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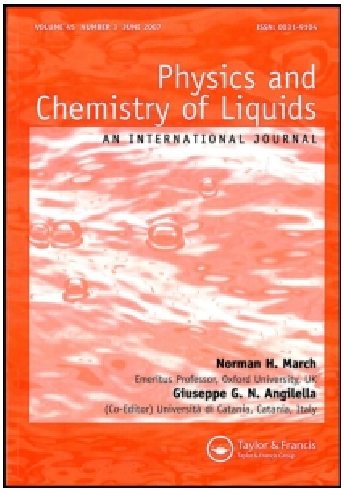

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Review article: ion pair potentials for alkali halides and some applications to liquids and defect studies

M. Dixon[a][b]; C. S. N. Murthy[c]
[a] Department of Theoretical Physics, University of Oxford, Oxford, England [b] Theoretical Physics Division, AERE Harwell, Oxon, England [c] Department of Chemistry, Royal Holloway College, Englefield Green, Surrey, England

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Review Article

Ion Pair Potentials for Alkali Halides and Some Applications to Liquids and Defect Studies

M. DIXON†

Department of Theoretical Physics, University of Oxford,
1, Keble Road, Oxford, OX1 3NP, England

and

C. S. N. MURTHY

Department of Chemistry, Royal Holloway College, Englefield Green, Egham,
Surrey, TW20 OEX, England.

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We review the basis on which interionic potentials for alkali halides are obtained. We find that the sizes of the van der Waals terms are known poorly and that the polarizable ion models lack the necessary thermodynamic corrections, however small they may be, to fit low temperature properties of the solid. Although the quantum statistical calculations indicated some damping of van der Waals interactions due to ionic overlap, a systematic study of the basic and modified approaches shows them to be unsatisfactory.

Studies of the liquid structure and point defect properties are reported for a limited range of salts. It is shown that at longer wavelength the charge charge dynamical structure factor is substantially changed by the inclusion of ionic polarization in the interionic potential. Ionic polarizability produces a relatively small change in the structure. The polarizable ion models give encouraging values for the cation and anion vacancy migration energies compared with the values derived from recent experimental studies of the crystal.

1 INTRODUCTION

It is now well established that molecular dynamics can provide valuable insights into the physical processes in condensed matter. While the formalism of statistical mechanics provides a well defined procedure for studying condensed matter, the system still has to be defined in terms of a set of

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† Attached to Theoretical Physics Division, AERE Harwell, Oxon, OX11 ORA England.

interacting particles. In limiting cases such as perfect crystals in the harmonic approximation, most of the basic physics is well established. Anharmonic and disordered systems (especially alloys[1]) have been studied using perturbation theory based on perfect harmonic crystal properties. But it is precisely when the harmonic model is least satisfactory as a starting point, or when there is substantial structural disorder, that molecular dynamics is especially effective. However, it is evident that use of molecular dynamics requires that the interaction between particles is known as a function of separation. The simulation can be only as good as the potential is reliable.

In what follows we shall be concerned with alkali halides in the condensed state. A large part of the interaction then arises from the electrostatic potential which is known exactly. The short range part representing the remaining terms in the potential has to be determined. There are three classes of models of interionic potentials which have been proposed:

(a) *rigid ion models* which consist of a point Coulombic interaction plus a short range repulsion which arises from the overlap of the electron density on different ions.

(b) *point polarizable ion models* which extend the rigid ion model by including a constant electronic polarizability.

(c) *polarizable ion models* which couple together the electronic and short range polarization. These models include some many body forces.

In this review we will discuss briefly (1) the underlying physical concepts beneath each model (2) the limitations of each model (3) show how the parameters of models have been derived and (4) the use of the models in simulations. We propose to restrict ourselves to the alkali halides since these are generally regarded as being the test bed for ionic models. Much of the work on alkali halides has been covered already in the extensive review by Sangster and Dixon[2] and we shall therefore emphasise developments since that review. There is now a Handbook of Interatomic Potentials compiled by Stoneham[3] from contributed potentials, although these do not include rigid ion potentials.

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2 ELECTROSTATIC INTERACTION

2.1 Point Coulombic ion models

The simplest form for the electrostatic interaction is for each ion to have an integer charge located at its centre of mass; the ions are treated as point ions. This form appears to be reasonable for the simulation of structures, but is known to be completely inadequate for dynamical properties since

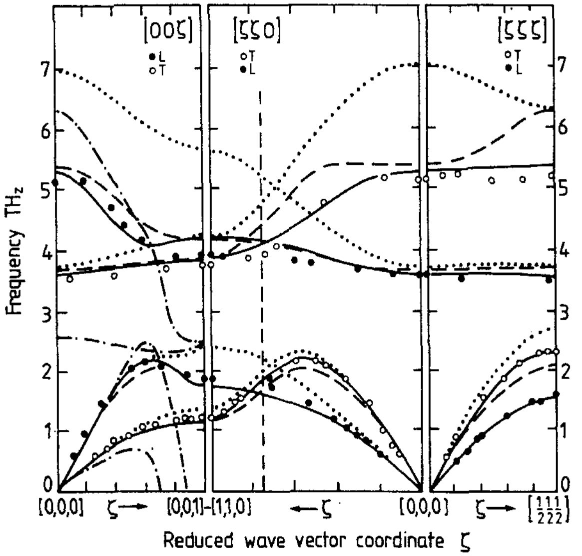

FIGURE 1 Comparison of Phonon Dispersion Curve for NaI: ○ ● experiment; · · · · rigid ion model; —·— · rigid ion + point dipole; — — — shell model; ——— breathing shell model.

it gives the high frequency dielectric constant $\varepsilon_\infty = 1$. However, a point Coulombic ion model should be regarded as the essential starting point for computer simulation studies.[4] The model fails for dynamical properties because the Coulombic field of one ion polarizes the charge distribution on other ions and this substantially modifies the dynamical properties of the ions (see Figure 1). Such a model would also be unsuitable for static defect calculations.

2.2 Point Polarizable ion models

It is possible to go beyond point Coulombic ion models by giving each ion a dipole moment which is proportional to the effective field acting on it; the constant of proportionality being the polarizability of the ion. Lyddane and Herzfeld[5] showed that the point polarizable ion models led to a very poor description of the dynamics of the regular crystal and gave rise to a structural instability at certain wave vectors as shown by Woods *et al.*[6] (see Figure 1). Faux and Lidiard[7] reported that this class of model was unsuitable for defect calculations because the polarization of each ion depends not only on the electrostatic forces but also on the short range forces; a point first suggested by Lyddane and Hertzfeld.[5]

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The omission of the latter consistently underestimates the Schottky defect formation energy by about 25% and leads to a static dielectric constant which is over estimated in defect structures. Phenomenalogically this situation has been improved either by choosing[8] the repulsive potential or adopting[9] model polarizabilities to fit the static dielectric constant.

2.3 Shell models

Dick and Overhauser[10] proposed this class of shell models to couple the electrostatic forces to the short range forces, see Figure 2. The ion is modelled by a charged massless shell through which short range forces act. The shell is coupled through a harmonic spring to a charged core which has the mass of the ion. In order to reproduce the experimental dispersion curves for the lattice vibrations as closely as possible (see Figure 1 and Ref. 11), an extra degree of freedom allowing the deformation of the shells has been introduced. Further Bilz *et al.*[12] have incorporated the overlap-charge polarization effects centred at the positive ion corresponding to the introduction of 'pseudo-deformabilities' for the positive ion. However, we confine ourselves in this review to the rigid shell models. The relation between the shell parameters and the dielectric constants has been given by Cowley.[13]

Taking

$$A_{ij} = \frac{2V}{e^2}\left|\frac{d^2\phi_{ij}^{NC}(r)}{dr^2}\right|_{r=r_0}$$

and

$$B_{ij} = \frac{2V}{e^2}\left|\frac{1}{r}\frac{d\phi_{ij}^{NC}(r)}{dr}\right|_{r=r_0}$$

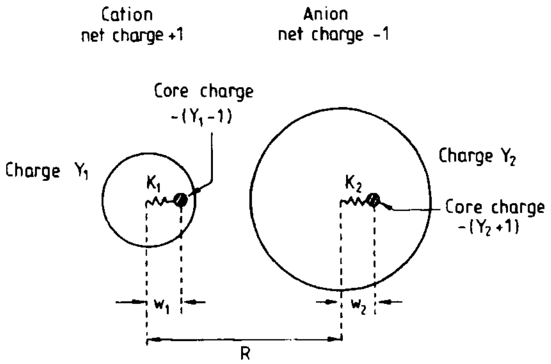

FIGURE 2 Shell model.

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where r_0 is nearest neighbour lattice distance; $\phi_{ij}^{NC}(r)$ is the short range non-coulombic part of the potential.

We define

$$b_0 = \frac{3}{4\pi}\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2}; \qquad b_\infty = \frac{3}{4\pi}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2};$$

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)};$$

and

$R_0 = f(A_{+-} + 2B_{+-})$ with $f = 1$ for the NaCl structure and $f = 4/3$ for the CsCl structure. Then extending Peckham's[14] formulation for two polarizable ions, we have for the static lattice

$$\begin{vmatrix} b_0 & Y_1 & Y_2 & Z \\ Y_1 & k_1 + R_0 & -R_0 & R_0 \\ Y_2 & -R_0 & k_2 + R_0 & -R_0 \\ Z & R_0 & -R_0 & R_0 \end{vmatrix} = 0,$$

$$\begin{vmatrix} b_\infty & Y_1 & Y_2 \\ Y_1 & k_1 + R_0 & -R_0 \\ Y_2 & -R_0 & k_2 + R_0 \end{vmatrix} = 0,$$

and

$$\begin{vmatrix} \frac{3}{4\pi} & Y_1 & Y_2 & Z \\ Y_1 & k_1 + R_0 & -R_0 & R_0 \\ Y_2 & -R_0 & k_2 + R_0 & -R_0 \\ Z & R_0 & -R_0 & R_0 - \frac{V\mu}{e^2}\omega_0^2 \end{vmatrix} = 0,$$

where Z is the ionic charge, ω_0 is the transverse optic frequency, ε_0 is the static dielectric constant, and ε_∞ is the high frequency dielectric constant.

We now have three equations in five unknowns for each crystal. The short range interactions are coupled to the polarizability through the term R_0 appearing in these equations. This is why it is incorrect just to add a polarizability term to a point Coulombic ion potential in an ad hoc way.[2,15]

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We will now follow the solution of these equations recently presented by Sangster and co-workers.[16] It is assumed that the ions are fully ionic. They determine for each ion a set of crystal independent ionic parameters Y_i and k_i/V by a least squares fit to the rocksalt structure; R_0 is also determined for each crystal.

In adopting a shell model formulation which is valid for static crystal, it has been customary to use low temperature dielectric data and we do not have an assessment of the extent of the error that this introduces. This thermodynamic inconsistency has been recently stressed by Eggenhoffner *et al.*[17] Further the different procedures adopted by various authors[16,18] may lead to unphysical values for the shell model parameters (see Table 7, ref. 17).

It is appropriate to mention here how the shell model can be implemented within a molecular dynamics simulation. The zero mass shells have been introduced to account for the experimentally observed high frequency dielectric constants of the crystals. These high frequency dielectric constants arise from the distortion of the electron density of the ions by high frequency electric fields. On time scales appropriate to the molecular dynamics simulation, the shells may be assumed to relax instantly to experience zero force. This is included in the simulation by a simple but very successful algorithm because the force constant k_i turns out to be very large. A small change in the position of a shell produces a much larger change in the force between a shell and its own core than in any of the other forces on the shell. Thus the following molecular dynamics cycle was used:

(a) calculate the forces on the cores;

(b) move cores according to Newton's equations;

(c) calculate the force F_s on each shell and obtain $S = \sum_s F_s^2$;

(d) displace each shell by $\Delta_s = \frac{3}{4}F_s/k_s$ until S is within the error of the calculation of the forces.

It is found that the least number of iterations was required if the shells were initially given the same displacements as their own core. The error in the position of the shells can be reduced to around 5×10^{-6} Å. The procedure is an order of magnitude more expensive than a corresponding rigid ion simulation. If one wishes to run the molecular dynamics with a timestep comparable with that of a rigid ion simulation then a scaling of the velocities by 1/2000 is necessary to conserve energy rigorously. However, if the timestep is halved this scaling is unnecessary. The separation of a shell from its core can be as large as 0.25 Å. The use of a simple expansion method leads to temperature drifting[15] which becomes the more severe the greater the importance of ion polarizability.

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3 VAN DER WAALS INTERACTION†

It is the time average of the distribution of the electrons in an ion which is spherically symmetrical. At any instant there will be distortions in the distribution around an ion A due to electron correlations in A. These distortions will induce a transient dipole in a well separated neighbour B. Similarly electron correlations in B will induce a transient dipole moment in A. These induced dipoles will induce higher order multipoles. The interaction between these induced moments is usually referred to as the van der Waals energy. It is written within the perturbation theory framework as an asymptotic expansion in r^{-6}, r^{-8} ... This expansion breaks down at small r. Further, exchange and overlap correlation effects are missing from the van der Waals energy as discussed by Tosi[19] and Murrell.[20]

The term quenching is used to indicate that the ions are interacting sufficiently strongly that the correlation energy between electrons on different ions is overestimated by the r^{-6}, and r^{-8} terms. In this region Cohen and Pack[21] have suggested that the following prescription can be used for the pair potential,

$$\Phi^{(r)}_{vdw} = \frac{\Phi^{(r_Q)}_{vdw}}{\Phi^{(r_Q)}_{corr}} \Phi^{(r)}_{corr}.$$

Boswarva and Murthy[22] have estimated. on the basis of quantum statistical calculations, that for unlike ions in the crystal r_Q is about 1.0 r_0; for anions r_Q is about $\sqrt{2}\, r_0$; for cations quenching appears to be absent. It is incorrect to appeal to quenching to equate the van der Waals energy to zero for a pair interaction over the whole range.[18]

Now we discuss briefly the methods which have been used to estimate the van der Waals coefficients.

3.1 Ab initio quantum mechanical calculations

Andzelm and Piela[23] have carried out some ab initio calculations for LiF and NaF. However, for the van der Waals coefficients they consider only the asymptotic values and do not examine the effect of the overlap of the ions on these terms. Consequently no conclusions can be drawn about the magnitude of the quenching of this interaction.

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† The physical origin of this term involves the polarizability of the ions. In an interionic potential this term is not responsive to a high frequency electric field caused by the lattice vibrations. Nor does it account for the polarization caused by defects in the crystal. Consequently it is conventionally included as a rigid model contribution.

3.2 Optical absorption experiments

From knowledge of either the optical density[24] or dielectric data[25] one can estimate the van der Waals coefficient C_{ij}. This involves choosing the appropriate energy limits for the individual ionic absorptions. In practice this choice can be arbitrary because the energies of optical excitations of anions and cations overlap. However, even in overlapping cases if the complete absorption spectrum is available, a composite van der Waals coefficient can be obtained.

The dipole-dipole van der Waals energy of two ions can be written as

$$\Phi^{(r)}_{vdw} = -C_{ij}r^{-6} = -6r^{-6}\sum_{b'(i)}\sum_{b(j)}\frac{|M_{ab}|^2|M_{ab'}|^2}{E_a + E_{b'}}$$

where i, j indicate different ions and where $M_{ab} = < b \mid - \mathrm{e}x \mid a >$ for electron states a and b; E_a is energy of electron state a.

This equation when combined with the absorption coefficient

$$\mu(E) = \frac{4\pi^2 N}{hcn(E)} L(E)E\sum_{c}|M_{ac}|^2\delta(E - E_c)$$

where $n(E)$ is the refractive index, gives

$$C_{ij} = \frac{3}{8\pi^4 N^2}\iint\frac{\varepsilon_2(E)\varepsilon_2(E')\,\mathrm{d}E\,\mathrm{d}E'}{(E + E')L(E)L(E')}$$

N is the density of ion pairs, $L(E)$ is the local field correction and where ε_2 is the imaginary part of the dielectric constant of the material. The extent to which the local field correction should be used does not appear to have been resolved.[25]

3.3 Empirical methods

It is customary to use London's perturbation formula[26]

$$C_{ij} = \frac{3}{2}\frac{\alpha_i\alpha_j E_i E_j}{(E_i + E_j)}$$

where E_i and E_j are excitation energies corresponding to the strongest absorption frequencies. This usage is based on the assumption that all the excited states fall in a narrow energy range and that the polarizability is expressible in terms of a one level formula which is

$$\alpha_i = \frac{n_i e^2 h^2}{4\pi^2 m E_1^2}$$

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where n_i is the effective number of electrons responsible for the polarization and m is the mass of the electron. The arbitrariness of choosing either the value of n_i or some scale factors to the first exciton peaks to obtain the E_i gives rise to major uncertainities in the values of C_{ij} derived from this approach.

An alternative approach is to treat the van der Waals dipole-dipole interaction coefficient as an adjustable parameter in the interionic potential to be determined from a fitting procedure[18] or a hybrid of these empirical routes.[16]

We have reported the dipole-dipole coefficients obtained from the above described methods in Table I for ion pairs in LiF, NaF, and NaCl.

3.4 Neutron scattering experiments

At long wavelength the r^{-6} term in the potential gives rise to a term in k^3 in the structure factor,

$$S(k) \rightarrow S(0) + sk^2 + \frac{\pi^2 nA}{12k_BT} S^2(0)\, k^3.$$

For a molten alkali halide Rovere *et al.*[27] have shown that

$$A = \tfrac{1}{2}(C_{++} + C_{--} + 2C_{+-}).$$

Thus, although one cannot determine the independent values of C_{ij} one could determine limits on the composite magnitude. Mitchell *et al.*[28] are carrying out this experiment for NaCl. These experiments would facilitate assessing the estimates from optical data analysis and thus indirectly throw some light on the extent of the local field effects. Further they would reflect on the credibility of the existing estimates.

3.5 Summary

The entries in Table I are remarkable for the range of disagreement shown. Comparison of columns 8 and 9 indicate that it is necessary to consider the effects of the quenching of these interactions. It should, however, be noted when using optical spectra to determine these coefficients[29] that it seems that the separation of the anion and cation valence electron absorptions is not completely arbitrary for most of the alkali halides and that there are ways to gauge the role of the effective local field. It would be useful to augment these estimates and the quenching effects with ab initio calculations.

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TABLE 1

van der Waals dipole-dipole coefficients (C_6, in units of 10^{-60} ergs cm^{-6})

			Fitted			Semi-empirical (Ref. 22)			
Ion pairs	Mayer Ref. 24	ab initio Ref. 23	CDN I Ref. 18	CDN II	SA[b] Ref. 16	(a)	(b)	Quenched values (b′)	r_0 (Å)
$Li^+ - Li^+$	0.073	0.065	20.4	0[a]	0.09	0.09	0.07	—	1.489
$F^- - F^-$	17.5	31.7	20.4	42.9	38.3	25.3	20.5	10.8	3.736
$Li^+ - F^-$	0.8	1.30	0	0	1.64	1.27	1.04	0.54	2.697
$Na^+ - Na^+$	1.68	1.30	18.7	0[c]	4.96	4.69	3.80	—	1.885
$F^- - F^-$	16.5	31.7	18.7	42.9	38.3	25.3	20.5	14.6	3.736
$Na^+ - F^-$	4.5	5.58	0	0	13.0	10.5	8.49	5.70	2.873
$Na^+ - Na^+$	1.68	1.30	46.6	0[a]	4.96	4.69	3.80	—	1.885
$Cl^- - Cl^-$	122		46.6	265	311	161	154	123	4.253
$Na^+ - Cl^-$	11.2		0	0	34.9	23.3	21.4	16.9	3.158

[a] The authors assume that the total (repulsive + attractive) short range interaction energy is zero for positive ions and strictly $C_{++} \neq 0$.

[b] The authors actually adopt a semi-empirical approach but the model polarizabilities are obtained from a fit to dielectric properties.

[c] The effective number of electrons (n_i) responsible for the polarization of the ions is for (a) n_i = outershell electrons and (b) n_i corresponds to the isoelectronic rare gas atom.

4 SHORT RANGE INTERACTION

Two main approaches have been developed to determine the short range interactions between ions. One takes the crystal as its starting point. The other starts from an isolated ion pair applying a simple quantum statistical model to the interactions. Of course there have been hybrids of these alternative approaches.[18] Each of these approaches is complicated by the uncertainty associated with the van der Waals terms which we have just discussed since the empirical parameters will be modified by the error associated with van der Waals coefficients.

4.1 Crystal based potentials

In this approach it has become recent practice to fit the equilibrium condition of the static lattice to the *lattice parameter*. The lattice parameter of the 0K crystal is about 1% larger because of zero point vibrations. This confusion leads to only a small error in the compressibility but the error in the pressure can be several kilobars.

A fit to the *static dielectric constant* ε_0 of the static crystal is effectively a fit to the nearest neighbour force constant at r_0, since

$$V\left(\frac{3}{4\pi}\right)\frac{(\varepsilon_0 - 1)}{(\varepsilon_0 + 2)} = \frac{Y_i^2}{k_1/V} + \frac{Y_2^2}{k_2/V} + Z^2 V\left[\frac{1}{R_0} + \frac{1}{k_1} + \frac{1}{k_2}\right]$$

$$- 2Z\left(\frac{Y_1}{k_1/V} - \frac{Y_2}{k_2/V}\right)$$

Lattice stability requires that the derivative of the static lattice energy with respect to the nearest-neighbour distance must be zero for the equilibrium spacing. The lattice energy per ion pair for the NaCl structure is

$$\Phi^{\mathrm{NaCl}}(r) = -\frac{\alpha_M Z^2 e^2}{r} + 6\Phi_{+-}^{NC}(r) + 6[\Phi_{++}^{NC}(\sqrt{2}r) + \Phi_{--}^{NC}(\sqrt{2}r)]$$

with $\alpha_M = 1.7476$.

The lattice energy per ion pair for the CsCl structure is

$$\Phi^{\mathrm{CSCl}}(r) = -\frac{\alpha'_M Z^2 e^2}{r} + 8\Phi_{+-}^{NC}(r) + 3\left[\Phi_{++}^{NC}\left(\frac{2r}{\sqrt{3}}\right) + \Phi_{--}^{NC}\left(\frac{2r}{\sqrt{3}}\right)\right]$$

with $\alpha'_M = 1.7267$.

In each case we have assumed the potentials to be truncated at the second nearest neighbour distances. Such a truncation would be appropriate for the repulsive part of the potential. Extending the stability condition to include the van der Waals long range interaction[2], we get

$$B_{+-} + 2B_{++} + 2B_{--} = -\frac{2}{3}\alpha_M - \frac{2V}{e^2}\left(\frac{C''}{r_0^8} + \frac{D''}{r_0^{10}}\right)$$

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where

$$C'' = 0.5952 = C_{+-} + 0.1533\,(C_{--} + C_{++})$$
$$D'' = 0.19427\,D_{+-} + 0.0334\,(D_{--} + D_{++})$$

For the CsCl structure the stability condition is

$$B_{+-} + 2B_{++} + 2B_{--} = -\frac{2}{3}\alpha'_M - \frac{2V}{e^2}\left(\frac{C''}{r_0^8} + \frac{D''}{r_0^{10}}\right)$$

where

$$C'' = 2.7088\,C_{+-} + 1.02225\,(C_{++} + C_{--})$$
$$D'' = 2.9436\,D_{+-} + 0.9317\,(D_{++} + D_{--})$$

Substitution of numerical values in these expressions shows that the stability is determined by the nearest neighbour force constant B_{+-}. It is also seen that the $++$ and $--$ interactions occur with the same weight. Expressions for the *elastic constants* of the static crystal in terms of these parameters are recorded in Appendix I.

With the elastic constants also it is seen that the $++$ and $--$ interactions occur with the same weight. Pair potentials give rise to central forces. These, when taken together with the stability condition, require $C_{12} = C_{44}$ which is unphysical.

In order to relate any of the experimental quantities to interionic potentials it is necessary to assume a parametric form for the interactions. For the short-range non-coulombic potential, Φ^{NC}, the Born-Huggins-Mayer form is often used. It can be written as

$$\Phi_{ij}^{NC} = H_{ij}\exp(-\alpha_{ij}r) - C_{ij}r^{-6} - D_{ij}r^{-8}$$

The repulsive parameters are generally determined by fitting to the equation of state of the solid under standard thermodynamic conditions[19, 30] and this seems to give a fit to some of the equilibrium properties at high pressures and temperatures.[31] Following the Fumi and Tosi procedure,[30] Boswarva[32] has recently recalculated the repulsion parameters for the rigid ion model with more recent crystal data at room temperature and atmospheric pressure. Interionic potentials of this type have become available[33–35] for crystals with CsCl structure.

By contrast to these well established procedures, the polarizable ion models adopt the static lattice stability condition for a low temperature crystal. In Section 2.3 it was pointed out that the determination of shell model and short range potential parameters is not an independent fitting procedure. Both fits involve the application of low temperature crystal data in a static lattice formulation.

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The potentials are fitted to the crystal dielectric properties and lattice stability and in some cases to the elastic constants. For the underlying physical assumptions involved, we refer the reader to the original papers[16, 18] and that by Eggenhoffner *et al.* [17]. It is important to recall that the fits are around the regular crystal sites for all models.

4.2 Potentials based upon the electron density of the ions

The model consists of a positive nucleus surrounded by a spherically symmetrical electron distribution for which the density is calculated from SCF Hartree Fock wavefunctions. No distortion of the separate electronic densities is allowed to occur as the two ions interact so the total density is the sum of the two ionic densities. The short range interaction energy is assumed following Wedepohl[36] to be

$$\Phi^{SR}(r) = \left(\frac{E_{\text{kin}}(r) + E_{\text{ex}}(r)}{4\pi}\right)$$

where

$$E_{\text{kin}}(r) = \frac{3h^2\pi^2}{10m}\left(\frac{3}{\pi}\right)^{2/3}\int_{V_{\text{overlap}}}[\rho^{5/3} - (\rho_1^{5/3} + \rho_2^{5/3})]\,\mathrm{dv}$$

and

$$E_{\text{ex}}(r) = \frac{-3e^2}{16\pi}\left(\frac{3}{\pi}\right)^{1/3}\int_{V_{\text{overlap}}}[\rho^{4/3} - (\rho_1^{4/3} + \rho_2^{4/3})]\,\mathrm{dv}$$

where the total density $\rho = \rho_1 + \rho_2$. The integral is over the overlap volume for the kinetic energy and exchange energies. There then exist a series of modifications of this procedure in order to obtain effective pair interactions between two isolated ions:

(a) a density dependent correlation energy is introduced following Gordon and Kim,[37]

$$E^L_{\text{corr}}(r_s < 0.7) = 0.0311 \ln r_s - 0.048 + 0.009 r_s \ln r_s - 0.01 r_s$$

and

$$E^l_{\text{corr}}(r_s > 10) = -0.438 r_s^{-1} + 1.32 r_s^{-3/2} - 1.47 r_s^{-2} - 0.4 r_s^{-5/2}$$

where

$$\rho = \frac{4\pi}{3} r_s^3.$$

with interpolation in range $0.7 < r_s < 10$. Murrell[20] states that this model is more successful than one would reasonably expect in the attractive part

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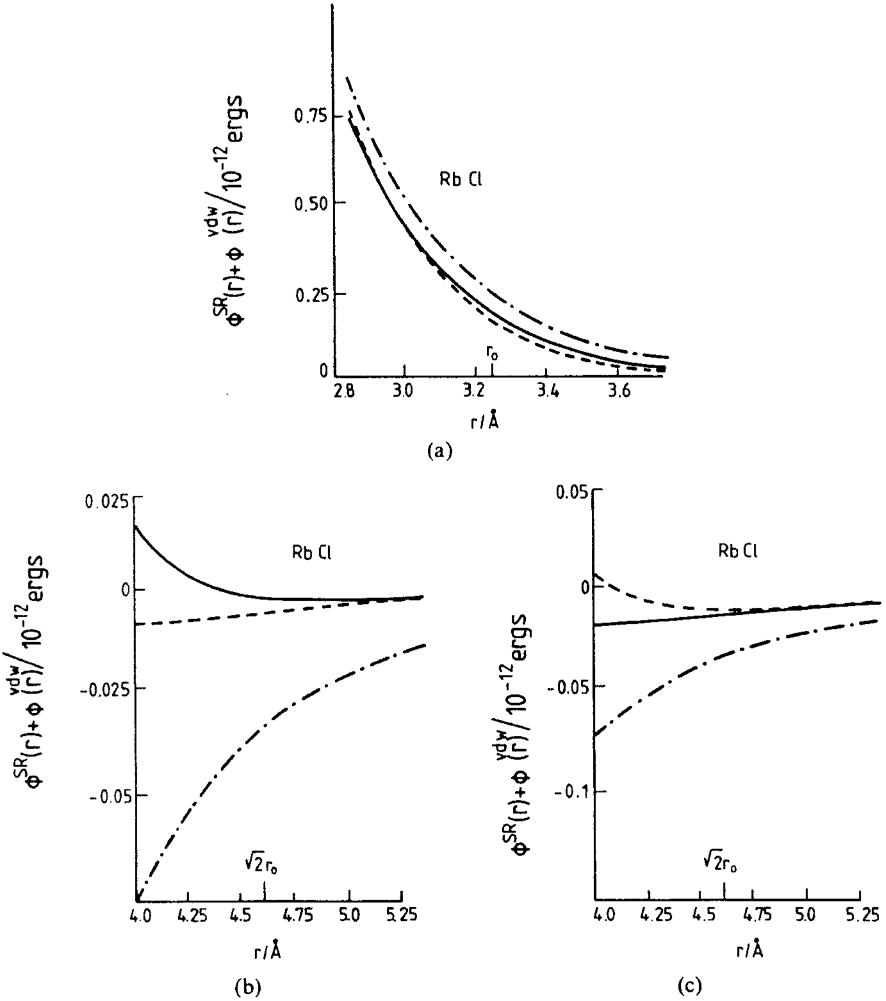

(a)

(b)

(c)

FIGURE 3 Comparison of potentials for RbCl: (a) Φ^{NC}_{RbCl}; (b) Φ^{NC}_{RbRb}. Short range and van der Waals: (c) Φ^{NC}_{ClCl}; ——— Tosi Fumi rigid ion; ------ Sangster, Schroder, and Atwood shell model; -·-· Catlow, Diller, and Norgett shell model.

of the potential. However, this is probably fortuitous; for example, the long range correlation energy is predicted to be overlap dependent and decays rapidly but we know from perturbation theory that that is not the case. In addition Murrell pointed out that models which assume no distortion of electron density will overestimate the repulsive energy at small r.

(b) the correct asymptotic form of the dispersion energy is added and the exchange energy is modified to remove the self energy.

(c) scaling factors for the kinetic and exchange energy terms have been determined so as to produce the correct values of the corresponding terms in an isolated atom, isoelectronic with the interaction of interest.

Boswarva and Murthy[38] have derived these potentials and assessed them using the lattice energy, the equilibrium distance, and the Smith's stiffness parameter

$$\left.\frac{-r^2 \dfrac{d^2}{dr^2}\Phi_L^{NC}(r)}{r\dfrac{d}{dr}\Phi_L^{NC}(r)}\right|_{r=r_0}$$

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5 LIQUID STRUCTURE AND DYNAMICS

In this section we shall focus on the comparison between rigid ion and shell model potentials used in the simulation of ionic melts. The potentials used in this section are given in the papers referred to. The simulations of NaI by Dixon and Sangster[39] showed a clear structural difference between the polarizable ion model and the rigid ion model; this was confirmed by their work on NaCl.[40] In each case the simulations predicted marked differences between the ionic distribution functions $g_{++}(r)$ and $g_{--}(r)$. Comparison with the experimental neutron scattering data of Edwards *et al.*[41] showed that for NaCl the polarizable ion model was in better accord with experiment. Mitchell *et al.*[42] then performed a similar experiment on RbCl. We show in Figure 4 a comparison between the simulations of Dixon and Sangster[43] and that experiment.

We may summarize the comparison as follows:

(a) The overall agreement between the experimental peak heights and positions and those found by simulation is good.

(b) There is some disagreement between simulation and experiment over several details: (1) the width of the main peak of $g_{+-}(r)$; (2) the deep well in the experimental $g_{+-}(r)$ at 5.2Å; (3) the amplitude of oscillation of $g_{++}(r)$ and $g_{--}(r)$.

(c) The agreement between the rigid ion model and the polarizable ion model for the *ion pair distribution functions* is so close that it would appear to be unnecessary to use a polarizable model for situations in which both ions have considerable polarizabilities since these appear to neutralize each other.

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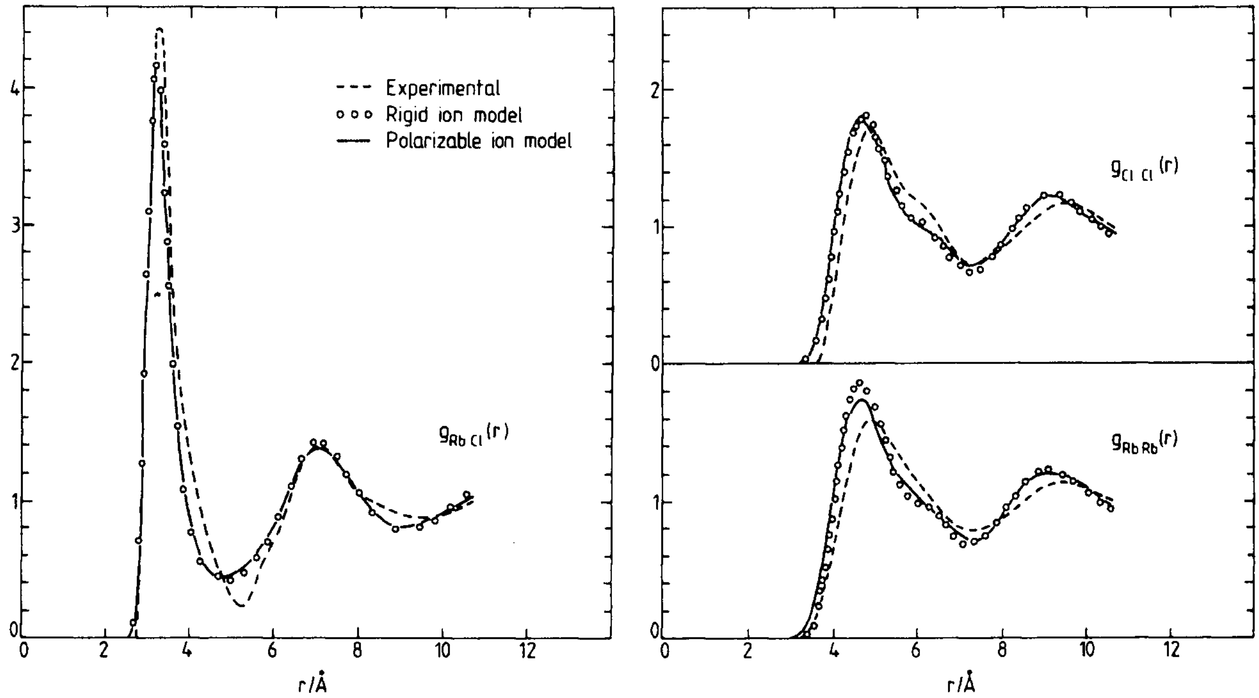

FIGURE 4 Comparison of rigid ion model, polarizable ion model, and experimental partial pair distribution functions for RbCl.

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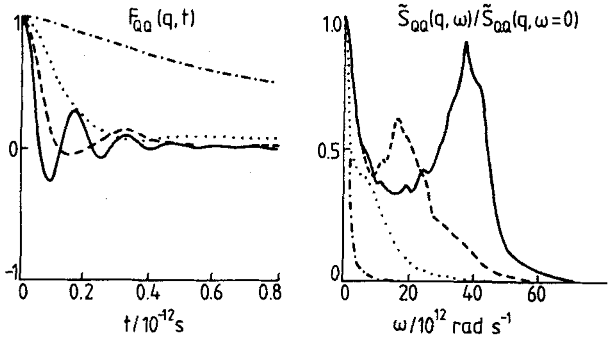
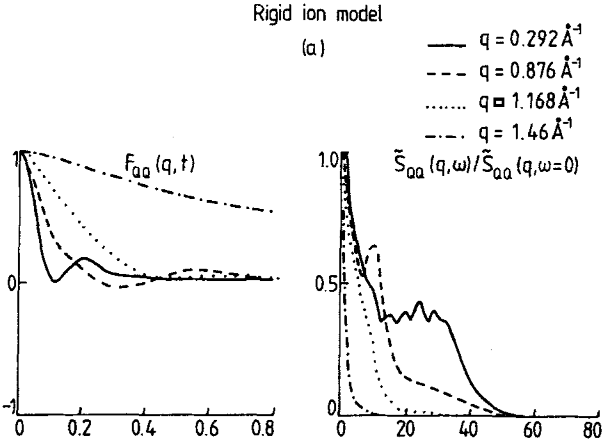
Dixon and Sangster[43] reported quite good agreement between the two models for both the velocity and the force autocorrelation functions. For each autocorrelation the rigid ion model produced a function which oscillated with a slightly higher frequency and which was of slightly stronger intensity. The main effect on the single particle dynamics was seen to come through the increased diffusion coefficients. Recently Dixon[44] has calculated the quasi-electric neutron scattering spectrum for molten NaI. That work shows that the lower diffusion constant for the rigid ion model causes a much higher central peak by enhancing the incoherent scattering terms. Overall the effects of ionic polarization on the mass and number density auto-correlation functions are relatively small. We show in Figure 5 the



Rigid ion model

(a)



Polarizable ion model

(b)

FIGURE 5 Charge density auto-correlation function and dynamical structure factor for molten NaI. Temperature is circa 1000 K.

charge density autocorrelation function $F_{QQ}(q,t)$ for several wavevectors. The $F_{QQ}(q, t)$ show substantially different behaviour for the two models; the rigid ion model has oscillations which are both much stronger in intensity and shorter in time. For both models at low q the melt supports charge density oscillations. Increasing q results in a damping of the oscillations and a lowering of their frequency. There is then a radical change in the characteristics of $F_{QQ}(q, t)$ as we approach the peak in the structure factor $F_{QQ}(q, t = 0)$. The oscillations disappear and the half width at half maximum height becomes comparable with those of the mass and number density auto-correlation functions. Fourier transforming $F_{QQ}(q, t)$ in conjunction with a window function gives the dynamical structure factors, $S_{QQ}(q\omega)$. The $S_{QQ}(q, \omega)$ emphasise the points we have already made about the $F_{QQ}(q, t)$.

From the work on NaI we can formulate three tentative conclusions on the effect of ionic polarizability on the dynamics of the melt.

(a) the inclusion of ionic polarizability into a simulation of the melt leads to a substantial modification of the charge density fluctuations for low q values.

(b) the charge density fluctuations for higher q, and the mass and number density fluctuations for all q are relatively unaffected by ionic polarizability.

(c) ionic polarizability increases the diffusion coefficients and hence reduces the intensity of the incoherent contribution to the central peak of the quasi-elastic neutron scattering function.

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6 DEFECT CALCULATIONS

In order to obtain information on the interionic potentials at distances other than the regular crystal distances it may be expected that defect calculations of the type performed with standard computer packages like "HADES"[45] may be helpful. An earlier extensive review by Barr and Lidiard[46] deals with the experimental and theoretical studies of point defects in ionic crystals. It has been known for some time that the point-polarizable ion models used in defect calculations underestimate the Schottky defect formation energies (h_s) and yield unrealistic values for the activation energies of cation (Δh_c) and anion (Δh_a) vacancies. However, the trend for the relative mobilities of cation and anion vacancies is correctly predicted. This situation has been partially remedied[7,8] by adopting a fit to the static dielectric constant of the crystal which gets overestimated in

TABLE 2

Vacancy formation and activation energies

Solid	Defect energies (ev)	Expt. Ref. (47–49)	Theoretical estimates CDN I	 CDN II	 SD	 SA
			Ref. 50		Ref. 51	
NaCl	h_s	2.44	2.32	2.54	2.25	2.30
	Δh_c	0.69	0.67	0.66	0.81	0.70
	Δh_a	0.77	0.72	0.71	1.16	0.92
NaI	h_s	2.00	1.71	2.14	—	1.98
	Δh_c	0.58	0.61	0.57	—	0.61
	Δh_a	0.77	0.67	0.68	—	0.79
KCl	h_s	2.54, 2.50	2.50	2.56	2.33	2.54
	Δh_c	0.73, 0.68	0.67	0.70	0.88	0.73
	Δh_a	0.85, 0.85	0.69	0.69	0.92	0.82

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the defect structures. The two modified versions of the point polarisable models used in defect calculations[7,8] discussed in section 2.2 give rise to h_s values in reasonable agreement with experiment.

We show in Table II, the formation (h_s) and migration (Δh_c and Δh_a) energies for NaCl, NaI and KCl for which reasonably good experimental analyses[47–49] involving both ionic conductivity and diffusion measurements are available. These energies are compared with the theoretical estimates[50–51] for the class of polarizable ion models proposed for the family of NaCl-type alkali halides. The activation energies (Δh_c and Δh_a) appear to be quite sensitive to the details of the interaction potential but the agreement between the limited number of recent extensive combined measurements and theoretical estimates is encouraging. For the heavier alkali halides, computed motional energies for the cation and anion vacancies are nearly equal for all the models and the spread of the experimental values is too large (see Table II in Ref. 51) to allow reliable conclusions to be drawn. There is thus a need for systematic experimental investigation for a majority of the salts in the family of alkali halides.

7 CONCLUSIONS

We restrict our discussion to sets of interionic potentials which have been constructed from fits over the family of alkali halides. Apart from the Fumi Tosi potentials[30] there is the thermodynamic inconsistency of using low temperature crystal data in static lattice calculations. The uncertainties

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in the van der Waals coefficients are expected to affect all potentials. The $\{\Phi_{ij}^{SR}(r) + \Phi_{ij}^{vdw}(r)\} = \Phi_{ij}^{NC}(r)$ RbCl are shown in Figure 3 to illustrate the differences between the potentials. There are large discrepancies between the potentials, particularly for like ion interactions. Eggenhoffner *et al.*[17] discuss the underlying physical approximations of these and other models.

Sangster *et al.*[16] have shown that it is possible to derive reasonably good shell model parameters which are independent of the particular environment in which the ion is found. Although Verma and Singh[52] have studied many body effects within the shell model formulation and Murrell *et al.*[53] have carried out quantum mechanical calculations of them in LiF, there remains the need for further investigation of many body effects. Singh has just completed an extensive review of many body effects in binary ionic solids.[54]

Boswarva and Murthy[38] have shown that the lattice parameter, predicted by various quantum statistical calculations is in error by about 10%. We believe this is far too large to be accepted for use in simulation work. Part of this is certainly due to the failure to include the electrostatic field in calculating ion densities. Using shell models, Mackrodt and Stewart[55] have demonstrated the importance for electrostatic fields in calculating the ion densities. Strictly one has to allow for the deformations of the free ion electron densities by the total crystal field and a self-consistent treatment in $\rho(r)$ has to be carried out. Work is in progress[56] using Kohn–Sham density functional method for the ionic deformations in alkali halides.

Eggenhoffner *et al.*[17] have made a detailed assessment concerning the quality of the predicted or fitted equilibrium properties at low temperatures for the various polarizable ion potentials. Here we discuss briefly point defect energetics, structure and dynamics of liquids. Schottky defect formation energies are in reasonably good agreement with experiment and the activation energies of vacancies appear to be satisfactory for a few ionic solids.

The changes in the structure of the liquid caused by ionic polarizability are relatively small. Preliminary work on molten NaI suggests that the effect of ionic polarizability is seen primarily in the diffusion coefficients and the long wave length charge density fluctuations.

In order that confidence can be placed in the details of an interionic potential and properties obtained by simulation we believe that quantum mechanical calculations should be carried out to derive some potentials in crystals from first principles. Since the gross characteristics of ionic systems are dominated by the Coulombic interactions it is to be expected that these will still be obtained with the present empirical potentials but that more sensitive properties will not. In particular, there is need for reliable information on more disordered states and defect structures to probe other parts of the potential than the regular lattice distances.

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Appendix 1

ELASTIC CONSTANTS FOR NaCl AND CsCl STRUCTURES

The static *elastic constants* for the NaCl lattice within the non-deformable shell model[13,2] can be written as

$$C_{11} = \frac{e^2}{Vr_0}\left[\tfrac{1}{2}(A_{+-} + A_{++} + A_{--} + B_{--} + B_{++}) - 2.55604Z^2\right] - \frac{V_{11}}{V}$$

$$C_{12} = \frac{e^2}{Vr_0}\left[\tfrac{1}{4}(A_{--} + A_{++} - 5B_{--} - 5B_{++} - 2B_{+-}) + 0.11298Z^2\right] - \frac{V_{12}}{V}$$

$$C_{44} = \frac{e^2}{Vr_0}\left[\tfrac{1}{4}(2B_{+-} + A_{--} + A_{++} + 3B_{--} + 3B_{++}) + 1.27802Z^2\right] - \frac{V_{44}}{V}$$

with

$$
\begin{aligned}
V_{11} &= r_0^{-6}[3.4759C_{+-} + 1.3831(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[1.3162D_{+-} + 0.4353(D_{++} + D_{--})] \\
V_{12} &= r_0^{-6}[3.6171C_{+-} + 0.6881(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[1.4784D_{+-} + 1.0498(D_{++} + D_{--})] \\
V_{44} &= r_0^{-6}[1.2367C_{+-} + 0.0747(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[0.7016D_{+-} + 0.0162(D_{++} + D_{--})]
\end{aligned}
$$

The analgous expressions for the CsCl lattice[13,16] are:

$$C_{11} = \frac{e^2}{Vr_0}[\tfrac{1}{6}(A_{+-} + 2B_{+-}) + \tfrac{1}{4}(A_{--} + A_{++}) + 1.40179Z^2] - \frac{V_{11}}{V}$$

$$C_{12} = \frac{e^2}{Vr_0}[\tfrac{1}{6}(A_{+-} - 4B_{+-}) - \tfrac{1}{4}(B_{--} + B_{++}) - 1.37935Z^2] - \frac{V_{12}}{V}$$

$$C_{44} = \frac{e^2}{Vr_0}[\tfrac{1}{6}(A_{+-} + 2B_{+-}) + \tfrac{1}{4}(B_{--} + B_{++}) - 0.70089Z^2] - \frac{V_{44}}{V}$$

with

$$
\begin{aligned}
V_{11} &= r_0^{-6}[0.2187C_{+-} + 0.1191(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[0.0291D_{+-} + 0.0199(D_{++} + D_{--})] \\
V_{12} &= r_0^{-6}[0.1270C_{+-} + 0.1093(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[0.0139D_{+-} + 0.0171(D_{++} + D_{--})] \\
V_{44} &= r_0^{-6}[0.0220C_{+-} + 0.0343(C_{++} + C_{--})] \\
&\quad + r_0^{-8}[0.0036D_{+-} + 0.0073(D_{++} + D_{--})]
\end{aligned}
$$

Appendix 2

SOME QUANTUM MECHANICAL CALCULATIONS

A2.1 Diatomic molecules

Brumer and Karplus[57] have shown that a consistent perturbation treatment which includes terms of second order in the potential and second order in the overlap leads to a pair potential which has been referred to as the dis-

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tortion dipole model by analogy with the shell model. It has the following form:

$$V_{ij}(r) = \frac{Z_i Z_j e^2}{r} + \left[\frac{H_{ij} + G_{ij}(\alpha_i - \alpha_j)}{2r^2}\right]\exp(-\alpha_{ij} r)$$
$$- \frac{(\alpha_i + \alpha_j)}{2r^4} - \frac{C_{ij}}{r^6}$$

where α_i and α_j are the free ion polarizabilities. Several assumptions were made by them in arriving at this function. They modified the original Rittner[58] function for diatomic molecules. An r^{-7} term which arises from higher order perturbation theory has been dropped; this term is included implicitly in the shell model description.[2] The new term in G_{ij} refers to second order energies which are overlap dependent. All of these assumptions can be tested by comparison with ab initio calculations for alkali halide systems.

Bounds *et al.*[59] have performed conventional SCF MO calculations on LiCl giving rise to a good representation of the LiCl potential curve and properties of the LiCl molecule. But these ab initio 2-body alkali halide potentials lead to completely unphysical lattice energies for the solids. In a perfect static lattice the electrostatic field at each lattice site is zero so that the dipolar induction term is zero. Bounds and Hinchcliffe[60] report some unpublished work of Bounds and Klein who have obtained effective pair potentials in the condensed phase by removing the induction term, $\bar{\alpha}(r)/2r^4$, from the 2-body potentials for molecules; $\bar{\alpha}$ is the mean polarizability. Bounds and Hinchcliffe claim that these effective pair potentials yield reasonable values for the lattice energies and other static properties although they do not present supporting data. The unreliability of potentials for the alkali halide crystals from the studies of diatomic molecules is known[2,31].

A2.2 Ions and crystals

Very recently, Murrell *et al.*[53] have estimated the many body contributions to the intermolecular potential for LiF clusters and crystals. They point out that by taking the same exponential dependence for G_{ij} terms as well as H_{ij} terms (representing first order exchange) in the distortion dipole function of Brumer and Karplus,[56] a severe approximation is probably being made. They follow an alternative approach to second order terms which are overlap dependent; they calculate charge transfer states. In contrast to the induction energy there will be 4-body terms for the charge transfer energy. Contributions to the many body energies from exchange and dispersion are not considered as they are expected to be negligible for ionic systems.

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The approach of Murrell *et al.*[53] to obtaining effective pair potentials for the solid does not involve diatomic alkali halide potentials and their calculations in the crystal environment are rather elegant. Calculations are made on a small number of ions contained within an inner zone at the centre of a finite lattice for which the Coulomb potential in the central region closely approximates the Coulomb potential in the unit cell of the infinite lattice. They find 1) that 3-body energies in the crystal are much smaller than for the isolated clusters and 2) that the charge transfer terms make an important contribution to the 3-body energies. An explicit functional form of the whole 3-body energy from ab initio calculations has yet to be devised. They claim the addition of such a polarization function to the 2-body pair potentials should be both more accurate and also computationally cheaper than using the shell model because the number of dynamical variables is halved. Murrell has since suggested that this could be complemented by a small constant dipole moment term. It is difficult to make a direct comparison of these suggestions either with original work of Dick and Overhauser[10] who envisaged charge transfer effects as an *additional* term in the polarization or with the work of Verma and Singh[52] who suggested that charge transfer made only a small modification to the dynamics. Without a functional form for the 3-body terms it is not possible to make an estimate of the relative computational cost.

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