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Many-body contributions to the intermolecular potential in alkali halide crystals and clusters

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SCFMO calculations have been made on lithium fluoride clusters both within the crystal and as isolated species. Calculations have been made with different bases in order to separate exchange, charge–transfer and induction energies. Calculations confirm the conclusion from perturbation theory that charge–transfer is an important contribution to three-body energies and gives a small four-body energy. The three-body energies in the crystal environment are much smaller than for the isolated clusters.

1. INTRODUCTION

The considerable interest in the static and dynamic properties of ionic crystals, both perfect and defective lattices, and ionic melts, provides a continuing incentive to obtain accurate interionic potential functions. There has indeed been no lack of effort on this front ; the first alkali halide potentials which gave a good fit to the lattice energy were obtained by Huggins and Mayer in 1933 [1].

The total potential for a finite cluster of ions can be written as a many-body expansion. The first term will be the sum of pair potentials, the second we refer to as the three-body term, etc. The pair potentials contain the Coulomb energy, which is dominant at large distances and the exchange energy which provides the short range repulsion. There will be other smaller terms, some long range and some short, such as dispersion, induction and charge transfer, whose relative importance depends on the internuclear separation. There are however problems relating to whether these energies make separate and additive contributions to the two-body energy [2]. For polar molecules and particularly for ions it has generally been considered that the inductive energies are the most important contribution to the higher *n*-body terms. These energies are associated with the polarization of one atom or molecule in the total electric field arising from its neighbours. As the component fields must be combined vectorially the polarization depends on the relative positions of the neighbours.

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Each neighbour does not therefore make a separate contribution to the inductive energy, that is, the inductive energy is not pair additive.

In a perfect alkali halide crystal lattice the electrostatic field at the lattice sites is zero so that the dipolar induction term (dipole polarization in a uniform field) is zero. Thus, the static properties of the perfect lattice can be interpreted quite well using pair potentials only, or effective pair potentials which incorporate small many-body terms. There is, however, evidence from lattice dyanamics and neutron scattering that many-body terms cannot be ignored completely [3].

For isolated ionic clusters there is no doubt that many-body energies can be quite large but a recent SCFMO study of the clusters $[\mathrm{Li}_n\mathrm{Cl}]^{(n-1)+}$ ($n=1$ to 4) by Bounds and Hinchliffe [4] has shown that these are confined almost entirely to the three-body term and they are as large as the non-Coulombic part of the two-term body. We might expect that for problems involving the imperfect ionic lattice, such as defect structure, ionic immobility and particularly molten salt dynamics, three-body energies would have to be considered. Nevertheless the majority of such problems have been tackled with a pair potential.

The only widely used alternative to the pair potential is the shell model [5]. In this each ion is divided into an inner core which has the nuclear mass and a point charge X, and a massless outer shell of charge Y ($X+Y$ is the net charge of the ion). The core and shell are coupled by a harmonic potential. Core–core, shell–shell and core–shell interionic potentials are defined and usually only the latter has non-Coulomb terms. The parameters entering the model are determined from ion polarization or from dielectric constants.

We have no personal experience of using the shell model but note that it has its limitations. With parameters optimized for solid state properties it gives a poor representation of the diatomic alkali halide equilibrium properties [3]. Moreover in molecular dynamics calculations shell models are much more time consuming than calculations based on non-polarizable ion pair potentials [3]. We see no reason why, for such calculations, the introduction of polarization energies by three-body terms should not be more accurate and computationally cheaper. (In comparison with the shell model more terms have to be calculated to obtain the potential but the number of dynamical variables is halved.)

In this paper we use a standard SCFMO technique to investigate the pair and many-body potentials of alkali halides in the crystal lattice and as isolated clusters. Our main interest is in interpreting the many-body terms, particularly their dependence on the geometry of the interacting ions. Only when this has been achieved can we have a rational approach to accurate potentials either empirical or *ab initio*. We begin with a few observations on the perturbation theory of interionic potentials.

2. PERTURBATION THEORY OF INTERIONIC POTENTIALS

The most detailed analysis of the alkali halide pair potential using perturbation theory was given by Brumer and Karplus [6] using the exchange perturbation theory of Murrell and co-workers [7, 8]. They showed that to second order in the interaction potentials and second order in overlap a potential is obtained that can be represented qualitatively by a modification of the Rittner function [9]. This they called the distortion–dipole function ; it has the following form (in atomic units):

$$V_{mx}{}^{\mathrm{DD}}(R) = (A + B(\alpha_x - \alpha_m)/2R^2)\exp(-R/\rho) - R^{-1} - (\alpha_x - \alpha_m)/2R^4 - C/R^6, \qquad (1)$$

where α_x and α_m are the free ion polarizabilities and A, B, C and ρ are constant parameters of the system.

An R^{-7} term in the Rittner function was dropped on the grounds that it would arise from a higher order perturbation. The term in B is an addition and has its origins in second-order energies which are overlap dependent. Several assumptions were made by Brumer and Karplus [6] in arriving at this function and probably the most serious was that the B-term has the same exponential dependence on R as the A-term (which represents first-order exchange).

An alternative approach to second-order terms which are overlap dependent is through charge–transfer states [7, 10]. If the variational method is used to obtain the wavefunction of the interaction systems with a small basis of functions then charge–transfer states are the most efficient functions to provide these energies.

First-order exchange energies involve the overlap of occupied orbitals of the ground states of the interacting systems. This overlap has roughly an exponential dependence on R and is accounted for in expression (1) by the A term. Charge–transfer energies, in contrast, depend on the overlap of an occupied orbital of the donor (the halogen anion) and a vacant orbital of the acceptor (the metal cation). In other words, for the alkali halide molecule the charge transfer state is a covalent state of the system and the acceptor orbital is typically a valence orbital of the neutral metal. The overlap of these donor and acceptor orbitals is much larger (for the same value of R) than the overlap responsible for exchange energy and hence we expect the charge transfer energy to decay exponentially with R at a much slower rate than does the exchange energy.

Let us now consider the polarization of a system D (atom, molecule or ion) in the electric field of all neighbours. Polarization can be related to the excitation of electrons from occupied to vacant orbitals and the excitation $\phi_d \rightarrow \phi_{d'}$ is associated with a contribution to the induction energy

$$-\Big[\int \phi_d \phi_{d'} \sum_{K \neq D} V^K \, dv\Big]^2 / \Delta E_{dd'}\,; \qquad (2)$$

V^K is the potential energy of an electron in the field of system K. The pair-additive part of (2) is

$$-\sum_K{}' \Big[\int \phi_d \phi_{d'} V^K \, dv\Big]^2 / \Delta E_{dd'} \qquad (3)$$

and the non-pair additive part is

$$-\sum_K{}' \sum_{L \neq K}{}' \int \phi_d \phi_{d'} V^K \, dv \int \phi_d \phi_{d'} V^L \, dv / \Delta E_{dd'}. \qquad (4)$$

It has been pointed out by Claverie [10] that the non-pair additive part of the induction energy arises in three-body terms but not in higher terms. For neutral atoms V^K decays exponentially away from the centre of K and hence the integrals appearing in (3) and (4) are generally small. For ions V^K decays as R^{-1} and therefore the induction energies will be much larger.

An expression for the charge-transfer energy can be obtained which is analogous to (2) and has been investigated for its non-pair additive features by Williams and co-workers [11]. Associated with the transfer of an electron from ϕ_d of D to ϕ_a of A there is a contribution to the energy of

$$-[\int (\phi_d\phi_a - S_{ad}\phi_d^2) \sum_{K\neq D} V^K \, dv]/\Delta E_{da}. \tag{5}$$

(Expression (5) becomes identical with (3) if ϕ_a is an orbital of D (say $\phi_{d'}$) because in this case S_{ad} will be zero.)

Each integral in (5) couples the donor and acceptor with the potential of the acceptor or the potential of some third atom ($K\neq D, A$). The pair-additive terms in (5) are

$$-[\int (\phi_d\phi_a - S_{ad}\phi_d^2)V^A \, dv]^2/\Delta E_{da} \tag{6}$$

and there will be three-body terms which couple ϕ_d and ϕ_a to the potential of a third atom K. In contrast to the induction energy there will also be four-body terms of the type

$$-\sum_K{}'' \sum_{L\neq K}'' \int (\phi_d\phi_a - S_{ad}\phi_d^2)V^K \, dv \cdot \int (\phi_d\phi_a - S_{ad}\phi_d^2)V^L \, dv/\Delta E_{da} \tag{7}$$

but no higher terms.

The contributions to the two-body induction and charge transfer terms, (3) and (6), are all of the same sign and will accumulate to stabilize the system. The three- and four-body terms, however, can be of either sign and their net contribution will be larger or smaller depending on the situation.

There are other contributions to the many-body energies from exchange and dispersion but these are expected to be small and can be ignored for ionic systems [11].

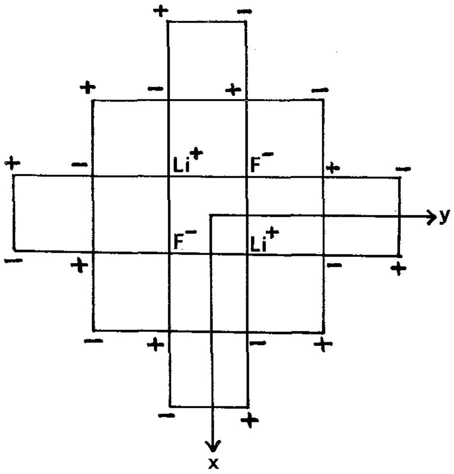
3. CALCULATIONS

We shall compare calculations on lithium fluoride clusters both isolated and within a crystal environment. We wish to analyse the induction and charge-transfer energies in both situations and do this by a suitable choice of basis.

To calculate the energy in the crystal environment we follow a procedure used before [12] to study the SCF energy levels of the F-centre defect and define a finite lattice whose Coulomb potential in the central region closely approximates the Coulomb potential in the unit cell of the infinite lattice. SCFMO calculations are then made on a small number of ions contained within an inner zone at the centre of the finite lattice.

The coordinates of ion sites in the finite lattice are given in table 1 and the figure shows the ion position in the (0, 0, 0) plane. Only the electrons of the four central ions in this plane have been included in the SCF calculations, other sites entering the calculation only as point charges.

The Coulomb potentials along the x and y axes of the figure are zero by symmetry as in the infinite lattice. The charges on the outer two shells listed in table 1 were chosen to make the Coulomb potential at the four central sites equal to the Madelung potential of the infinite lattice and to make the potential at the eight points with coordinates $(O, \pm R \pm R)$ and $(\pm R, O, \pm R)$ equal to zero as it should be in the infinite crystal. With these charges, 0·7211 and



Representation of the $z=0$ plane of the lattice used in the calculations.

Table 1. Specification of the finite lattice used for the crystal calculations. R is half the lattice distance which for LiF is 3·7965 a_0. r is the distance of the appropriate shell from the centre of the lattice.

r^2/R^2	Coordinates/R $\lvert x\rvert$, $\lvert y\rvert$, $\lvert z\rvert$	Charge $\lvert q\rvert$	Number of centres
2	1, 1, 0	1	4
6	1, 1, 2	1	8
10	3, 1, 0	1	8
14	3, 1, 2	1	16
18	1, 1, 4	1	8
18	3, 3, 0	1	4
22	3, 3, 2	1	8
26	5, 1, 0	1	8
26	3, 1, 4	0·7211	16
30	5, 1, 2	0·2476	16

0·2476 as shown in table 1, the Coulomb potential in the region occupied by the central ions is very close to that in the unit cell of the complete crystal.

Calculations have been made with three different bases. Firstly we used an extended basis of gaussian functions ; (6*s*, 4*p*) for lithium [13, 14] and (8*s*, 4*p*) for fluorine [13]. This basis allows for charge transfer, which is primarily from the 2*p* orbitals of fluorine to the 2*p* orbitals of lithium but the amount of polarization allowed by the basis is very small. Li$^+$ has a very low polarizability and most of the polarizability of F$^-$ is associated with *p*–*d* excitations. To introduce polarization and hence induction energies, we added to the fluorine basis a single gaussian *d* orbital with exponent $\zeta=0·24$ which maximizes the F$^-$ polarizability ($\alpha_{\text{calc}}=2·6\ \text{e}^2\ a_0{}^2\ E_{\text{h}}{}^{-1}$). Calculations were also made at the minimal basis level, (1*s*) for lithium and 2*s*, 1*p*) for fluorine, the contraction coefficients being obtained by calculations on Li^+ and F^- using the extended basis. In minimal basis there is no charge transfer or induction energy.

Tables 2, 3 and 4 show the calculated energies in the three bases for free clusters and for clusters within the crystal. In all cases the Coulomb energy has been removed, this being calculated on the assumption of point charges at the nuclei (i.e. assuming 100 per cent ionic character and no overlapping electron densities). For the crystal calculation this Coulomb energy is the same for all clusters because a lattice site is either occupied by an ion or by the appropriate point charge. All clusters are based on the square array shown in the figure with lattice spacing $a = 3{\cdot}7965\ a_0$. Thus the Li^+–F^- separation is equal to a and the Li^+–Li^+ and F^-–F^- distances are $2^{1/2}\,a$. The energies have been analysed into many body terms : $E(2, n)$, for example, is the two-body energy in the n-atom cluster, the Coulomb energy not being included.

In the minimal basis all the two-body energies are positive and this can be attributed to the exchange energy. There is little difference between the crystal and free cluster energies and three-body terms are only a few per cent of two-body. In other words, in the absence of charge transfer and induction energies the two-body energy dominates and is very similar in and outside the crystal.

From table 3 it can be seen that charge-transfer and the small amount of induction from this basis lead to negative two-body energies except in the case of $(F^-)_2$. However, the exchange energy increases rapidly at shorter distances and there must of course be a balance between attractive and repulsive forces in the equilibrium crystal lattice.

The two-body energies are substantially more negative for the free cluster than for the crystal. We should expect this for the induction energy as the field is zero at the lattice sites in the crystal. It is apparently also true for the charge-transfer energy and this can be attributed to the fact that in the crystal the ions are sitting in the deep Coulomb hole produced by the lattice which favours a high ionic character for the system. In the crystal we find about 99 per cent ionic character for Li^+F^- but as a free cluster it is only about 85 per cent ionic. (These numbers are approximate because neither the dipole moment nor the orbital populations give an unambiguous measure of ionic character.)

Previous calculations on LiF [15, 16] have shown that there is appreciable ionic–covalent mixing even at a separation of 11 a_0 which is the ionic–covalent diabatic crossing point. This is evidence that the charge-transfer contribution to the energy falls off slowly with distance even though it is formally an exponentially decaying term. In comparison to the results of table 2 the three-body terms in table 3 are quite large and can certainly not be neglected in comparison with the non-coulombic part of the two-body energy. The results are entirely consistent with those of Bounds and Hinchliffe : we find the four-body term to be unimportant.

Increasing the polarizability of the fluoride ion gives the results in table 4. The two-body energy for $(F^-)_2$ is substantially lowered (there is negligible charge-transfer for this species) but that for Li^+F^- is not. This is an important point that has been noted in calculations on $H_2(^3\Sigma_u{}^+)$. When a basis is used which gives an appreciable amount of charge-transfer then only a small extra stabilization can be obtained from induction terms [17].

Table 2. Calculated energies of ion clusters with minimal basis. The top figure in each case refers to clusters within the crystal and the bottom (in parenthesis) to the free cluster. $E(k, n)$ is the k-body energy (excluding Coulomb energy) for the n-ion cluster.

Structure	E/E_h	$E(2, n)/E_h$	$E(3, n)/E_h$	$E(4, n)/E_h$
Li^+	−7·23514	—	—	—
	(−7·23514)	—	—	—
F^-	−99·07872	—	—	—
	(−99·07896)	—	—	—
$(Li^+)_2$	−14·47028	0	—	—
	(−14·47028)	(0)	—	—
$(F^-)_2$	−198·15613	0·00131	—	—
	(−198·15686)	(0·00106)	—	—
Li^+F^-	−106·30982	0·00404	—	—
	(−106·30952)	(0·00458)	—	—
$(Li^+)_2F^-$	−113·54092	0·00808	0	—
	(−113·54019)	(0·00916)	(−0·00011)	—
$Li^+(F^-)_2$	−205·38335)	0·00939	−0·00016	—
	(−205·38201)	(0·01022)	(−0·00017)	—
$(Li^+)_2F^-)_2$	−212·61057	0·01747	−0·00032	0
	(−212·60938)	(0·01938)	−0·00056	(0)

Table 3. Calculated energies of ion clusters with the basis Li(6s, 4p), F(8s, 4p). Analysis as in table 2.

Structure	E/E_h	$E(2, n)/E_h$	$E(3, n)/E_h$	$E(4, n)/E_h$
Li^+	−7·23520	—	—	—
	(−7·23520)	—	—	—
F^-	−99·36143	—	—	—
	(−99·36160)	—	—	—
$(Li^+)_2$	−14·47051	−0·00011	—	—
	(−14·47073)	(−0·00034)	—	—
$(F^-)_2$	−198·72278	0·00008	—	—
	(−198·72358)	(−0·00038)	—	—
Li^+F^-	−106·60070	−0·00407	—	—
	(−106·61985)	(−0·02305)	—	—
$(Li^+)_2F^-$	−113·83712	−0·00825	0·00296	—
	(−113·86210)	(−0·04644)	(0·01634)	—
$Li^+(F^-)_2$	−205·96570	−0·00806	0·00042	—
	(−205·99340)	(−0·04648)	(0·01148)	—
$(Li^+)_2(F^-)_2$	−213·20296	−0·01631	0·00676	−0·00015
	(−213·23245)	(−0·09292)	(0·05564)	(−0·00157)

Table 4. Calculated energies of ion clusters with the basis Li(6*s*, 4*p*), F(8*s*, 4*p*, 1*d*). Analysis as in table 2.

Structure	E/E_h	$E(2, n)/E_h$	$E(3, n)/E_h$	$E(4, n)/E_h$
Li^+	−7·23520	—	—	—
	(−7·23520)	—	—	—
F^-	−99·36143	—	—	—
	(−99·36160)	—	—	—
$(Li^+)_2$	−14·47051	−0·00011	—	—
	(−14·47073)	(−0·00034)	—	—
$(F^-)_2$	−198·72598	−0·00312	—	—
	(−198·73023)	(−0·00703)	—	—
Li^+F^-	−106·60186	−0·00523	—	—
	(−106·62153)	(−0·02473)	—	—
$(Li^+)_2F^-$	−113·83925	−0·01057	0·00315	—
	(−113·86640)	(−0·04980)	(0·01540)	—
$Li^+(F^-)_2$	−205·97039	−0·01358	0·00125	—
	(−205·99743)	(−0·05649)	(0·01746)	—
$(Li^+)_2(F^-)_2$	−213·20844	−0·02415	+0·00880	−0·00017
	(−213·23573)	(−0·10629)	(0·06572)	(−0·00155)

The three-body induction energy should be small for the cluster $(Li^+)_2F^-$ because the polarizing fields from the lithium ions are orthogonal. We note that $E(3, 3)$ for this species is very similar in tables 3 and 4. Finally we note that the four-body terms are very similar in these two tables confirming our analysis in § 2 that four-body terms arise from charge-transfer.

Table 5 gives the energies of defect vacancies of the crystal which have been obtained by removing an ion from one of the four central sites. Although these vacancies lower the symmetry of the electrostatic field in which the cluster sits the two-body and three-body energies are still much closer to the values obtained for the perfect crystal than for the free cluster. It appears therefore

Table 5. Calculated energies of clusters adjacent to vacancy defects. The vacancy is located in one of the four central sites and the cluster occupies the other three sites. Results are given for minimal (i), extended (ii) and polarization (iii) bases as described in the text.

Vacancy	Structure		E/E_h	$E(2, 3)/E_h$	$E(3, 3)/E_h$
F^-	$(Li^+)_2F^-$	(i)	−113·54065	0·00836	0
		(ii)	−113·84131	−0·01150	0·00321
		(iii)	−113·84230	−0·01075	0·00341
Li^+	$Li^+(F^-)_2$	(i)	−205·38261	0·00922	−0·00025
		(ii)	−205·97458	−0·01350	−0·00018
		(iii)	−205·99414	−0·01895	0·00160

that the symmetry of the crystal can be broken quite severely without changing greatly the two-body and three-body terms and particularly by not increasing the relative importance of three-body to two-body terms.

Further calculations would be needed to establish the nature of two-body and many-body terms in other distorted crystal structures and in particular whether effective two-body terms can be obtained which will be adequate for approximate dynamical calculations. We have obtained two-body potentials for some symmetrical distortions of the central ions in our lattice. For example, by displacing the two Li^+ ions along the (1, 1, 0) axis we have obtained a two-body potential for $Li^+–Li^+$. All we can conclude at this point, however, is that these potentials have a functional dependence on the inter-ionic distance which is similar to that for the free ion pair but we do not know whether this potential can be applied in less symmetrical situations.

4. CONCLUSIONS

There are two important conclusions from this work. Firstly, the many-body contributions to the inter-ionic potential within the crystal are smaller, relative to the two-body term, than for free ion clusters. Secondly, charge-transfer terms make an important contribution to the three-body energies and for lithium fluoride clusters appear to be more important than induction terms.

If this second point is found to be generally true for ionic systems then there seems to be little point in making further developments of the shell model, which can only simulate induction energies. A more profitable approach would be to obtain an explicit functional form of the whole three-body energy, induction and charge-transfer, by *ab-initio* calculations.

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