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Short-Range Contributions to the Polarization of Cations

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Charge-overlap cluster calculations [Wheatley, R. J. *Chem. Phys. Lett*. **1998**, *294*, 487], in which the electronic structure of a central ion is modified self-consistently by the frozen densities of its neighbors, are used to model induced dipoles in the condensed-phase alkali metal halides. Two distinct effects of overlap are identified: exchange-repulsion and Coulomb corrections. For anions, both substantially reduce the dipole from its asymptotic value; for cations, the two short-range effects are opposed, producing small net short-range corrections of different sign for different alkali metal cations.

I. Introduction

The dipoles and quadrupoles induced by interionic interactions play important roles in determining the properties of condensed ionic systems.[1,2] The contribution of the polarization effects to the interaction potential can be significant. They may determine the choice of crystal structure, affect phonon dispersion relationships, and strongly influence the local structure in ionic melts and clusters.[3−10] Additionally, the induced dipole moments have a direct experimental signature in the infrared spectrum of the material.[11,12] It has long been recognized that multipoles may be induced by short-range effects, on the length scale of the overlap between the electron densities of the individual ions, as well as by the Coulombic fields caused by the charges (and induced multipoles) on surrounding ions. Such short-range effects are incorporated, according to a particular mechanical representation, in the description of polarization interactions in the classical shell model,[13,14] for example. In previous work we have examined the short-range contribution to the polarization of anions[3,15,16] in electronic structure calculations of distorted clusters. Accurate, physically based representations of this contribution which are suitable for incorporation in computer simulations have been devised and are found to be transferable between different materials. Systematic simulation studies of a range of materials have clarified the role of anion polarization effects on their structural and dynamical properties.[3,17]

Although the anion is normally the main polarizable species in an ionic material when the cation is heavy, or does not have a noble gas electronic configuration, the cation polarizability may become very large. For example, the Cs^+ and Sn^{2+} cations have polarizabilities of ∼15 au, approaching the in-crystal polarizability of Cl^- (∼20 au in NaCl), and comfortably exceeding those of F^- (∼6 au in LiF) and O^{2-} (∼11 au in MgO). Cation polarization has been shown to have a marked effect on the properties of such materials. For example, dipole polarization of Sn^{2+} accounts quantitatively for the distinctive litharge structure of SnO (which is normally attributed to the Sn^{2+} lone pair),[18] and quadrupole polarization of Ag^+ is often invoked to explain its high mobility in the solid state.[19−21] Short-range cation polarization effects may be expected to influence these properties. For reasons to be described below, it has not hitherto been possible to study cations in crystals with electronic structure calculations of the type used to characterize anion polarization.

In the present paper we use a model of the in-crystal environmental potential, which has been successfully used to treat the anion polarization problem,[22,23] to explore the physical effects which contribute to the short-range cation polarization. Significant differences are found between the way that cations and anions respond to distortions in their coordination environment.

The plan of the paper is as follows. In section II we survey the way in which ions in a condensed phase are polarized by interaction with their neighbors, and how this effect has been studied in the anion case. Section III summarizes the "charge-density-overlap" method which we use to model the environmental potential in electronic structure calculations of the induced moments. In section IV we separate the contribution to the induced dipole of an ion arising from Coulombic interactions with the charge densities of its neighbors from the contribution arising from "exchange repulsion"[24,25] (i.e., from the orthogonalization of the associated wave functions) and we compare their effects for cations and anions. Finally (section IV.C), we present results for the short-range polarization of alkali metal cations and Ag^+ and discuss the implications for interionic interactions in the condensed phase.

II. Mechanisms for Ion Polarization

A. Anion Polarization: Reprise. The anion polarization effect was characterized by performing electronic structure calculations (Hartree−Fock + Møller−Plesset) on clusters of ions in which an anion was surrounded by a first coordination shell of cations, and this cluster placed in a lattice of point charges to ensure that the variation of the Madelung potential close to the anion site was similar to that in an infinite crystal. In this way the effects of coordination on the anion electronic

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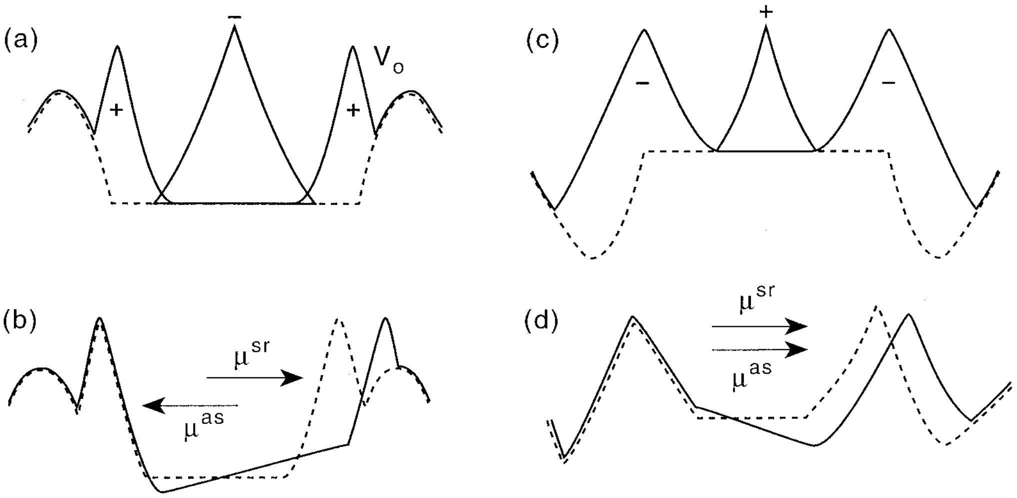

Figure 1. (a) Origin of the spherical confining potential which acts on the electrons around an anion in a cubic crystal. A cross section through the spherical potential, V_0, is shown: the dashed line shows the Coulombic (Madelung) contribution, associated with the point ionic charges. This is enhanced by the exclusion from the region occupied by the electron density of the other ions. (b) Origin of the asymptotic and short-range dipole moments associated with the motion of a single nearest-neighbor cation (on the right of the figure) outward. (c) Origin of the potential acting on a central cation surrounded by a shell of anions. The line styles are as in part a. (d) Origin of the asymptotic and short-range dipole moments associated with the motion of a single nearest-neighbor anion outward assuming that the exchange effects are dominant.

properties were replicated. When carried out on undistorted clusters, representative of perfect crystals, such calculations reveal that the properties of the anion are profoundly affected by this environment, so that the polarizability of the in-crystal anion, for example, is much reduced from that of an isolated anion in the gas phase.[15,26,38] In a perfect cubic crystal, this environmental effect can be viewed as the consequence of a *spherical* confining potential which compresses the electron density of the anion.[1,3,33]

If the cluster is deformed to simulate the environmental effect in a distorted crystal, the anion becomes polarized. The multipole moments induced in this way can be described as the sum of two terms—an “asymptotic” multipole, arising from the electric fields and field gradients at the anion site, i.e., the terms which would be obtained in a Taylor (or multipole[24]) expansion of the Coulomb potential at the anion site, and a “short-range” multipole, which accounts for the corrections to this asymptotic term. The calculations showed that this correction could be viewed as caused by the anisotropic deformation of the confining potential (or “dent in the wall”) when a near-neighboring cation is displaced, and this localized picture informs the way that the effect is mimicked in the computer simulations (see Figure 1). In the undistorted cluster the anion electron density is isotropically compressed by the confining potential. When one of the ions in the first coordination shell is displaced outward, it causes an electric field (potential gradient) at the anion site. This field is responsible for the asymptotic dipole. However, the displacement also makes a “dent” in the wall of the confining potential, so that the anion charge density may expand into this space giving a dipole which *opposes* the asymptotic moment. The effect may be substantial: in an alkali metal halide the short-range term may reduce by $\sim$40% the dipole induced in an anion by small displacements of a first-neighbor cation, and the reduction of the quadrupole may be twice as large.[16,27]

At a more fundamental level, these short-range corrections arise from two sources, both of which originate in the overlap of the anion charge density with the charges of neighboring ions. Stone[24] has discussed the generalization of the conventional theory of long-range, nonbonding interactions to allow for overlapping charge distributions. First, there is a correction to the Coulomb potential as the Taylor (multipole) expansion of the Coulomb potential between classical charge distributions fails when the charge distributions overlap: we will refer to this as the “Coulomb overlap correction”. There is a second effect whose origin lies in the Pauli exclusion principle, which restricts the extent to which the anion electrons can penetrate the charge clouds of the surrounding cations: this is the “exchange-repulsion correction” to the induced dipole. As we shall show below, the reason that the simple picture of the dent in the confining potential describes the short-range anion polarization so well is that the second of these effects outweighs the first.

B. Cation Polarization. For the polarization of cations, the confining-potential picture, which successfully rationalizes anion behavior, leads to the expectation that the short-range polarization will enhance the asymptotic one. This reasoning is illustrated in panels c and d of Figure 1. The spherically averaged Coulomb potential at the cation site in a perfect crystal arising from all other charges (i.e., the Madelung potential) is a plateau.[1] In the figure this is ringed by a barrier to indicate the presumed exclusion of the cation electrons from the charge clouds of the anions. For main-group elements the effect of this potential on the cation charge density is much smaller than for the anions, as can be seen from the similarity of the polarizabilities of free and in-crystal cations.[27,28] When a first shell anion is displaced radially, the electron flow induced by the electric field at the cation site and that induced by the dent in the barrier are in the same direction—giving rise to the enhancement anticipated above. There is empirical evidence to support such an enhancement in some cases,[29,30] but not in others.[18] Clearly, some guidance from electronic structure calculations would be helpful.

The difficulty in obtaining such guidance can be traced to problems with applying cluster electronic structure calculations of the type described above to the cation case. An analogous calculation would have a cation surrounded by a shell of anions subjected to certain distortions. Conventionally, the moments induced in the entire cluster are obtained from an ab initio (Hartree–Fock + MP2) calculation on the distorted cluster, and the moment induced on the central ion is extracted after correcting for the dipoles induced on the shell, dipole–induced dipole (DID) effects, and basis set superposition error (BSSE).

When cations surround anions, these corrections are small compared to the moment on the central ion, either because the cations have low intrinsic polarizabilities or because the special basis sets used do not allow the cations to polarize. Such basis sets cannot be constructed for anions without introducing uncontrollable BSSE. Since a shell of six anions will typically be much more highly polarized than a central cation, the induced moment on the cation is a small part of the total moment of the cluster and cannot be extracted reliably from all-electron cluster calculations.

However, it has recently been shown that a simplified type of electronic structure calculation, first developed to study the effect of (weak) overlap corrections to long-range forces,[25] also accurately recovers the results of the full, all-electron cluster calculations of anion polarization.[23] In these calculations the environmental potential acting on the electrons of the central ion is calculated from the static ground-state electron densities of the surrounding ions. The subsequent electronic structure calculation therefore involves only the electrons of the central ion subjected to this environmental potential. Hence, these calculations yield the induced moment on the central ion directly, without correction for polarization and BSSE of the surrounding shell. This approach should therefore avoid the main problems which beset the all-electron approach to the cation polarization.

In the next section we summarize this charge-density-overlap model, and then describe a series of calculations to explore the physical effects that contribute to the short-range cation polarization (analogous to the calculations used to establish the dent-in-the-wall picture for anions). The new calculations show that the picture of short-range cation polarization, represented in Figure 1c,d, is oversimplified. Results for the short-range polarization of various simple cations allow some general conclusions about the cation polarization to be drawn.

III. The Charge-Density-Overlap Model

In a crystal, the environmental potential on the electrons of an ion is dominated by interactions, both Coulombic and exchange, between that ion and its nearest neighbors. In the calculations to be described below, Coulomb and exchange interactions with the frozen densities of the neighbors are included in the Hamiltonian for the ion of interest, and a self-consistent calculation is performed for its electronic structure in the presence of this perturbing potential. Similar calculations, in which the environmental potential is calculated directly from the electron density of surrounding atoms, have been performed previously, in order to study the effect of the environment-induced compression on the effective interaction potentials.[31−34] So far as we are aware, no such calculations have been made for the polarization effects.

The charge-density-overlap model proposed by Wheatley[25] approximates the exchange repulsion between two (closed-shell) ions A and B by assuming that it is proportional to the overlap of their electron densities:

$$E^{AB}{}_{\mathrm{exch}} = k_{AB} \int \rho_A(\mathbf{r})\, \rho_B(\mathbf{r})\, \mathrm{d}\mathbf{r} \qquad (3.1)$$

where k_{AB} is an adjustable parameter to be determined (see below). Note that this energy reflects, in addition to a normal exchange energy, the consequences of the orthogonalization of the orbitals of A to those of B,[24] which would occur in a full self-consistent electronic structure calculation, and which results in an increase of the kinetic energy.[35] The identification of the best functional of the density through which to express this energy is a matter of active research.[36,37] As we shall discuss below, the functional given in eq 3.1 seems to perform well for the current applications.

If B is the ion whose electronic structure we wish to calculate in the presence of the static charge density of A, the environmental potential on the orbitals $\{\phi^B{}_i\}$ of B arising from A is obtained from the (functional) derivative of this energy (eq 3.1) with respect to $\phi^B{}_i$, i.e.

$$v_{\mathrm{exch}}(\mathbf{r})\, \phi^B{}_i(\mathbf{r}) = k_{AB}\, \rho_A(\mathbf{r})\, \phi^B{}_i(\mathbf{r}) \qquad (3.2)$$

Together with the Coulomb potential from the electrons of A

$$v_{\mathrm{coul}}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho_A(\mathbf{r}')\ (3.3) \qquad (3.3)$$

and the Coulomb potential due to the nucleus of A, this constitutes the environmental potential to be added to the normal Hamiltonian for ion B.

To specify the potential fully, a value for k_{AB} is required. It is fixed from a Heitler−London calculation of the exchange energy for the ion pair, as follows. Obtain wave functions for the isolated species A and B in separate calculations. Now perform a Heitler−London calculation of the energy of the AB dimer at the separation relevant to the crystal by antisymmetrizing the two monomer wave functions over all the electrons of the dimer. This gives a total interaction energy

$$\Delta E^{HL} = \Delta E^{HL}{}_{\mathrm{coul}} + \Delta E^{HL}{}_{\mathrm{exch}} \qquad (3.4)$$

In the final step, the charge-density overlap of A and B is calculated using the first step of an SCF calculation of B in the exchange-repulsion potential (eq 3.2) of A, setting k_{AB} to 1 au and switching off the Coulomb interaction between the two systems. The total energy in the first step of the self-consistent cycle, before the density of B has relaxed, is

$$E_{1,B} = E_{0,B} + \int \rho_A(\mathbf{r})\, \rho_B(\mathbf{r})\, \mathrm{d}\mathbf{r} \qquad (3.5)$$

where $E_{0,B}$ is the energy of the isolated B system and $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ are the densities of the isolated systems A and B. Simple proportionality gives k_{AB} as

$$k_{AB} = \frac{\Delta E^{HL}{}_{\mathrm{exch}}}{E_{1,B} - E_{0,B}} \qquad (3.6)$$

With the value of k_{AB} fixed, the polarization of an ion due to interaction with its neighbors is calculated using a distorted cluster in which the electron densities of the first shell of ions around the ion of interest are “frozen” and included in the Hamiltonian only through the environmental potential. The induced dipole is obtained from the first moment of the self-consistent wave function for this Hamiltonian. The reliability of these procedures was extensively tested in ref 22.

Use of the charge-density-overlap model in cluster calculations has some clear advantages. The size of the system is only that of the central ion, and so the calculations can be taken to a high level of theory and large single-particle basis sets may be used. BSSE is no longer a problem, and DID interactions are absent, as the compressing cation has a rigorously frozen density and adds no variational freedom for the anion electrons.

When the method has been applied to calculate the properties of an anion, we have made use of the fact that the neighboring cation densities are insensitive to the crystalline environment: $\rho_B(\mathbf{r})$ in eq 3.1 is therefore a constant function obtained from a good-quality electronic structure calculation on an isolated cation. When cation properties are of interest, the neighbors are anionic, and some questions of principle arise: should the frozen anion density be that of the free ion, the ion confined by the Madelung potential, or the fully compressed in-crystal anion? Fortunately, the effects are small, and in the halide systems studied here free-ion densities were used, though alternative choices of anion density have negligible effect on the result.

The earlier anion calculations allayed possible reservations about the crude approximation of the exchange-repulsion energy by linear functions of the two densities. In particular k_{AB} was found not to depend strongly on the interionic separation over a physically significant range, and the values obtained for the polarizabilities and for the induced dipoles in distorted cluster calculations accord well with those obtained from the conventional all-electron approach. These features may be expected to carry over to cation-centered calculations.

Extension to Cation Properties. Preliminary calculations of the type described above for cations gave results for the short-range polarization which appeared difficult to reconcile with the physical pictures described in section II.B. The procedure was modified to separate the contributions to the induced dipole arising from the Coulombic and exchange repulsion interactions of the central ion with the charge densities of its neighbors. Calculations were carried out with the environmental potential represented at three levels, approximating progressively more closely to reality.

Point charge model (XTAL): At the lowest level, all the ions surrounding the ion of interest are simple point charges (formal ionic charges).

Coulomb potential model (COUL): The exchange-repulsion parameter k_{AB} is set to zero, so that electrons of the central ion experience the pure Coulomb potential of the full frozen charge densities of the surrounding ions plus the point charge interaction with the rest of the lattice. Comparison of the XTAL and COUL results will enable us to identify the effect of overlap of charge densities on the Coulomb potential.

Charge-overlap model (FULL): In the FULL calculations, k_{AB} is set to the value determined from the Heitler−London procedure described above[22] and a calculation is carried out for the central ion embedded in a cluster of frozen neighbors surrounded by a point charge lattice fragment. Comparison of the FULL and COUL results enables us to isolate the exchange-repulsion contributions to the induced dipoles.

IV. Results

In all cases calculations of the induced dipole are performed on clusters representing fragments of rock-salt-structured crystals where one of the ions in the first shell around the ion of interest has been displaced radially inward or outward by a small amount. The results of the electronic structure calculations (μ_α) are interpreted by identifying the short-range contributions to the dipole as the difference between the calculated dipole (μ_α^{SR}) and the asymptotic dipole (μ_α^{ASY}) induced by the electric field at the central ion (**E**) calculated from the formal charges on the other ions

$$\mu_\alpha^{SR} = \mu_\alpha - \mu_\alpha^{ASY} \tag{4.1}$$

where

$$\mu_\alpha^{ASY} = \alpha E_\alpha = -\alpha \sum_i \frac{Q^i r_\alpha^i}{(r^i)^3} + ... \tag{4.2}$$

and Q^i and $\mathbf{r}^i$ are the charge and position, relative to the central ion, of neighbor i. In this equation α is the (isotropic) polarizability of the central ion at the appropriate level of calculation (XTAL, COUL, or FULL). The asymptotic dipole describes the dipole which would be found if all overlap effects were negligible. In principle, eq 4.2 contains higher order terms reflecting hyperpolarization effects, but for the cations which are our central interest, these corrections are extremely small. For anions, the hyperpolarization can be significant and has been included in our previous work.[16,23]

TABLE 1: Anion and Cation Polarizabilities from the Present Charge-Overlap Calculations[a]

system	calculation	R (au)	α (au)
$F^-(Li^+)_6$	XTAL	3.7965	7.57
$F^-(Li^+)_6$	COUL	3.7965	8.20
$F^-(Li^+)_6$	FULL	3.7965	5.23
$Li^+(F^-)_6$	FULL	3.7965	0.18
$Na^+(F^-)_6$	FULL	4.3785	0.97
$K^+(F^-)_6$	FULL	5.0512	5.34
$Rb^+(F^-)_6$	FULL	5.3290	9.05
$Na^+(Cl^-)_6$	FULL	5.3290	0.97
$K^+(Cl^-)_6$	FULL	5.9451	5.34
$Rb^+(Cl^-)_6$	FULL	6.2191	9.05
$Ag^+(F^-)_6$	FULL	4.6580	9.05

[a] Column 1 indicates the nature of the central ion (F^- anion or M^+ cation). Column 2 shows the level of calculation (see text), while columns 3 and 4 list the equilibrium ionic separations and central ion polarizabilities, respectively.

A. Anion Polarization: The F⁻ ion in LiF. To set the stage for the cation case, we first present results for the induced dipole on an F^- ion in a distorted LiF crystal. The short-range polarization of this ion has been discussed at length previously.[27] Here, by contrasting the COUL and FULL results we will be able to separate the short-range contributions of exchange repulsion and Coulomb overlap.

Induced dipoles are obtained in six distorted geometries and at different levels of calculation. One Li^+ ion in the first coordination shell is displaced radially by ±0.05, ±0.1, and ±0.5 au. Analysis of the short-range effects for a central anion has the complication that the anion polarizability itself differs at different levels of calculation, so that a direct comparison of the induced dipoles does not reflect simply the differences in the perturbing potentials. For this reason, we compare the results for the induced dipole divided by the polarizability appropriate to each level of calculation (separately determined). These polarizabilities are listed in Table 1. This ratio can be viewed as the effective field which acts upon the ion to give the dipole.[39]

The values of the μ/α ratio obtained in the different types of electronic structure calculations are shown by symbols in Figure 2. Also shown, with a full line, is the asymptotic electric field to which all the calculated results would reduce if there were no charge-overlap effects. It can be seen that even for the XTAL calculations with point charge neighbors there is a short-range correction which reduces the dipole below that expected for the asymptotic electric field; this "dent-in-the-wall" effect was discussed previously.[27] When XTAL results are contrasted with COUL results (full Li^+ electron density, but no exchange repulsion), we see that the dipole is increased slightly by the overlap of anion and cation electron densities. As anion electrons penetrate the charge clouds of the closest cation, they experience an increased nuclear charge and are drawn in the same direction as μ^{ASY}. Finally, when COUL results are contrasted with FULL results, we see the effect of exchange repulsion. The anion electrons are excluded from the region of the cation charge density, hence opposing μ^{ASY}. Exchange-repulsion acts in the

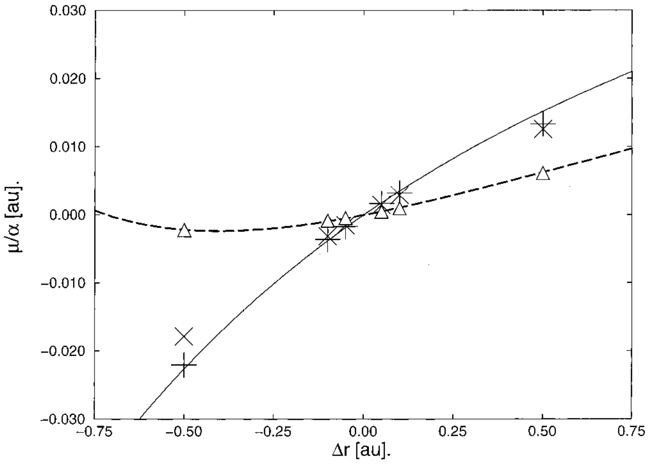

Figure 2. Induced dipoles from the ab initio calculations for a central F^- anion surrounded by six Li^+ cations at the equilibrium lattice parameter, plotted against the radial displacement of a single first-shell cation. +, XTAL; ×, COUL; △, FULL; full line, dipole predicted from the asymptotic polarizability; dashed line, dipole predicted from the short-range damping model (see text for details). The dipoles are divided by the anion polarizability appropriate to the level of calculation as discussed in the text.

same direction as the net short-range Coulomb correction, but is substantially more important. It can be shown directly that the exchange-repulsion effects swamp the Coulomb contribution by running a FULL calculation but with Coulomb contributions to the interionic potential switched off; the net induced dipole obtained in this case arises from exchange repulsion alone (since there are no ionic charges to create the Coulombic polarization). These net dipoles are very similar to the short-range dipoles obtained in the FULL calculations.

For anions it is therefore seen that the dominant short-range correction to the asymptotic dipole comes from the exchange-repulsion effect, as has been tacitly assumed in the way that the correction has been modeled in simulation work.[3,16] In this model the short-range dipole is regarded as the effect of a "field" acting through the ionic polarizability, i.e.

$$\mu_\alpha{}^{SR} = \alpha E_\alpha{}^{SR} \tag{4.3}$$

where E^{SR} is a short-range function of the positions of neighboring ions

$$E_\alpha^{SR} = \sum_i \frac{Q^i r^i_\alpha}{(r^i)^3}\left[c^i \sum_{k=0}^{4} \frac{(b^i r^i)^k}{k!} e^{-b^i r^i}\right] \tag{4.4}$$

At small r^i, the factor in square brackets reduces to c^i times the contribution of that ion to the Coulomb field (eq 4.2), so that with c^i negative, the effect is to damp the asymptotic dipole. For $r^i \gg 1/b^i$ the factor reduces to zero, so that b^i sets the range of the short-range correction—effectively the range of the overlap effects between the cation and anion. For many systems, b^i is found to be proportional to the sum of cation and anion radii (with a "universal" constant of proportionality).[16] This gives a useful way of estimating the corrections for systems on which full calculations have not yet been made. The dashed line in Figure 2 shows the total dipole calculated with the short-range model determined in earlier work.[16]

B. Analysis of the Cation Cases. In Figure 3a−c, we show analogous results for the cation polarization in NaF, NaCl, and LiF. For cations the polarizabilities obtained at different levels of calculation differ little from each other, so that the unscaled data directly reflect the induced dipoles.

The cation figures show a different picture from the familiar anion case. First, the XTAL and asymptotic calculations are in much closer agreement, showing that the short-range corrections for polarization of the cation by a point charge lattice are much smaller than in the anion case. This can be attributed to the more contracted nature of the cation charge distribution, which does not extend as far as the nuclei of the first shell of neighbors, so that the corrections for the breakdown of the multipole representation of the electric field are much smaller.

On the other hand, when the full anion charge densities are introduced in the COUL calculations, we find substantial differences with respect to the XTAL (and asymptotic) predictions. The effect of this Coulomb overlap correction is to oppose the asymptotic dipole, and it is much larger than in the anion case discussed above. The sign of the effect is rationalized by noting that the cation electrons which penetrate the anion electron density are subjected to a less effectively screened anion nuclear charge, and hence on average experience a smaller Coulombic field than would be produced by a point at the anion site carrying a single negative charge. That the Coulomb overlap correction is much more important for cations than for anions reflects the difference in their sizes. The anion (considered as the polarizable species) is sufficiently diffuse to detect non-multipolar terms in the point charge potential, which show up in the difference between the asymptotic and XTAL calculations. The cation is sufficiently compact that the point charge approximates its potential quite well. On the other hand, when considering the polarization of the cation, its charge density does not overlap the anion site (asymptotic ≅ XTAL) but does penetrate the diffuse anion charge density and hence sees a potential appreciably different from that produced by a point charge.

The dashed lines in the figures show the Coulomb overlap correction to the cation dipole predicted by the same functional form used to represent the short-range anion dipole (eq 4.4) with the same range parameter b as for the anion case (but with a different value for c). This confirms that the results are consistent with the physical picture of the origin of both cation and anion short-range polarization effects in the overlap of their electron densities.

Finally, the comparison of the COUL and FULL calculations shows that the exchange-repulsion term pushes the electrons in the same direction as the asymptotic electric field and in the opposite direction to the Coulomb overlap correction. This is straightforwardly explained as exclusion of the cation electrons from the region of the anion charge density.

In contrast to the anion case, the net short-range correction to the asymptotic-predicted dipole on a cation can take either sign. For anions, a damping of the asymptotic dipole is always found. For cations, short-range effects can enhance (LiF case) or damp (NaCl case) the asymptotic dipole, depending upon the relative size of the Coulomb overlap and exchange-repulsion corrections. For NaF we see that the two corrections almost cancel, so that the net dipole is extremely close to the asymptotic prediction. It had previously been argued,[21,29] by analogy with the anion case, that the short-range effect should enhance the cation dipole. We now see that this argument, which is based on the sign of the exchange-repulsion effect and fails to take into account the importance of the Coulomb overlap effect for cations, is wrong in general. A general statement which can be made is that the magnitude of the short-range cation dipole, relative to the asymptotic one, is much smaller than in the anion

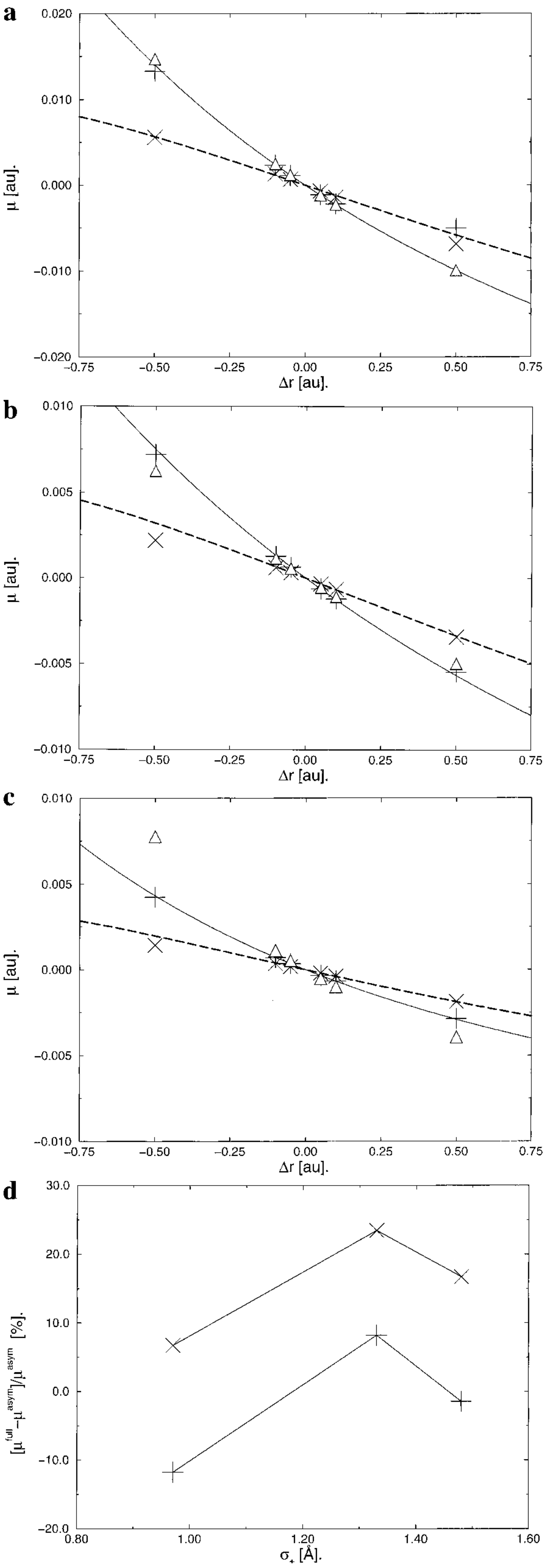

Figure 3. Induced dipoles from the ab initio calculations for a central M^+ cation surrounded by six X^- anions at the equilibrium lattice parameters, plotted against the radial displacement of a single first-shell anion for (a) NaF, (b) NaCl, and (c) LiF. +, XTAL; ×, COUL; △, FULL; full line, dipole predicted from the asymptotic polarizability; dashed line, dipole predicted from the short-range damping model (see text for details). Panel d shows the difference in the XTAL and FULL dipole moments for a single (0.1 au) inward displacement plotted against cation radius in order to highlight the similar trends observed for the fluorides (×) and chlorides (+).

case. For the alkali metal cations considered here the correction is of the order of 10−25% and therefore unlikely to exert any substantial influence on ionic interactions in the condensed phase or clusters. For this reason, we have not pursued the development of a model to represent the net short-range dipole in the cation case.

C. Other Systems. In addition to the systems discussed above, we have also calculated the net induced dipole (at the FULL level) on the cation in KF, KCl, RbF, and RbCl. Rather than present results for the full set of distorted geometries, we will simply present results for the configuration in which the anion is displaced inward by 0.1 au. The pattern of results for the other geometries can be readily envisaged from this value, taken with the generic behavior already illustrated in Figure 3 for smaller cations.

In Figure 3d we show the scaled dipole correction, $(\mu - \mu^{ASY})/\mu^{ASY}$, for the 0.1 au inward distortion in the alkali metal fluorides and chlorides (excluding Li, for which polarization effects are, in absolute terms, very small). This quantity is a measure of the relative importance of the short-range term, and a positive value indicates a dominance of the exchange repulsion over the Coulomb overlap effect. The results are plotted against the cation radius ($\sigma_+ = 0.97$ Å for Na^+, 1.33 Å for K^+, and 1.48 Å for Rb^+), and confirm the efficient cancellation of the exchange-repulsion and Coulomb overlap effects, already illustrated above for the lighter alkali metals; for the alkali metals the magnitude of the short-range dipole is always less than 25% of the asymptotic dipole. They also suggest that the degree of cancellation depends on the radii of the ions involved. The chlorides and fluoride series show the same pattern for the dependence of the short-range dipole on the cation radius. For the more diffuse chloride ion, the Coulomb overlap term is larger for a given cation.

We have also calculated the distortion-induced dipole on the Ag^+ ion in AgF; here we might expect larger short-range effects than for the closed-shell cations. The polarizability of the Ag^+ ion has been seen to be more sensitive to environmental effects than the alkali metals,[28] presumably because of their influence on the filled 4d orbitals which lie close in energy to empty 5s and 5p orbitals. Furthermore, it has been suggested[21] that quadrupole polarization effects might become large enough to explain characteristic differences in the material properties between silver and alkali metal halides as a consequence of a proposed *enhancement* of the induced moments by short-range effects. The results of the present calculations do *not* confirm this proposal: the value of $(\mu - \mu^{ASY})/\mu^{ASY}$ for the 0.1 au inward distortion is −26%. The Ag^+ ion does, therefore, seem to exhibit a larger short-range effect than the alkali metals, but the sign corresponds to a damping of the asymptotic dipole. Similar damping of the quadrupole moment is observed in FULL calculations for this system (−38% at the same distorted geometry).

V. Conclusion

The charge-overlap technique has allowed calculations of the induced dipoles on cations in distorted clusters which model the condensed-phase environment. The results show significant differences between the way in which cations and anions are polarized by short-range interactions with neighboring ions (i.e., by effects which arise from the overlap of their electron densities). The net short-range contribution to the induced dipole on the cation is seen to arise from opposing effects of similar magnitude. These are an exchange repulsion (exclusion of the cation electrons from the region occupied by the electrons of the surrounding anions) and a correction to the Coulomb potential (arising from the diffuse nature of the anion charge clouds). For anions, the two effects are of the same sign, and exchange repulsion is dominant. For cations, the cancellation means that the short-range corrections to the induced dipoles on the cations tend to be small, compared to the normal "asymptotic" dipole induced by the electric field. The magnitudes of the two effects seem to depend sensitively on the relative size of the cation and anion charge densities, so that for the alkali metal ions even the sign of the net short-range term is unpredictable. Only for the silver ion (among the cases studied) is the short-range correction large enough to influence material properties. In this case, the short-range effect opposes the asymptotic dipole, contrary to earlier suggestions.[21]

VI. Appendix

All calculations used the program written by R. J. Wheatley (density-overlap model) and the uncontracted basis sets used in ref 23. Dipole polarizabilities were calculated at uncorrelated (coupled Hartree–Fock) level. Equilibrium separations are given in Table 1.

Where finite fragments of rock salt type lattices were needed for embedding the (cation)(anion)$_6$ clusters, cubic $5 \times 5 \times 5$ fragments were constructed, taking nominal interior and scaled exterior charges. A scaling factor of $(1/2)^f$ was applied to each charge shared by $f = 1, 2, 3$ faces of the cube.

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