sAA}}(x_{\text{AA}}\,R)$ (2.16*b*), excluding the dispersion energy is attractive.

(*c*) *The oxide–oxide interaction*

(i) *Ab initio potentials*

The data presented in Appendix 5 shows that the Lloyd & Pugh (1977) and Waldman–Gordon (1979) modifications of electron-gas theory both predict uncorrelated short-range O^{2-}–O^{2-} interactions which are too repulsive for $R \geqslant 3.5$ compared with that computed by using the RIP program. That program yields the exact uncorrelated potential given the oxide wavefunctions predicted with description (2.18) of the crystalline environment. Furthermore, both the electron-gas approaches fail to reproduce the attractive tail of the true potential $V^0_{\text{sAA}}(\surd 2R)$ for $R > 4.25$.

The significance of the differences between the electron-gas potentials and that computed with the RIP program is shown by the comparison, table 10, between the crystal properties

Table 10. MgO crystal properties predicted from different methods of computing the uncorrelated short-range oxide–oxide interaction

	method of computing $V^0_{\text{sCC}}(\surd 2R) + V^0_{\text{sAA}}(\surd 2R)$				
		electron-gas			
	omitted	LP	WG	RIP	experiment⁽²⁾
D_e	2997	2878	2936	3020	3038
R_e	3.99	4.16	4.12	4.09	3.98
B	17.9	16.0	16.7	18.8	17.5

(1) See first note to table 5. All calculations use wavefunctions computed from descriptions (2.18) and (2.20) of the environment: compute $V^0_{\text{sCA}}(R)$ from RIP, include $V^{\text{corr}}_{\text{sCA}}(R)$ and damped dispersion, $V^{\text{corr}}_{\text{sCC}}(\surd 2R)$ and $V^{\text{corr}}_{\text{sAA}}(\surd 2R)$ included in last three calculations.

(2) See third note to table 6.

predicted with the different O^{2-}–O^{2-} potentials. In all these calculations, table 10, the Mg^{2+}–O^{2-} potential is calculated exactly with the RIP program, the correlation and damped dispersion energies are both included while the short-range interaction between a pair of cations, although included, is negligible. The results show that neglect of the short-range O^{2-}–O^{2-} interaction predicts too small a lattice energy (column 1, table 10) which is further reduced (columns 2 and 3) on inclusion of the purely repulsive short-range $V^{T}_{sAA}(\sqrt{2R})$ (see (2.16 *b*)) O^{2-}–O^{2-} electron-gas potentials. However, introduction of the RIP short-range oxide–oxide potential increases the predicted lattice energy to a value close to experiment because the total oxide–oxide short-range contribution (equal to $6V^{T}_{sAA}(\sqrt{2R})$) to the crystal binding energy (2.15) is attractive by 17.2 and 42.2 kJ mol^{-1}, for $R = 4.0$ and 4.25 a.u. respectively.

(ii) *Comparison of semi-empirical and ab initio non-point coulomb interactions*

The total non-point coulombic interaction (4.1) between a pair of oxide ions calculated with the RIP program is compared in table 11 both with the predictions of electron-gas theory and with those derived (Catlow *et al.* 1976) from a semi-empirical fit to observed properties of MgO. That potential was constructed by first fitting the function $A \exp(-\sqrt{2R}/\rho) - C_{--}(\sqrt{2R})^{-6}$ to the results of *ab initio* Hartree–Fock molecular orbital calculations for the dimer $(O^{-})_2$ (Catlow 1977) and then using this function to describe the MgO crystal adjusting further the constant C_{--} to reproduce experimental data. This constant, predicted to be 34.1 a.u. from the *ab initio* calculation, is only changed to 48.4 a.u. on the further adjustment. As simple molecular orbital theory predicts two O^{-} ions to form a covalent bond of unit bond order, it is hardly surprising that the resulting non-point coulombic interaction (Table 11) is purely attractive decreasing monotonically with decreasing R. However, the O^{2-} ion wavefunction input to the RIP program, unlike an O^{-} ion, has a closed outer electronic shell so that two O^{2-} ions repel at intermediate separations as shown by the RIP results presented in table 11. Thus the semi-empirical description (Catlow *et al.* 1976) can only be appropriate if MgO crystals are composed not of O^{2-} but of O^{-} ions with the remaining electrons occupying a band delocalized over the entire crystal while the RIP method is only realistic if the crystal is composed of separate clearly identifiable O^{2-} ions. The adjustment to reproduce experimental data can only ensure that the semi-empirical potential (Catlow *et al.* 1976) is realistic for those R values close

TABLE 11. NON-POINT COULOMB OXIDE–OXIDE POTENTIALS $V^{npc}_{AA}(\sqrt{2R})$ IN MgO (ATOMIC UNITS)⁽¹⁾

	method of calculating $V^{0}_{sAA}(\sqrt{2R})$			
	electron-gas⁽²⁾			
R	LP	WG	RIP	semi-empirical⁽³⁾
3.0	0.03883	0.03035	0.03041	−0.00807
3.5	0.01577	0.01003	0.00406	−0.00328
3.75	0.01022	0.00544	−0.00069	−0.00217
4.0	0.00785	0.00381	−0.00186	−0.00148
4.25	0.00394	0.00050	−0.00451	−0.00103
4.5	0.00272	−0.00023	−0.00454	−0.00073
5.0	0.00093	−0.00130	−0.00438	−0.00039
5.5	0.00006	−0.00168	−0.00385	−0.00022

⁽¹⁾ Oxide wavefunctions computed by using environmental description (2.18).
⁽²⁾ See second note to table 7. ⁽³⁾ Catlow *et al.* (1976).

to R_e which determine the input experimental data. Although use of the RIP program and the semi-empirical approach (Catlow *et al.* 1976) predict not dissimilar non-point coulombic attractions for R close to R_e their slopes $(\mathrm{d}V_{AA}^{npc}(\sqrt{2}R)/\mathrm{d}R)$ have opposite sign.

Ab initio calculations for the dimer composed of two ten electron atoms having nuclear charge 8.8553 a.u., chosen to reproduce the experimental polarizability of one O^{2-} ion, predict (Kendrick & Mackrodt 1983, fig. 4) non-point coulombic interactions similar to those (table 11) derived from the electron-gas theories. This corresponds to using the potential $-0.88553 r_A^{-1}$ to represent the effect of the crystalline environment on an electron in the O^{2-} ion which potential is shown by the discussion of §2*b* to be unrealistic. For the O^{2-}–O^{2-} interaction this provides a further reason in addition to those discussed in §4*a* and §4*b* (ii) for distrusting the results of the polarization adjusted dimer calculations of Kendrick & Mackrodt (1983).

The results (table 11) computed with the RIP program show that the non-point coulombic attractions between the neighbouring pairs of O^{2-} ions stabilize the MgO lattice by 11, 29 and 71 kJ mol^{-1} at $R = 3.75$, 4.0 and 4.25 respectively. The use of either of the two most reliable electron-gas approximations (Lloyd & Pugh 1977; Waldman & Gordon 1979) with the same oxide wavefunctions fails to reproduce these stabilizations predicting destabilization.

5. Comparison with previous calculations

(*a*) *The electron-gas method*

The crystal properties predicted by using both the Waldman–Gordon and Lloyd & Pugh modifications of electron-gas theory are compared in table 12 both with experiment and with the corresponding calculations in which the uncorrelated short-range interactions are computed with the RIP program. The damped dispersion term (2.22) and the unmodified electron-gas correlation energy were included in all these calculations which therefore differ only in the

Table 12. Comparison of electron-gas and RIP predictions of crystal properties⁽¹⁾

	calculated electron-gas⁽²⁾				calculated electron-gas⁽²⁾			
	LP	WG	RIP	experiment⁽³⁾	LP	WG	RIP	experiment⁽³⁾
	LiF				NaF			
D_e	1044	1081	1038	1035	917	945	938	923, 931
R_e	3.86	3.77	3.89	3.80	4.45	4.36	4.38	4.38
B	8.00	9.29	8.16	6.98–8.67	5.18	5.91	5.69	5.14, 5.17
	NaCl				AgF			
D_e	762	794	778	773, 786	786	819	944	942, 953
R_e	5.45	5.29	5.36	5.33	5.37	5.22	4.64	4.66
B	2.58	3.03	2.99	2.66, 2.74	2.59	3.44	6.37	
	PbF_2				MgO			
D_e	2355	2433	2433	2491	2963	3062	3020	3038
R_e	5.08	4.97	4.87	4.86	4.09	4.01	4.09	3.98
B	5.89	6.77	6.56	6.08, 627	17.1	19.0	18.8	17.5

⁽¹⁾ See first note to table 5. All calculations use wavefunctions computed with the descriptions (2.18) and (2.20) of the environment, and include all $V^{0}_{\mathrm{sXY}}(x_{XY}R)$ correlation and damped dispersion.

⁽²⁾ Electron-gas method used to compute $V^{0}_{\mathrm{sCA}}(R)$, $V^{0}_{\mathrm{sCC}}(x_{CC}R)$ and $V^{0}_{\mathrm{sAA}}(x_{AA}R)$. See also second note to table 7.

⁽³⁾ See third note to table **6**.

uncorrelated short-range potentials, the Waldman–Gordon and Lloyd & Pugh calculations using electron-gas theory to compute the cation–anion as well as the anion–anion and cation–cation uncorrelated short-range potentials. In the Lloyd & Pugh calculations, the effective number of electrons needed to derive the exchange correction factor for each pair potential was taken to be the sum of the number (see §3*a*) of electrons contributed by each of the two ions. In the Waldman–Gordon calculations, the correction factors for the Ne–Ne interaction were used to derive all the uncorrelated short-range interactions excepting the Li^+–F^- and Li^+–Li^+ potentials. The latter pair of potentials were calculated by using the correction factors (Waldman & Gordon 1979) for the He–Ne and He–He systems respectively. Ion wavefunctions derived from the environmental potentials (2.18) and (2.20) were used to compute all the results presented in table 12. There is, in principle, a slight inconsistency in the electron-gas calculations because these used relativistic electron densities while retaining the non-relativistic energy functionals of electron-gas theory. However, it has been shown (Pyper *et al.* 1977), even for the interaction of two Hg atoms, that substitution of the relativistic kinetic energy functional for the non-relativistic one scarcely changed the predicted interaction potential.

The results presented in table 12 show that use of either electron-gas method introduces appreciable errors compared both with experiment and with the RIP calculations to which the electron-gas approach is an approximation. The data presented in Appendix 5 show the Waldman–Gordon method to underestimate the cation–anion short-range repulsion in all three alkali halides and MgO, thereby explaining why this approach overestimates the cohesion of these four crystals. The excess of the LiF and MgO bindings compared with experiment do not arise from the omission of the correlation correction factors (Waldman & Gordon 1979) of 0.45 for Li^+–F^- and 0.51 for the remaining interactions because the cation–anion plus anion–anion uncorrected electron-gas correlation energies only contribute 23 kJ mol^{-1} and 55 kJ mol^{-1} respectively to the crystal cohesions of LiF and MgO at $R = 3.75$ a.u. The Lloyd & Pugh method overestimates (Appendix 5) the repulsion between an Na^+ ion and a halide ion while underestimating the Li^+–F^- and $Mg^{2+}-O^{2-}$ interactions, these errors being propagated into the predictions (table 12) of the crystal cohesion. Both electron-gas methods predict (Appendix 5) an uncorrelated short-range Pb^{2+}–F^- repulsion of slightly incorrect shape, this being too repulsive at short distances yet insufficiently repulsive at longer distances when compared with the RIP potential. It should be noted that the errors in the electron-gas cation–cation and anion–anion potentials may either reinforce or partly cancel those of the electron-gas cation–anion interaction in the prediction of the crystal properties.

Both electron-gas methods are seen to fail completely for AgF, the crystal cohesion being underestimated (table 12). Use of even the original uncorrected electron-gas method (Gordon & Kim 1972), which is known to underestimate the short-range repulsion of most systems, only predicts a lattice energy of 873 kJ mol^{-1} at $R_e = 4.99$ a.u. This failure arises from the already elucidated origin (Wood & Pyper 1981) which causes the total (including the point coulomb $-1/R$ term) attraction between a free Ag^+ and a free F^- ion to be underestimated.

(*b*) *Previous more exact calculations*

The previous calculations of the properties of the LiF and NaF crystals (Andzelm & Piela 1977, 1978) neglected terms in the uncorrelated short-range potentials involving products of more than two overlap integrals between pairs of atomic orbitals. These calculations also differ from those reported here in the inclusion of short-range 3-body terms (Löwdin 1956), the exclusion of the short-range overlap correlation energy, the absence of damping of the dispersion energy and in the method of adapting the ion wavefunctions to the crystalline environment. Nonetheless, the uncorrelated short-range interactions computed with free ion wavefunctions are directly comparable with corresponding calculations with the RIP program. Although the computations of Abarenkov & Antonova (1970) included neither correlation nor dispersion damping, their predictions of the short-range interactions, which used free ion wavefunctions, are even more directly comparable with corresponding RIP results because no expansion in powers of atomic orbital overlap integrals was used.

Comparison of the present and previous results is facilitated by specializing to the NaCl structure the result (2.16) for the crystal binding energy and then rewriting this as

$$U_{\mathrm{L}}(R) = -M/R + 6[V^{0\mathrm{F}}_{\mathrm{sCA}}(R) + V^{0\mathrm{F}}_{\mathrm{sAA}}(\surd 2R)] + U^{\mathrm{F}}_{\mathrm{corr}}(R) + U_{\mathrm{disp}}(R) + U^{\mathrm{F}}_{3\mathrm{B}}(R) + U^{\mathrm{en}}(R), \tag{5.1}$$

$$U^{\mathrm{F}}_{\mathrm{corr}}(R) = 6[V^{\mathrm{corr\,F}}_{\mathrm{sCA}}(R) + V^{\mathrm{corr\,F}}_{\mathrm{sAA}}(\surd 2R)]. \tag{5.2}$$

Here $V^{0\mathrm{F}}_{\mathrm{sab}}(x_{\mathrm{ab}}R)$ and $V^{\mathrm{corr\,F}}_{\mathrm{sab}}(x_{\mathrm{ab}}R)$ are the uncorrelated short-range and electron-gas overlap correlation contributions to the potential (2.16*b*) between the ions a and b computed by using free ion wavefunctions. The quantity $U^{\mathrm{F}}_{3\mathrm{B}}(R)$ is the short-range 3-body term predicted by using free ion wavefunctions, while $U^{\mathrm{en}}(R)$ is the sum of the contributions arising from the environmentally induced modifications to the uncorrelated short-range potentials, the electron-gas correlation energy and the short-range 3-body term. These three terms, which all arise from the environmentally induced modification of the ion wavefunctions, are given by

$$U^{\mathrm{en}}(R) = U^{\mathrm{en}}_{\mathrm{s0}}(R) + U^{\mathrm{en}}_{\mathrm{corr}}(R) + U^{\mathrm{en}}_{3\mathrm{B}}(R), \tag{5.3}$$

$$U^{\mathrm{en}}_{\mathrm{s0}}(R) = 6[V^{0}_{\mathrm{sCA}}(R) - V^{0\mathrm{F}}_{\mathrm{sCA}}(R) + V^{0}_{\mathrm{sAA}}(\surd 2R) - V^{0\mathrm{F}}_{\mathrm{sAA}}(\surd 2R)] + E^{\mathrm{A}}_{\mathrm{re}}(R), \tag{5.4}$$

$$U^{\mathrm{en}}_{\mathrm{corr}}(R) = 6[V^{\mathrm{corr}}_{\mathrm{sCA}}(R) - V^{\mathrm{corr\,F}}_{\mathrm{sCA}}(R) + V^{\mathrm{corr}}_{\mathrm{sAA}}(\surd 2R) - V^{\mathrm{corr\,F}}_{\mathrm{sAA}}(\surd 2R)], \tag{5.5}$$

$$U^{\mathrm{en}}_{3\mathrm{B}}(R) = U_{3\mathrm{B}}(R) - U^{\mathrm{F}}_{3\mathrm{B}}(R). \tag{5.6}$$

Here $U_{3\mathrm{B}}(R)$ is the short-range 3-body energy computed by using the crystal wavefunction (2.1). The cation–cation short-range interactions are negligible for Li^{+} and Na^{+} and therefore omitted from (5.1). It is also useful to decompose $V^{0\mathrm{F}}_{\mathrm{sab}}(x_{\mathrm{ab}}R)$ into a purely 'coulombic' contribution $V^{\mathrm{pen}}_{\mathrm{sab}}(x_{\mathrm{ab}}R)$, present even if inter-ionic electron exchange is ignored, plus a term $V^{kx}_{\mathrm{ab}}(x_{\mathrm{ab}}R)$ arising entirely from exchange of electrons between the ions. The latter has contributions from both one-electron and two-electron terms:

$$V^{0}_{\mathrm{sab}}(x_{\mathrm{ab}}R) = V^{\mathrm{pen}}_{\mathrm{sab}}(x_{\mathrm{ab}}R) + V^{kx}_{\mathrm{ab}}(x_{\mathrm{ab}}R), \tag{5.7}$$

$$V^{\mathrm{pen}}_{\mathrm{sab}}(x_{\mathrm{ab}}R) = -q_{\mathrm{a}}\,q_{\mathrm{b}}/(x_{\mathrm{ab}}R) + \iint \rho_{\mathrm{Ta}}(\boldsymbol{r}_1)\,\rho_{\mathrm{Tb}}(\boldsymbol{r}_2)\,|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-1}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2. \tag{5.8}$$

Here $\rho_{\mathrm{Ta}}(\boldsymbol{r}_1)$ is the total charge density of the ion a composed of an electronic plus a nuclear term.

The contributions $6V^{0\mathrm{F}}_{\mathrm{sCA}}(R)$ to the crystal binding energy made by the uncorrelated short-range cation–anion interaction predicted from the RIP program by using relativistic wavefunctions agree satisfactorily (table 13) with those computed by using non-relativistic

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TABLE 13. COMPARISON BETWEEN RIP AND PREVIOUS PREDICTIONS OF FREE ION UNCORRELATED SHORT-RANGE CATION–ANION CONTRIBUTION TO CRYSTAL COHESION (DATA IN KILOJOULES PER MOLE)

	LiF $6V^{0F}_{sCA}(R)$		NaF $6V^{0F}_{(R)}$			NaCl $6V^{0}_{sCA}(R)$	
R/a.u.	RIP	AA†	RIP	AA†	R/a.u.	RIP	AA†
3.5	429.1	440.1	900.5	922.5			
4.0	174.4	176.9	348.0	352.1	5.0	255.5	260.7
4.5	73.6	73.9	141.0	141.5	5.25	173.0	176.4
5.0	32.0	32.0	60.0	59.7	5.5	118.1	120.0

† Abarenkov & Antonova (1970).

wavefunctions (Abarenkov & Antonova 1970). For these light systems relativistic effects on the interaction potential are only a few tenths of a kilojoule per mole as shown both by the RIP program result $6V^{0F}_{sCA}(5.25) = 173.2$ kJ mol^{-1} for NaCl computed non-relativistically and by the comparison between the relativistic RIP results (table 13) for LiF and NaF with their non-relativistic counterparts (table 14) also computed by using the RIP program. The present non-relativistic calculations were done simply by first running the Oxford atomic Dirac–Fock program with an artificially large value of the velocity of light thus generating non-relativistic ion wavefunctions which then form the input for a standard run of the RIP program. Although the agreement (table 14) between the RIP and previous results (Abarenkov & Antonova 1970) for the interaction $(6V^{0F}_{sAA}(\surd 2R))$ of free non-relativistic fluoride ions is not unsatisfactory, for the Cl$^-$–Cl$^-$ interaction the non-relativistic RIP results of $6V^{0F}_{sAA}(5.25\surd 2) = -4.9$ kJ mol^{-1} differs significantly from the previous value of

TABLE 14. COMPARISON BETWEEN RIP AND PREVIOUS CALCULATIONS OF THE COHESIVE ENERGIES OF LiF AND NaF (DATA IN KILOJOULES PER MOLE)⁽¹⁾

		LiF ($R = 4.0$)		NaF ($R = 4.0$)		NaF ($R = 4.4$)	
	RIP	AP1⁽²⁾	AA⁽²⁾	RIP	AA⁽²⁾	RIP	AP2⁽²⁾
$6V^{pen}_{sCA}(R)$	21.6	21.6	21.4	−78.3	−78.8	−36.2	−39.9
$6V^{kx}_{CA}(R)$	152.6	155.8	155.5	426.9	430.9	204.8	210.7
$6V^{0F}_{sCA}(R)$	174.2	177.4	176.9	348.6	352.1	168.6	170.8
$6V^{pen}_{sAA}(\surd 2R)$	−42.9	−43.5	−42.7	−42.9	−42.7	−18.3	−17.3
$6V^{kx}_{AA}(\surd 2R)$	40.6	40.4	38.4	40.6	38.4	15.1	14.3
$6V^{0F}_{sAA}(\surd 2R)$	−2.3	−3.1	−4.3	−2.3	−4.3	−3.2	−3.0
$U^{F}_{3B}(R)$	—	−8.9	−26	—	−49	—	−18.4
$U^{en}_{3B}(R)$	—	+2.3	—	—	—	—	1.7
$U_{3B}(R)$	—	−6.6	−26	—	−49	—	−16.7
$U^{en}_{s0}(R)$	−26.6	−24.5	—	—	—	−22.2	−13.4
$U^{en}_{corr}(R)$	4.8	—	—	—	—	6.5	—
$U^{F}_{corr}(R)$	−22.6	—	—	—	—	−22.8	—
$U_{disp}(R)$	−15.6	−24.9	—	—	—	−19.7	−25.2
$-M/R$	−1147.1	−1147.1	—	—	—	−1042.8	−1042.8
$U_{L}(R)$	−1035.2	−1028.8	—	—	—	−935.6	−930.8
$U^{un}_{disp}(R)$	−26.5	—	—	−66.0	—	−35.0	—

(1) For definitions see text.

(2) AP1: Andzelm & Piela (1977); AP2; Andzelm & Piela (1978); AA: Abarenkov & Antonova (1970).

-20.8 kJ mol^{-1} (Abarenkov & Antonova 1970). Both the RIP and Abarenkov & Antonova (1970) calculations use numerical wavefunctions (2.13) for the ions constituting the crystal thereby avoiding the uncertainties that can arise through the use of basis sets. However, both programs use an angular momentum expansion to express a function on one centre in terms of functions on another centre. The RIP program is almost certainly the more accurate of the two both because it includes 18 terms in the expansion compared with 7 in the 1970 calculation and because it avoids using angular momentum expansions in the calculation of coulomb integrals (Wood & Pyper 1986). Furthermore, the results presented in table 2 of Abarenkov & Antonova (1970) show errors of 0.0003 a.u. on a single integral, whereas the total potentials $V^0_{\mathrm{ab}}(x_{\mathrm{ab}}R)$ (2.14) computed with the RIP program show errors no greater than 0.000004 a.u. as gauged by the difference between the results computed by using 17 and 18 functions in the angular momentum expansions.

The small discrepancies (table 14) between the RIP predictions of the uncorrelated short-range potentials and those computed (Andzelm & Piela 1977, 1978) by using analytic basis set ion wavefunctions (2.13) almost certainly arise either from failure of the overlap expansion or more probably from basis set inadequacies. That the latter should not be underestimated, particularly for anion–anion interactions, is shown by the prediction (Andzelm & Piela 1977, 1978) by using a less good basis for the F^-–F^- interaction of $6V^0_{\mathrm{sab}}(4\sqrt{2}) = +5.4$ kJ mol^{-1} which even has the wrong sign. However, it should be stressed (see §4*b*(i)) that both the previous calculations (Abarenkov & Antonova 1970; Andzelm & Piela 1977, 1978) agree with the RIP program in predicting an uncorrelated short-range attraction between a pair of free fluoride ions separated by a distance $4\sqrt{2}$ a.u.

The uncorrelated short-range 2-body contributions $U^{\mathrm{en}}_{\mathrm{so}}(R)$ to the binding energy arising from the environmentally induced modifications of the ion wavefunctions predicted in the present calculations are lower (table 14) than the previous estimates (Andzelm & Piela 1977, 1978) because the model (2.18) for the potential acting on an anion electron is more realistic than the potential generated by a point charge lattice, as discussed in §2*b*. This discrepancy is larger for NaF than for LiF simply because the Na^+ is larger than the Li^+ ion. For these light systems the total contributions $(U^{\mathrm{F}}_{\mathrm{corr}}(R)+U^{\mathrm{en}}_{\mathrm{corr}}(R)+U_{\mathrm{disp}}(R))$ arising from correlation effects predicted here are larger than those previously calculated (Andzelm & Piela 1977, 1978) even though dispersion damping was omitted from the latter calculations. The total crystal binding energies predicted here are similar (table 14) to those previously presented (Andzelm & Piela 1977, 1978) because the greater environmental and correlation contributions are partly offset by the short-range 3-body term of Andzelm & Piela (1977). As the further 3-body interaction arising in the theory of long-range inter-atomic forces (Axilrod & Teller 1943) can be expected to contribute positively to the crystal binding energy, the total 3-body contributions may well have smaller magnitudes than those of the short-range terms reported in table 14. The Axilrod–Teller interaction contributes between 2% and 9% (0.5–1.5 kJ mol^{-1}) of the binding energy of an inert gas crystal (Maitland *et al.* 1981) which is dominated by the two-body dispersion energy. The closer inter-nuclear separations of ionic compared with inert gas crystals and the inverse ninth power dependence of the Axilrod–Teller term on these separations are both relevant in the comparison of these systems. Thus it can be argued that it may be more consistent to omit all 3-body terms, which are in any case small, rather than to include just the short-range 3-body term.

(*c*) *Uppsala group calculations*

The calculations of the properties of ionic crystals by the Uppsala group (Löwdin 1950, 1956; Fröman & Löwdin 1962; Mansikka & Bystrand 1966; Vallin *et al.* 1967; Petterson *et al.* 1967, 1968; Calais *et al.* 1967, 1971; Hayns & Calais 1973) invoked various approximations such as the neglect of integrals involving charge densities constructed as products of different atomic orbitals belonging to the same centre. Comparison of calculations involving the Uppsala approximations with exactly corresponding computations with the RIP program which avoids these approximations showed the former calculations to underestimate the uncorrelated cation–anion short-range repulsion in halide crystals (Wood & Pyper 1986). Thus comparison of calculations, all with free ion wavefunctions and retaining only the Madelung and uncorrelated cation–anion short-range energies, showed that use of the Uppsala approximations yielded a spuriously good agreement with experiment.

The changes in the crystal properties predicted by using Uppsala approximations upon introducing the anion–anion short-range interactions are compared in table 15 with the corresponding changes predicted by using the RIP program. Although the Uppsala and RIP calculations use different wavefunctions, these remain unchanged within each set of calculations thereby demonstrating the effect of introducing the short-range anion–anion interaction. The instability of the free O^{2-} ion renders the MgO lattice energies (table 15), measured relative to Mg^{2+} and O^{2-} ions, experimentally inaccessible although the true value has been stated to lie between 3780 and 4070 kJ mol^{-1} (Calais *et al.* 1971). The results (table 15) show very clearly that the Uppsala approximations overestimate drastically the uncorrelated short-range

Table 15. RIP and Uppsala predictions of the dependence of crystal properties on the short-range anion–anion interaction(1)

		Uppsala group(2)				RIP(5)	
		$V^0_{sCA}(R)$ only free ion	$V^0_{sCA}(R)+V^0_{sAA}(\sqrt{2}R)$ free ion(3)		$V^0_{sCA}(R)+V^0_{sAA}(\sqrt{2}R)$ scaled(4)	$V^0_{sCA}(R)$ only	$V^0_{sCA}(R)+V^0_{sAA}(\sqrt{2}R)$
NaF	D_e	952(7)	887(7)	873(8)	879(8)	906	901
	R_e	4.20	4.60	4.65	4.59	4.43	4.48
	B	5.0	5.98	5.1	4.1	4.89	4.88
NaCl	D_e	763(9)	648(9)	—	—	739	732
	R_e	5.1	6.40	—	—	5.46	5.56
	B	2.54	1.39	—	—	2.23	2.29
MgO	D_e(6)	3858(10)	3126(11)	—	3194(11)	3975	3956
	R_e	< 4.0	5.10	—	4.91	4.06	4.17
	B	—	11.9	—	6.0	16.8	17.0
AgF	D_e	927(12)	888(12)	—	—	853	847
	R_e	—	—	—	—	4.83	4.87

(1) For units see first note to table 5. Correlation and dispersion excluded from all calculations.

(2) All calculations used non-relativistic wavefunctions.

(3) Free ion wavefunctions excepting O^{2-}; 3-body terms excluded.

(4) Ion wavefunctions scaled in crystal to satisfy virial theorem.

(5) All calculations used relativistic wavefunctions computed with the descriptions (2.18) and (2.20) of the environment.

(6) Relative to Mg^{2+} and O^{2-} ions.

(7) Vallin *et al.* (1967).

(8) Petterson *et al.* (1968).

(9) Petterson *et al.* (1967).

(10) Calais *et al.* (1967).

(11) Calais *et al.* (1971).

(12) Hayns & Calais (1973).

anion–anion repulsions because these are predicted to decrease the lattice energies of NaF, NaCl and MgO by 65, 115 and 732 kJ mol^{-1} respectively while increasing substantially the predicted R_e values, those of NaCl and MgO being increased by as much as 1.3 a.u. and 1.1 a.u. By contrast the RIP results (table 15) show that introduction of the short-range anion–anion potential $V^0_{SAA}(\surd 2R)$ only decreases the lattice energies by less than 20 kJ mol^{-1} while increasing the R_e values by at most 0.1 a.u.

TABLE 16. COMPARISON OF RIP AND UPPSALA UNCORRELATED SHORT-RANGE POTENTIALS (IN ATOMIC UNITS)$^{(1)}$

crystal	R	$V^0_{SCA}(R)$ Uppsala$^{(2)}$	$V^0_{SCA}(R)$ RIP	$V^0_{SAA}(\surd 2R)$ Uppsala$^{(2)}$	$V^0_{SAA}(\surd 2R)$ RIP
NaF	4.0	0.01291	0.02213	0.00867	−0.00014
	4.4	0.00626	0.01070	—	−0.00020
NaCl	5.0	0.00989	0.01622	0.04943	—
	5.25		0.01099	—	−0.00031
	5.5	0.00540	0.00750	0.02007	—
MgO	4.0	0.04628	0.11978	—	0.00097
	4.5	0.02247	0.09235	0.05466	−0.00180
	5.0	0.01120	0.07782	0.02482	−0.00241

(1) Free ion wavefunctions used throughout excepting O^{2-}.

(2) NaF data from Vallin *et al.* (1967); NaCl from Petterson *et al.* (1967); $V^0_{SCA}(R)$ for MgO from Calais *et al.* (1967); and $V^0_{SAA}(\surd 2R)$ for MgO from Calais *et al.* (1971).

The comparison (table 16) between the RIP and Uppsala predictions of the uncorrelated short-range potentials all computed by using free cation and free halide wavefunctions confirms the failure of the Uppsala approximations deduced from table 15. There is very little resemblance between the two sets of results, the Uppsala approximations predicting, in particular, Cl^-–Cl^- short-range repulsions which are excessively large. The enormous discrepancies between the Uppsala and the RIP results for MgO cannot conceivably arise from the differences in the oxide ion wavefunctions used and thus demonstrate the breakdown of the Uppsala approximations.

6. CONCLUSION

It has been shown that the cohesive energies, lattice constants and compressibilities of polar solids containing the heaviest ions can be accurately predicted from fully relativistic calculations which are also in principle fully *ab initio*. Such predictions require that the wavefunctions of the constituent ions be adapted at least approximately to the crystalline environment, that some estimate of the short-range correlation energy be introduced and that the dispersive attraction between the ions is included. Furthermore, it has been shown that the damping of the dispersion energy arising from the overlap of the ion wavefunctions cannot be neglected, and one approximate method of calculating these damping factors has been developed. It should be emphasized that both these factors and the dispersion coefficients can, in principle, be computed *ab initio* and that any resultant changes in the dispersion energy would not alter the uncorrelated short-range inter-ionic potentials. It would be a computationally trivial matter to revise the predicted crystal properties by using new inter-ionic dispersive attractions while retaining the uncorrelated short-range potentials presented in this paper.

It has been shown that use of previously reported approximations to the uncorrelated short-range inter-ionic potentials, here computed exactly with the RIP program, significantly degrades the quality of the predictions of the crystal properties. Thus the approximations used previously by the Uppsala group are unsatisfactory, while the electron-gas results vary from the unacceptable to those slightly but significantly poorer than the RIP predictions. The use of the electron-gas method to calculate even the uncorrelated short-range cation–cation and anion–anion potentials while retaining the RIP predictions for the cation–anion interactions still yields results of significantly degraded quality compared with those computed exactly with the RIP program. The electron-gas predictions of the anion–anion and cation–cation interactions differ significantly from those of the RIP program particularly for the heavier cations.

This work has also provided *ab initio* predictions of the uncorrelated short-range anion–anion and cation–cation interactions which are not currently available from semi-empirical fits to experimental data. The development of the RIP program has enabled the interactions between pairs of ions as heavy as Pb^{2+} to be computed *ab initio*, the size and relativistic nature of such ions having hitherto precluded such calculations.

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APPENDIX 1. PROOF THAT SPHERICAL COMPONENT OF ENVIRONMENTAL POTENTIAL DETERMINES RADIAL DEFORMATIONS

The operator $\hat{F}_{\text{env}}(\boldsymbol{r}_{\text{A},i};R)$ describes the potential, originating from the remaining ions in the crystal, which acts on electron i on ion A at a position $\boldsymbol{r}_{\text{A},i}$ relative to the nucleus of A. Although this operator has non-local contributions from exchange and overlap with the wavefunctions of neighbouring ions, it can still be expressed as sum of irreducible spherical tensor operators (Brink & Satchler 1968).

$$\hat{F}_{\text{env}}(\boldsymbol{r};R) = \sum_{J=0}^{\infty} \sum_{M=-J}^{J} \hat{F}^{(J)}_{M,\text{env}}(\boldsymbol{r};R). \tag{A 1.1}$$

Here M is the component and J the rank of the tensor. The Wigner–Eckart theorem enables the total energy $E_{\text{env}}(R)$ of ion A arising from its interaction with the environment to be written (Brink & Satchler 1968)

$$\begin{aligned} E_{\text{env}}(R) &= \left\langle \Phi^{(0)}_{\text{A}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\text{A}}) \left| \sum_{i=1}^{N_\text{A}} \hat{F}_{\text{env}}(\boldsymbol{r}_{\text{A},i};R) \right| \Phi^{(0)}_{\text{A}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\text{A}}) \right\rangle \\ &= \sum_{J=0}^{\infty} \sum_{M=-J}^{J} \begin{pmatrix} 0 & J & 0 \\ 0 & M & 0 \end{pmatrix} \left\langle \Phi^{(0)}_{\text{A}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\text{A}}) \left\| \sum_{i=1}^{N_\text{A}} \hat{F}^{(J)}_{\text{env}}(\boldsymbol{r}_{\text{A},i}) \right\| \Phi^{(0)}_{\text{A}}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\text{A}}) \right\rangle, \end{aligned} \tag{A 1.2}$$

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where the superscript 0 on the wavefunction denotes that this has zero total angular momentum. As all the $3j$-symbols in (A 1.2) vanish except that with $J = M = 0$, only the spherically symmetric part of the environmental potential contributes to the energy of the ion wavefunction if this is taken to have the same J of zero as that of the free ion.

In the Dirac–Fock scheme the wavefunction for ion A is written as an anti-symmetrized product of orbitals $|u_\alpha j_\alpha m\rangle$ having the standard central field form (Grant 1970), where j_α and m denote the total and z-components of the angular momentum. As the label α denotes the sub-shell (Grant *et al.* 1976), the wavefunction can be written

$$|\Phi_\mathrm{A}(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_\mathrm{A}})\rangle = \hat{\mathscr{A}}\left(\prod_\alpha \prod_{m=-j_\alpha}^{j_\alpha} |u_\alpha j_\alpha m\rangle\right). \tag{A 1.3}$$

This function describes a closed shell with $J = 0$ provided the radial parts of orbitals which differ only in the m quantum number are taken to be identical. The environmental energy is given by

$$\begin{aligned} E_\mathrm{env}(R) &= \sum_\alpha \sum_{J=0}^{\infty} \sum_{M=-J}^{J} \sum_{m=-j_\alpha}^{j_\alpha} \langle u_\alpha j_\alpha m|\hat{F}^{(J)}_{M,\mathrm{env}}|u_\alpha j_\alpha m\rangle \\ &= \sum_\alpha \sum_{J=0}^{\infty} \sum_{M=-J}^{J} \sum_{m=-j_\alpha}^{j_\alpha} (2j_\alpha+1)^{\frac{1}{2}}(-1)^{j_\alpha-m}\begin{pmatrix} j_\alpha & J & j_\alpha \\ -m & M & m\end{pmatrix}\langle u_\alpha j_\alpha\|\hat{F}^{(J)}_\mathrm{env}\|u_\alpha j_\alpha\rangle. \end{aligned} \tag{A 1.4}$$

As the $3j$-symbol vanishes unless $M = 0$ while

$$\sum_m (-1)^{j_\alpha-m}\begin{pmatrix} j_\alpha & J & j_\alpha \\ -m & 0 & m\end{pmatrix} = \delta_{J,0}(2j_\alpha+1)^{\frac{1}{2}}$$

only the $J = 0$ term contributes to (A 1.4), which agrees with the general result presented in the first paragraph.

APPENDIX 2. TESTS OF APPROXIMATIONS TO DIPOLE–DIPOLE C_6(ab) DISPERSION COEFFICIENTS

(*a*) *Isolated systems*

The most reliable values of the dipole–dipole C_6(aa) dispersion coefficients between like systems derived from either experimental oscillator strengths or from accurate *ab initio* calculations are presented in table A 2.1. These results are compared both with those predicted from the Slater–Kirkwood (1931), London (Eyring *et al.* 1944) and Salem (1960) formulae and with those computed (Fraga *et al.* 1976) from three approximations requiring only the ground state electronic wavefunction. The polarizabilities needed for the Slater–Kirkwood and London calculations are also reported in table A 2.1. The electron number in the Slater–Kirkwood formula was taken to be one for H and the alkali metals, two for the alkaline earths H_2, Hg and He, eight for the remaining inert gases and methane, and ten for N_2. For the inert gases, the results predicted when this number is taken to be six are presented in parentheses. The ionization potentials needed to evaluate the London formula were taken from Moore (1971).

The London formula seriously overestimates all the C_6(aa) coefficients except those of the inert gases which are underestimated (table A 2.1) The three formulae of Fraga *et al.* (1976) relate C_6(aa) to sums of the moments of the oscillator strength distributions which are in turn

Table A 2.1. Comparison of approximations to dipole–dipole dispersion C_6(aa) coefficients for interaction of like systems (atomic units)

					C_6(a, a)		Fraga[(5)]		
a	α[(1)]	P_a	exact[(2)]	Slater–Kirk[(3)]	London[(6)]	Salem[(4)]	1-body	2-body	up-b
He	1.385	1.430	1.462	1.73	1.30	1.641	1.66	1.65	1.71
Ne	2.676	4.455	6.93	9.29 (8.04)	4.26	8.32	6.94	6.89	7.71
Ar	11.096	6106	68.5	78.4 (67.9)	53.5	91.1	93.6	93.1	106
Kr	16.753	7.305	139	145 (126)	108	—	200	199	225
Xe	27.318	7.901	301	302 (262)	250	—	508	505	575
H	4.5	0.824	6.499	7.159	7.59	6.75	—	—	—
Li	164.5	0.773	1390	1582	4022	—	885	883	957
Na	165.0	0.988	1580	1590	3856	—	1213	1210	1257
K	293.1	1.030	3820	3763	10279	—	4108	4089	4414
Rb	319.5	1.153	4600	4283	11752	—	6071	6048	6173
Cs	402.6	1.484	7380	6059	17396	—	11373	11330	11528
Be	37.84	1.420	208	247	368	—	413	413	457
Mg	71.32	1.874	618	639	1072	—	1084	1081	1173
Ca	153.9	1.961	2005	2025	3991	—	4518	4505	4940
Hg	34.0	2.605	240	210	333	—	1416	1409	1534
H_2	5.33	—	13	13	—	—	—	—	—
N_2	11.9	—	73	97	—	—	—	—	—
CH_4	17.6	—	150	157	—	—	—	—	—

(1) He, Kr, Xe data from Appendix and K, Rb and Cs data from table V of Miller & Bedenson (1977); Li, Be, Ne data from Werner & Meyer (1976); Ar, Na, Mg, Ca data from Reinsch & Meyer (1976); Hg data from Stwalley & Kramer (1968).

(2) Taken from Clugston & Pyper (1979) (inert gases by averaging the results cited by Clugston (1978); Langhoff & Karplus (1970) (alkali metals, H_2 and N_2 from column 3 of table VI. Note experimental results of column 4 of table VI are unreliable for reasons discussed at bottom of p. 239); Be, Mg, Ca data from Maeder & Kutzelnigg (1976); Hg data from Stwalley & Kramer (1968); CH_4 from Dalgarno (1967).

(3) Predicted by Slater–Kirkwood formula with 'theoretical' electron numbers discussed in text.

(4) Salem (1960).

(5) Fraga *et al.* (1976): 1-body and 2-body based on equations (24) and (25) of Davison (1968) and up-b is the upper bound based on equation (6) of Pack (1970).

(6) London formula with excitation energy taken to equal the ionization potential.

computed from an approximate expression involving expectation values over the ground state electronic wavefunction only. The first two formulae are based on expressions (24) and (31) of Davison (1968) while the third uses result (6) of Pack (1970). The results presented in table A 2.1 show all three methods (Fraga *et al.* 1976) to be quite unreliable. The deficiencies come primarily from the approximate method of calculating the moments of the oscillator strength distributions, borne out by the dispersion coefficients being predicted satisfactorily if more accurate moments are used (Davison 1968; Pack 1970). The results (table A 2.1) show the Slater–Kirkwood formula to be much more trustworthy than the other five methods because it does not break down. Furthermore, the relatively small quantitative inaccuracies of the Slater–Kirkwood formula can be plausibly ascribed to ambiguities in the choice of the electron number especially for the heavier inert gases where there appears to be no *a priori* method for deciding between the values of 6 and 8.

In table A 2.2 the best current estimates of the dispersion coefficients between unlike atoms are compared with those predicted from the Slater–Kirkwood formula with the electron numbers chosen to reproduce exactly the coefficients (column 3 of table A 2.1) for the interaction of the like systems. These electron numbers are presented in the second column of table A 2.1. The good agreement between the two sets of results provides strong evidence for the reliability of the Slater–Kirkwood formula after the electron numbers have been fixed.

TABLE A 2.2. TEST OF DIPOLE–DIPOLE DISPERSION C_6(ab) COEFFICIENTS FOR INTERACTION OF UNLIKE SYSTEMS PREDICTED BY SLATER–KIRKWOOD FORMULA (ATOMIC UNITS)

pair	exact(1)		SK(2)
He Ne	3.0	3.1	3.2
He Ar	9.6	9.8	9.9
He Kr	13	13.6	13.9
He Xe	19	18.3	20.0
Ne Ar	20	20.7	21.0
Ne Kr	27	28.7	29.4
Ne Xe	38	37.8	41.6
Ar Kr	91	94	97
Ar Xe	130	129	142
Kr Xe	190	184	203
Xe Li	410	404	410
Xe Na	450	438	457
Xe K	630	669	641
Xe Rb	690	786	707
Xe Cs	830	945	900
Li Na	1470	1450	1480
Li K	2290	2320	2299
Li Rb	2510	2590	2524
Li Cs	3160	3150	3198
He Li	22	22.6	21.9
He Na	25	24	25
He K	34	38	34
He Rb	37	46	38
He Cs	45	56	48
Ne Li	42	44	43
Ne Na	48	48	48
Ne K	66	75	67
Ne Rb	72	91	74
Ne Cs	87	111	94
Na K	2440	2410	2435
Na Rb	2670	2690	2699
Na Cs	3350	3270	3390
K Rb	4190	4350	4191
K Cs	5300	5300	5309
Rb Cs	5820	5940	5826
Ar Li	180	175	172
Ar Na	190	189	192
Ar K	270	292	268
Ar Rb	290	349	296
Ar Cs	350	422	376
Kr Li	260	259	257
Kr Na	280	281	287
Kr K	400	433	401
Kr Rb	430	515	442
Kr Cs	520	621	562

(1) First column taken from column 3 of table VI of Langhoff & Karplus (1970). Second column from Tang *et al.* (1976).
(2) Prediction of Slater–Kirkwood formula with electron numbers taken from table A 2.1.

(*b*) *In-crystal ions*

The dipole–dipole dispersion coefficients between the ions in some alkali halide crystals have been derived from measurement of the optical spectra (Mayer 1933; Lynch 1967). Values for $C_6(\mathrm{Cl^-Cl^-})$ and $C_6(\mathrm{I^-I^-})$ in NaCl, KCl and KI were derived (Mayer 1933) by fitting the optical absorption to a mathematical function and then subtracting a cation contribution calculated from a semi-theoretical method that uses the cation polarizabilities of Pauling (1927). All three coefficients $C_6(\mathrm{AA})$, $C_6(\mathrm{CC})$ and $C_6(\mathrm{AC})$ in KCl, KBr and KI have been derived from a more complete set of optical absorption data (Lynch 1967). Although these data transcended the limitations of that (Mayer 1933) consisting solely of the optical density of thin films, the anion and cation contributions to the absorption overlapped significantly. It was therefore assumed that the absorption corresponding to an integrated intensity of up to six electrons could be ascribed to the anion leaving the rest to be attributed to the cation.

The dispersion coefficients derived from experiment are compared with those predicted from the Slater–Kirkwood formula in table A 2.3 taking the electron numbers to be the same as those of the iso-electronic inert gases (table A 2.1). The polarizabilities of $\mathrm{Na^+}$ and $\mathrm{K^+}$ are known from accurate *ab initio* calculation to be 1.002 and 5.339 a.u. and to be independent of the crystal (Fowler & Pyper 1985). The halide polarizabilities are calculated by subtracting the cation values from the total molar polarizabilities reported by Wilson & Curtiss (1970). The results show all the cation–anion coefficients $C_6(\mathrm{AC})$ and all three dispersion coefficients for KCl to be well predicted by the Slater–Kirkwood formula (table A 2.3). For KBr and KI, $C_6(\mathrm{AA})$ appears to be overestimated while $C_6(\mathrm{K^+K^+})$ is apparently underestimated. However, these discrepancies do not come from the failure of the Slater–Kirkwood formula but from the assumption that an absorption corresponding to not more than six electrons can be ascribed to the anion. The failure of this assumption is shown by the polarizabilities (table A 2.3) which were also derived (Lynch 1967) from the absorption spectra. The values deduced for $\mathrm{K^+}$ in KBr and KI are too large compared with the accurate *ab initio* value of 5.339 a.u. which is only changed by less than 0.006 a.u. on entering the crystal (Fowler & Madden 1984). As the electron numbers of Kr and Xe are 7.305 and 7.901, the $\mathrm{Br^-}$ and $\mathrm{I^-}$ contributions to the absorption are likely to be underestimated by the assumption that this originates from not more than six electrons. This will cause too large a portion of the absorption to be ascribed to the $\mathrm{K^+}$ with consequent overestimation of the polarizability and $C_6(\mathrm{K^+K^+})$. Further uncertainties arise from the discrepancies (table A 2.3) between the accurate total molar polarizabilities of KBr and KI (Wilson & Curtiss 1970) and the sum of the cation and anion polarizabilities reported by Lynch (1967). The KCl results are, however, free from these difficulties not only because the sum of $\mathrm{K^+}$ and $\mathrm{Cl^-}$ polarizabilities of Lynch (1967) does reproduce the accurate molar polarizability (Wilson & Curtiss 1970) but also because the assumption that only six

Table A 2.3. Accurate polarizabilities and Slater–Kirkwood formula predictions of dipole–dipole dispersion coefficients for in-crystal ions compared with values derived from optical spectra (atomic units)

	α_C	α_A		$C_6(\mathrm{AA})$			$C_6(\mathrm{CA})$		$C_6(\mathrm{CC})$	
salt	opt(L)(1)	best(3)	opt(L)(1)	SK(4)	opt(L)(1)	opt(M)(2)	SK(4)	opt(L)(1)	SK(4)	opt(L)(1)
NaCl	—	21.15	—	180	—	122	14	—	—	—
KCl	5.60	22.86	22.54	203	191	137	64	65	22.9	24.0
KBr	6.95	30.63	30.37	343	271	—	82	87	22.9	31.1
KI	8.11	44.87	35.83	634	342	418	108	127	22.9	55.3

(1) opt(L) derived from optical spectrum by Lynch (1967).

(2) opt(M) derived from optical spectrum by Mayer (1933).

(3) Derived by subtracting cation polarizabilities (see text) from molar crystal polarizabilities (Wilson & Curtiss 1970).

(4) SK: prediction from Slater–Kirkwood formula with electron numbers taken to be those for the iso-electronic inert gases given in table A 2.1.

halide electrons contribute to the absorption is not unreasonable because the electron number of Ar is 6.106. Thus the optical absorption data do not provide any evidence that the Slater–Kirkwood formula is unreliable but even provide some further support for its validity.

The dispersion coefficients between pairs of free cations have been calculated (Mahan 1982) from frequency dependent polarizabilities computed with a non-empirical method in which exchange and correlation were introduced by a local density functional approximation. These predictions can be compared with in-crystal dispersion coefficients because s^2 and p^6 cation polarizabilities are insensitive to the environment. The agreement (table A 2.4) between the calculated polarizabilities and the most accurate values derived either from experiment or fully *ab initio* calculation provides evidence for the reliability of density functional approximations. The agreement (table A 2.4) between the Mahan (1982) non-empirical predictions for the $C_6(\mathrm{CC})$ coefficients and those calculated from the Slater–Kirkwood formula provides further evidence that the latter is trustworthy.

Table A 2.4. Comparison between Slater–Kirkwood and non-empirical predictions of dipole–dipole dispersion coefficients between like cations (atomic units)

	α of cation			$C_6(\mathrm{CC})$	
			SK	with[(3)]	Mahan
ion	best[(1)]	Mahan[(2)]	α (best)	α (Mahan)	computed[(2)]
Na^+	1.002	1.06	1.59	1.73	1.67
K^+	5.339	5.63	22.9	24.8	23.3
Rb^+	9.05	9.35	55.2	58.0	54.0
Mg^{2+}	0.486	0.506	0.63	0.57	0.57
Ca^{2+}	3.193	3.27	10.6	11.0	10.5
Sr^{2+}	5.15	5.92	23.7	29.2	27.7

(1) Best values from Fowler & Pyper (1985) derived from experiment for Rb^+ and Sr^{2+} or accurate *ab initio* calculation for Na^+, K^+, Mg^{2+}, Ca^{2+}.

(2) Computed by Mahan (1982) by using local approximations to exchange and correlations.

(3) Prediction of Slater–Kirkwood formula with electron numbers taken to equal those (table A 2.1) of the iso-electronic inert gas. Columns headed best and Mahan use the best and Mahan polarizabilities of columns 1 and 2 respectively.

Appendix 3. Tests of approximations to dipole–quadrupole $C_8(\mathrm{ab})$ dispersion coefficients

The most accurate current values of the dipole–quadrupole $C_8(\mathrm{aa})$ coefficients between like pairs are compared in table A 3.1 with those predicted by the formulae of Margenau (1939), Narayan (1977) and Starkschall & Gordon (1972). The accurate values are taken from *ab initio* calculations because experimental information is limited. The results show that neither the formula of Margenau (1939) nor that of Narayan (1977) is satisfactory. It should be noted that, for the interaction of like pairs, the Narayan formula depends only on the polarizability and not on the electron number. The previous test (Narayan 1977) of this formula is invalidated by the use of the ionic polarizabilities of Tessman *et al.* (1953) which are now known to be unreliable (Fowler & Pyper 1985), being too large for cations by factors of up to two.

The expectation values of r^4 and r^2 for the ground state entering the Starkschall–Gordon formula (2.26) were taken from the tables of Desclaux (1972). The results (table A 3.1) suggest that it may be preferable to consider all the electrons in the computation of these expectation values rather than just those belonging to the valence shell, namely the outermost s for the alkalis, alkaline earths and He, and the outermost s and p for the remaining inert gases.

TABLE A 3.1. COMPARISON OF APPROXIMATE METHODS OF DERIVING DIPOLE–QUADRUPOLE C_8(a a) DISPERSION COEFFICIENTS FROM THE INTERACTION OF LIKE SYSTEMS (ATOMIC UNITS)

		Starkschall–Gordon(2) considering electrons		Margenau(3) P_a from		
	best(1)	all	valence	theory	exp	Narayan(4)
He	13.9	14	14	4	6	3
Ne	74	60	61	8	15	11
Ar	1176	1142	1206	247	324	192
Kr	2581	2578	3053	674	738	437
Xe	7033	6677	8661	2062	2088	1162
H	124	146	146	66	80	32
Li	80890	129865	133011	203891	263766	42152
Na	109800	132443	171058	221558	224249	42408
K	383400	379178	588900	803780	780369	133818
Rb	524400	440246	781256	1015222	880505	159010
Cs	902500	605951	1198371	1913349	1289318	252481
Be	10270	9749	10008	6067	8545	2230
Mg	42230	34672	40885	27884	29759	7924
Ca	200000	150902	202069	155971	159073	36894

(1) Best values from Starkschall & Gordon (1972) for He, *ab initio* calculations of Doran (1974) for Ne, Ar, Kr and Xe, Maeder & Kutzelnigg (1979) for alkali and alkaline earths and Kolos (1967) for H.

(2) Computed with Starkschall–Gordon formula (1972) considering all electrons (column 2) and only valence electrons (column 3).

(3) Predicted by using Margenau (1939) formula. Column headed theory uses respectively the theoretical electron number (discussed in text) used to compute the C_6(aa) reported in table A 2.1. Column headed exp uses the electron numbers in column 2 of table A 2.1.

(4) $C_8(\mathrm{aa}) = \frac{3}{2}(27/26)\,\alpha_{\mathrm{a}}^2$. This is the simplification for like pairs of result (29) of Narayan (1977).

APPENDIX 4. TEST OF THE DISPERSION DAMPING FUNCTION AND THE CORRELATION ENERGY CALCULATION

The damping functions ($\chi_6^{\mathrm{aa}}(R)$ and $\chi_8^{\mathrm{aa}}(R)$ for the dipole–dipole and dipole–quadrupole dispersive attractions between a pair of hydrogen atoms have been calculated analytically (Koide 1976). The variation method was used to derive the first-order perturbed wavefunction needed to describe the polarizabilities at imaginary frequencies which are required to calculate the damping functions. These functions (Appendix 2 of Koide 1976) are extremely similar to (2.32) and (2.33) with $d_{\mathrm{a}1} = d_{\mathrm{a}2} = 2$.

The Koide formalism has also been used to compute more accurately, from an elaborate first-order perturbed wavefunction, the function $\chi_6^{\mathrm{aa}}(R)$ for the interaction of two Be atoms (Krauss & Newman 1979). The results presented in table A 4.1 show that the damping factors predicted from (2.32), with damping parameter calculated from the 2s and 2p orbital eigenvalues according to (2.41), accurately reproduces the *ab initio* values plotted in fig. 4 of Krauss & Newman (1979). A similar damping function is predicted (table A 4.1) from (2.32) if the two orbital eigenvalues in (2.41) are replaced by the experimental ionization potentials (in atomic units) of the ground (^{1}S) and first ^{1}P excited states.

The results of accurate *ab initio* calculations can be used to test not only the reliability of the expressions (2.32) and (2.33) for the dispersion damping function but also the calculation of the electron correlation contribution as the sum of the damped dispersion plus short-range correlation energy term computed from electron-gas theory. There is no substantial disagree-

Table A 4.1. Test of calculation of dispersion damping parameters and correlation energy for beryllium by *ab initio* calculation

				correlation contribution to interaction energy			
		$\chi_6^{aa}(R)$ (2.32)[2]		*ab initio*[3]		damped dispersion $+V_{saa}^{corr}(R)$[2]	
R	*ab initio*[1]	eigen	exp IP	basis 2	basis 5	eigen	exp IP
4.5	0.16	0.14	0.19	−0.0143	−0.0168	−0.0105	−0.0126
4.75	0.20	0.18	0.23	−0.0119	−0.0139	−0.0093	−0.0112
5.0	0.24	0.21	0.28	−0.0097	−0.0113	−0.0082	−0.0097
5.5	0.35	0.30	0.38	−0.0064	—	−0.0063	−0.0074
6.0	0.44	0.39	0.48	−0.0043	—	−0.0049	−0.0056
7.0	0.65	0.57	0.67	−0.0020	—	−0.0027	−0.0031
8.0	0.81	0.74	0.81	−0.0010	—	−0.0015	−0.0016
9.0	0.90	0.84	0.90	−0.0005	—	−0.0008	−0.0008

(1) From Krauss & Newman (1979).

(2) In columns headed eigen and exp IP, the dispersion damping parameters are calculated from (2.41) by using orbital eigenvalues and experimental ionization potentials respectively; $C_6 = 208$, $C_8 = 10270$; see tables A 2.1 and A 3.1.

(3) Harrison & Handy (1983). Basis 2 results communicated privately from which basis 5 results are derived as described in text.

ment (table A 4.1) over the entire range of inter-nuclear separations between the correlation contribution to the energy of interaction two Be atoms predicted *ab initio* (Harrison & Handy 1983) by using their basis 2 with that calculated as the sum of the damped dispersion plus electron-gas correlation energies. The three further *ab initio* values at short distances are derived by adding the difference between the total interaction energies predicted by bases 5 and 2 (Harrison & Handy 1983) to the results presented in column 5 of table A 4.1.

Appendix 5. Inter-ionic potentials predicted by using the descriptions (2.18) and (2.20) of the crystal environment

Table A 5.1. Lithium fluoride potentials†

		$V^0_{SCA}(R)$					$V^0_{SAA}(\surd 2R)$		
			electron-gas					electron-gas	
R	$V^{corr}_{SCA}(R)$	RIP	LP	WG	$E^A_{re}(R)$	$V^{corr}_{SAA}(\surd 2R)$	RIP	LP	WG
2.75	−0.00216	0.08522	0.06332	0.06022	0.03947	−0.00264	0.03370	0.04204	0.03617
3.0	−0.00159	0.05051	0.03772	0.03533	0.02465	−0.00195	0.01647	0.02371	0.01950
3.5	−0.00087	0.01897	0.01406	0.01274	0.00958	−0.00110	0.00404	0.00789	0.00572
3.75	−0.00065	0.01196	0.00879	0.00783	0.00600	−0.00084	0.00197	0.00462	0.00307
4.0	−0.00049	0.00766	0.00557	0.00488	0.00378	−0.00064	0.00095	0.00272	0.00161
4.5	−0.00027	0.00326	0.00232	0.00196	0.00153	−0.00037	0.00018	0.00095	0.00037
5.0	−0.00015	0.00144	0.00100	0.00081	0.00063	−0.00021	0.00002	0.00032	0.00003
5.5	−0.00008	0.00066	0.00044	0.00035	0.00026	−0.00012	0.0	0.00011	−0.00005

† $E^C_{re}(R) < 10^{-5}$ a.u.; RIP, LP and WG methods yield $V^0_{SCC}(2.75\surd 2) = 0.00002$, 0.00002 and 0.0 respectively. $V^{corr}_{SCC}(2.75\surd 2) = -0.00001$. All other cation–cation short-range energies are under 10^{-5}.

TABLE A 5.2. SODIUM FLUORIDE POTENTIALS†

		$V^0_{sCA}(R)$					$V^0_{sAA}(\sqrt{2}R)$		
			electron-gas					electron-gas	
R	$V^{corr}_{sCA}(R)$	RIP	LP	WG	$E^A_{re}(R)$	$V^{corr}_{sAA}(\sqrt{2}R)$	RIP	LP	WG
3.0	−0.00355	0.13265	0.13190	0.12536	0.05071	−0.00178	0.01867	0.02080	0.01707
3.5	−0.00193	0.04526	0.04731	0.04343	0.02211	−0.00093	0.00466	0.00645	0.00467
4.0	−0.00108	0.01677	0.01804	0.01591	0.00904	−0.00053	0.00118	0.00218	0.00128
4.25	−0.00082	0.01049	0.01135	0.00979	0.00577	−0.00040	0.00059	0.00128	0.00064
4.5	−0.00062	0.00666	0.00722	0.00609	0.00368	−0.00031	0.00028	0.00076	0.00029
5.0	−0.00036	0.00282	0.00301	0.00241	0.00151	−0.00018	0.00006	0.00026	0.00002
5.5	−0.00021	0.00124	0.00129	0.00098	0.00063	−0.00010	0.00001	0.00009	−0.00004
6.0	−0.00012	0.00056	0.00057	0.00040	0.00026	−0.00006	0.0	0.00002	−0.00004

		$V^0_{sCC}(\sqrt{2}R)$		
			electron-gas	
R	$V^{corr}_{sCC}(\sqrt{2}R)$	RIP	LP	WG
3.0	−0.00016	0.00078	0.00092	0.00065
3.5	−0.00004	0.00007	0.00009	0.00003

† $E^C_{re}(R) < 10^{-5}$ a.u.; $V^0_{sCC}(\sqrt{2}R)$ and $V^{corr}_{sCC}(\sqrt{2}R)$ all under 10^{-5} for $R \geqslant 4.0$ a.u.

TABLE A 5.3. SODIUM CHLORIDE POTENTIALS†

		$V^0_{sCA}(R)$					$V^0_{sCA}(\sqrt{2}R)$		
			electron-gas					electron-gas	
R	$V^{corr}_{sCA}(R)$	RIP	LP	WG	$E^A_{re}(R)$	$V^{corr}_{sAA}(\sqrt{2}R)$	RIP	LP	WG
4.0	−0.00245	0.06393	0.06376	0.05894	0.02911	−0.00246	0.01729	0.01779	0.01264
4.5	−0.00147	0.02721	0.02781	0.02496	0.01390	−0.00150	0.00555	0.00719	0.00435
5.0	−0.00089	0.01206	0.01251	0.01086	0.00646	−0.00093	0.00172	0.00293	0.00135
5.25	−0.00069	0.00814	0.00845	0.00721	0.00439	−0.00073	0.00092	0.00187	0.00069
5.5	−0.00054	0.00554	0.00577	0.00483	0.00298	−0.00058	0.00049	0.00119	0.00030
6.0	−0.00033	0.00267	0.00272	0.00219	0.00138	−0.00036	0.00011	0.00047	−0.00003
6.5	−0.00020	0.00130	0.00130	0.00101	0.00064	−0.00022	0.00001	0.00018	−0.00010
7.0	−0.00012	0.00064	0.00065	0.00047	0.00030	−0.00013	−0.00001	0.00006	−0.00010

† $E^C_{re}(R) < 10^{-5}$. Cation–cation potentials are identical to those given in table A 5.2.

TABLE A 5.4. SILVER FLUORIDE POTENTIALS

		$V^0_{\mathrm{sCA}}(R)$					$V^0_{\mathrm{sAA}}(\sqrt{2}R)$					$V^0_{\mathrm{sCC}}(\sqrt{2}R)$		
			electron-gas					electron-gas					electron-gas	
R	$V^{\mathrm{corr}}_{\mathrm{sCA}}(R)$	RIP	LP	WG	$E^{\mathrm{A}}_{\mathrm{re}}(R)$	$V^{\mathrm{corr}}_{\mathrm{sAA}}(\sqrt{2}R)$	RIP	LP	WG	$E^{\mathrm{C}}_{\mathrm{re}}(R)$	$V^{\mathrm{corr}}_{\mathrm{sCC}}(\sqrt{2}R)$	RIP	LP	WG
3.5	−0.00638	0.09926	0.18370	0.17374	0.02986	−0.00090	0.00483	0.00609	0.00439	0.00079	−0.00185	0.01013	0.02322	0.01933
4.0	−0.00385	0.03240	0.07597	0.06898	0.01271	−0.00049	0.00127	0.00199	0.00116	0.00016	−0.00079	0.00197	0.00519	0.00398
4.5	−0.00237	0.01131	0.03214	0.02776	0.00524	−0.00028	0.00031	0.00069	0.00026	0.00004	−0.00033	0.00043	0.00116	0.00070
4.75	−0.00187	0.00671	0.02103	0.01763	0.00336	−0.00022	0.00016	0.00040	0.00010	0.00002	−0.00021	0.00022	0.00053	0.00026
5.0	−0.00147	0.00406	0.01381	0.01120	0.00216	−0.00017	0.00007	0.00024	0.00001	0.00001	−0.00014	0.00011	0.00024	0.00007
5.5	−0.00092	0.00149	0.00600	0.00448	0.00090	−0.00009	0.00002	0.00008	−0.00004	0.0	−0.00005	0.00003	0.00004	−0.00002
6.0	−0.00057	0.00051	0.00262	0.00176	0.00038	−0.00005	0.0	0.00002	−0.00004	0.0	−0.00002	0.00001	0.0	−0.00002

TABLE A 5.5. LEAD FLUORIDE POTENTIALS

		$V^0_{\mathrm{sCA}}(R)$					$V^0_{\mathrm{sAA}}(\sqrt{(\frac{2}{3})}\,R)$					$V^0_{\mathrm{sCC}}(2\sqrt{(\frac{2}{3})}\,R)$		
			electron-gas					electron-gas					electron-gas	
R	$V^{\mathrm{corr}}_{\mathrm{sCA}}(R)$	RIP	LP	WG	$E^{\mathrm{A}}_{\mathrm{re}}(R)$	$V^{\mathrm{corr}}_{\mathrm{sAA}}(2R\sqrt{3})$	RIP	LP	WG	$E^{\mathrm{C}}_{\mathrm{re}}(R)$	$V^{\mathrm{corr}}_{\mathrm{sCC}}(2\sqrt{(\frac{2}{3})}\,R)$	RIP	LP	WG
4.0	−0.00468	0.07767	0.09581	0.08863	0.01576	−0.00145	0.00805	0.01304	0.01011	0.00125	−0.00057	0.00432	0.00230	0.00160
4.5	−0.00291	0.03419	0.04152	0.03668	0.00658	−0.00093	0.00245	0.00550	0.00377	0.00022	−0.00019	0.00085	0.00036	0.00014
4.75	−0.00230	0.02313	0.02744	0.02359	0.00424	−0.00075	0.00134	0.00361	0.00228	0.00009	−0.00011	0.00040	0.00013	0.00001
5.0	−0.00183	0.01578	0.01815	0.01514	0.00273	−0.00061	0.00069	0.00237	0.00135	0.00004	−0.00006	0.00017	0.00004	−0.00002
5.5	−0.00115	0.00750	0.00797	0.00617	0.00114	−0.00040	0.00015	0.00103	0.00042	0.0	−0.00002	0.00001	0.0	−0.00002
6.0	−0.00072	0.00364	0.00350	0.00245	0.00048	−0.00026	0.00001	0.00044	0.00008	0.0	−0.00001	0.0	0.0	−0.00001
6.5	−0.00049	0.00179	0.00154	0.00093	0.00020	−0.00016	−0.00001	0.00018	−0.00003	0.0	0.0	0.0	0.0	0.0

TABLE A 5.6. MAGNESIUM OXIDE POTENTIALS[1]

		$V^0_{\text{sCA}}(R)$					$V^0_{\text{sAA}}(\surd 2R)$				$V^0_{\text{CC}}(\surd 2R)$		
			electron-gas					electron-gas				electron-gas	
R	$V^{\text{corr}}_{\text{sCA}}(R)$	RIP	LP	WG	$E^{\text{A}}_{\text{re}}(R)$[2]	$V^{\text{corr}}_{\text{sAA}}(\surd 2R)$	RIP	LP	WG	$V^{\text{corr}}_{\text{CC}}(\surd 2R)$	RIP	LP	WG
3.0	−0.00366	0.22123	0.19393	0.18890	0.56348	−0.00378	0.04017	0.04858	0.04011	−0.00003	0.00007	0.00008	0.00004
3.5	−0.00224	0.10124	0.08930	0.08570	0.46132	−0.00270	0.01025	0.02196	0.01623				
3.75	−0.00179	0.07157	0.06318	0.06024	0.43000	−0.00235	0.00427	0.01519	0.01040				
4.0	−0.00144	0.05199	0.04582	0.04343	0.40673	−0.00206	0.00097	0.01067	0.00663				
4.25	−0.00118	0.03874	0.03412	0.03218	0.38907	−0.00183	−0.00085	0.00760	0.00416				
4.5	−0.00097	0.02977	0.02596	0.02440	0.37545	−0.00164	−0.00180	0.00546	0.00252				
5.0	−0.00068	0.01846	0.01605	0.01450	0.35617	−0.00135	−0.00241	0.00290	0.00067				
5.5	−0.00049	0.01230	0.01070	0.00997	0.34345	−0.00114	−0.00235	0.00155	−0.00019				

(1) $E^{\text{C}}_{\text{re}}(R) < 10^{-5}$; $V^0_{\text{sCC}}(\surd 2R)$ and $V^{\text{corr}}_{\text{sCC}}(\surd 2R)$ all under 10^{-5} for $R \geqslant 3.5$.

(2) Does not include the contribution from electron correlation $E^{\text{corr}}_{\text{re}}$: see (2.17).

The dispersion damping functions are not tabulated because they can be computed from the damping parameter reported in table 3 by using (2.32), (2.33), (2.35) and (2.37). All $\chi^{\text{CA}}_6(R)$ varied between 0.17 and 0.92, all $\chi^{\text{AA}}_6(x_{\text{AA}}R)$ varied between 0.25 and 0.97, while all $\chi^{\text{CC}}_6(x_{\text{CC}}R)$ were greater than 0.94 except for AgF for which $\chi^{\text{CC}}_6(x_{\text{CC}}R)$ ranged from 0.36 to 0.92. The ranges of all $\chi^{\text{CA}}_8(R)$, $\chi^{\text{AA}}_8(x_{\text{AA}}R)$ and $\chi^{\text{CC}}_8(x_{\text{CC}}R)$ were respectively 0.02–0.6, 0.06–0.8 and 0.67–1.0.