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An overlap model for exchange-induction: application to alkali halides

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Abstract

An existing method for estimating intermolecular exchange energies in weak Van der Waals interactions, based on the overlap between their ground-state charge densities, is extended to ionic interactions using the overlap between the polarised charge density of a negative ion and the ground-state charge density of surrounding positive ions. This enables the exchange-induction energy to be included in the model. One adjustable parameter for each ion pair is fitted to the dimer interaction energy. The prediction of in-crystal anion polarizabilities is excellent for the five alkali halides tested, and polarizabilities of anions in ionic dimers and trimers are reasonably well reproduced for lithium halides.

1. Introduction

Calculations of weak Van der Waals interactions often start by partitioning the interaction energy using a perturbation expansion in the intermolecular potential energy operator V:

$$V_{\mathrm{total}} = V_{\mathrm{Coul}} + V_{\mathrm{exch}} = \left(V^{(1)}_{\mathrm{Coul}} + V^{(2)}_{\mathrm{ind}} + V^{(2)}_{\mathrm{disp}} + \ldots\right) + V_{\mathrm{exch}}, \qquad (1)$$

where $V^{(1)}_{\mathrm{Coul}}$ is the first-order Coulomb interaction energy, involving the unperturbed ground-state charge densities; the second-order Coulomb energy consists of the induction energy $V^{(2)}_{\mathrm{ind}}$ and the dispersion energy $V^{(2)}_{\mathrm{disp}}$, and antisymmetrisation of the wavefunction gives the exchange energy V_{exch}. The perturbation expansion of the Coulomb energy converges reasonably quickly for weak interactions, and third-order and higher terms are generally ignored. However, there is no unique perturbation expansion of the exchange energy, and it is more difficult to calculate than the Coulomb energy. This subject has been extensively reviewed, for example in Refs. [1,2]. One approach involves expanding the exchange energy in powers of the overlap integral S; the leading term in the exchange energy is then a single exchange of electrons between the monomers, of order S^2. Alternatively, the Heitler-London exchange energy, which is calculated by antisymmetrising the ground-state monomer wavefunctions over all electrons of the dimer, can be used as the leading term in the exchange energy.

For stronger interactions, such as those between ions, the S^2 and Heitler-London exchange energies are both poor approximations to the total exchange energy, as S is large and the Heitler-London exchange energy does not include contributions such as the exchange-induction energy and the exchange-dispersion energy. The exchange-induction energy, which is expected to be particularly important for ionic clusters, describes the effect of polarisation of

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molecules or ions on the exchange-repulsion between them, or, equivalently, the change in induction energy caused by exchange. To obtain potential energy surfaces for ionic systems, it is important to have reliable representations both of the exchange-induction energy itself, and of the change in ionic polarizability, caused by exchange, in a cluster or crystal environment. The exchange-induction energy has been calculated by direct ab initio methods based on perturbation theory (for recent applications see Refs. [3,4]), but these calculations are expensive and are restricted to low orders of perturbation theory and to small clusters. More empirical methods have also been used [5–8], but none is completely satisfactory for one or more of the following reasons: they model either the ion polarizability or the exchange-induction energy, but not both; they are used to approximate only contributions of low order in S and V; they are applicable either to dimers or solids, but not both; they give unreliable results for some ions.

The need for a method of calculating exchange-induction and the related effect of exchange on ionic polarizability in solids has motivated the development of a new empirical model, based on the charge density overlap model [9]. The application of the model to a negative ion A surrounded by positive ions B is considered here. If the polarisation of the positive ions and the dispersion energy are ignored, the Coulomb interaction energy V_{Coul} (to infinite order) can be calculated using a finite field method:

$$\left(\hat{H}_{0\mathrm{A}} + V\right)\psi_{\mathrm{A}} = \left(E_{0\mathrm{A}} + V_{\mathrm{Coul}}\right)\psi_{\mathrm{A}}. \qquad (2)$$

Here $\hat{H}_{0\mathrm{A}}$ is the Hamiltonian of A and $E_{0\mathrm{A}}$ is its ground-state energy. The operator V includes the interaction of the electrons and nuclei of A with all the surrounding positive ions. However, since the wavefunction depends only on the electron coordinates of A, there is no exchange energy.

The charge density overlap model approximates the exchange energy by assuming that it is proportional to the overlap of the electron densities ρ^e of the ions,

$$V_{\mathrm{exch}} = \sum_B K \int \rho^e_{\mathrm{A}}(\mathbf{r})\,\rho^e_B(\mathbf{r})\,\mathrm{d}\mathbf{r}, \qquad (3)$$

where K is an adjustable parameter. The important generalisation made in this work is that ρ^e_{A} is no longer assumed to be the charge density of A in its ground state. Thus, when A is polarised, its overlap with its neighbours changes and the exchange energy also changes. This means that Eq. (3) is capable of modelling the exchange-induction energy as well as the exchange energy.

The implementation of Eq. (3) within an ab initio program is quite straightforward, and is described in Section 2. The lithium halides LiF and LiCl are chosen to test the model, since the cation polarizabilities are negligible; some results for the sodium and potassium halides are also presented. One advantage of using such small systems is that the ions are small enough to allow the basis set limit to be approached in test calculations, which minimises basis set effects. The calculations and results are presented in Section 2. Section 3 contains a discussion of the results and of the significance of the overlap model.

Atomic units are used in the following. The atomic unit of energy is the Hartree ($E_h = 4.3597482 \times 10^{-18}$ J), and the atomic unit of length is the Bohr ($a_0 = 5.29177249 \times 10^{-11}$ m).

2. Calculations and results

A finite-field calculation on anion A in the field of N cations B can be performed by modifying only the one-electron part of the Hamiltonian matrix for A:

$$h_{ij} = h^0_{ij} + \sum_B \sum_{k,l \in B} D_{kl} \int\!\!\int \phi_i(\mathbf{r}_1)\,\phi_j(\mathbf{r}_1) \times r_{12}^{-1}\phi_k(\mathbf{r}_2)\,\phi_l(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2, \qquad (4)$$

where ϕ_i and ϕ_j are basis functions of A, ϕ_k and ϕ_l are basis functions of B, D_{kl} is a density matrix element taken from a monomer ab initio calculation on B, and h^0 is the one-electron Hamiltonian matrix for monomer A.

The overlap model consists of adding an additional 'effective finite-field' term, which approximates the exchange energy, and has the form

$$h^{\mathrm{exch}}_{ij} = K \sum_B \sum_{k,l \in B} D_{kl} \int \phi_i(\mathbf{r})\,\phi_j(\mathbf{r})\,\phi_k(\mathbf{r})\,\phi_l(\mathbf{r})\,\mathrm{d}\mathbf{r}. \qquad (5)$$

This involves the same amount of additional work as the ordinary finite-field calculation described by Eq. (4), which is approximately N cycles of a direct SCF dimer calculation; subsequently, the Schrödinger equation is solved for the electrons of A only, which takes only the time required for a monomer calculation. There is a particularly significant saving in computer time, relative to an ab initio calculation on all $N+1$ ions, either if N is large or if correlation is included. For this initial study, the SCF approximation is employed.

A new SCF computer program is used to calculate the two-electron integrals in Eqs. (4) and (5), incorporate them into the Hamiltonian matrix for A, and solve the resulting matrix Hartree-Fock equations. The integrals in Eq. (4) are standard two-electron integrals and are obtained using a slight modification of the Head-Gordon and Pople recurrence relations [10] (see Ref. [11] and Eq. (98) therein). The integrals in Eq. (5) are obtained using the same method, but with different $[0]^m$ integrals over spherical Gaussian functions [11], which are easily written analytically. The energies, multipole moments and polarizabilities obtained from the SCF program have been checked against GAUSSIAN [12] and CADPAC [13] for several small molecules and ions with basis functions up to f symmetry. The program can also use basis functions of g, h and i symmetry in Cartesian form.

The calculations require large basis sets, which are chosen to be even-tempered [14]: for each angular momentum l, Gaussian exponents form a geometric progression with minimum exponent $\alpha_{l,\mathrm{min}}$ and common ratio β_l. These parameters are obtained by a rough optimisation of the SCF energy and anion polarizability. Basis set details are given in Table 1. The polarizabilities agree within about 0.2 atomic units with accurate Hartree-Fock calculations [15] on the fluoride and chloride ions.

Both all-electron (supermolecule) and finite-field calculations are used in this work. A supermolecule calculation on the AB dimer is denoted AB, and a finite-field calculation on A in the presence of B, using Eqs. (4) and (5), is denoted A[B]. For the supermolecule calculations, the lithium, sodium and potassium basis sets are contracted to minimal 1s, 2s1p and 3s2p basis sets respectively, in an attempt to remove any small effects from polarisation of the positive ions. Finite-field calculations are free from this complication, as the electrons of the positive ions are not included in the wavefunction. The SCF energies of the ions are the same for the contracted as for the uncontracted basis sets.

To use the overlap model, it is first necessary to obtain a value for the parameter K. For easy comparison with ab initio results, K is obtained in the present work using supermolecule SCF calculations, but it could equally be fitted to experimental data. The method is exemplified by the LiF dimer. A supermolecule calculation on the dimer (using the ionic separation taken from the crystal) gives an interaction energy of -0.261087 E_h, including the very small counterpoise correction. A value of K is then sought which will give an energy of -99.720407 E_h in a finite-field calculation on $F^-[Li^+]$, this being the sum of the SCF energy of

Table 1
Basis set details, SCF energies E and polarizabilities α for the ions, in atomic units

Ion	Li^+	Na^+	K^+	F^-	Cl^-
Uncontracted basis set	8s	14s9p	18s12p	20s10p4d1f	24s16p4d1f
$\alpha_{s,\mathrm{min}}$	0.5355	0.46162	0.2532	0.1168	0.08148
β_s	2.981	2.5434	2.353	2.22	2.1062
$\alpha_{p,\mathrm{min}}$		0.312	0.186	0.0615	0.03773
β_p		2.4858	2.32	2.545	2.1544
$\alpha_{d,\mathrm{min}}$				0.05	0.035
β_d				3.0	3.2
$\alpha_{f,\mathrm{min}}$				0.1	0.1
$-E$	7.236005	161.676219	599.016342	99.459320	459.576836
α				10.50	31.34

The basis set parameters $\alpha_{l,\mathrm{min}}$ and β_l are defined in the text.

free F^- and the interaction energy with Li^+. Using repeated finite-field calculations (Eqs. (4) and (5)) and varying K, a value of $K = 8.70$ is found to give the required energy to within about 10^{-6} E_h. The K parameters obtained are given in Table 2 for each of the six ion pairs.

Although not the main aim of this work, it is interesting to compare the dipole moments and polarizabilities from the two calculations. For the lithium halides, the polarizability of the lithium ion is only about 0.02 atomic units in the dimer basis set, so both calculations essentially give the anion polarizability directly. The dipole moment of the anion in the A[B] calculation can also be compared with the dipole moment of supermolecule AB minus the dipole due to the lithium cation B (assumed unpolarised). The results are given in Table 2, where the origin of the anion dipole μ_e is at the nucleus of the anion, and the positive direction of μ_e is towards the cation. In general, the prediction of the polarizability perpendicular to the bond is excellent. The predictions of dipole moment, and of the related polarizability parallel to the bond, are less satisfactory, especially for LiCl: the model predicts a polarizability too close to the free value, and hence a dipole moment which is too large. For both dimers, the (somewhat surprising) sign of the polarizability anisotropy is correctly obtained using the model. For NaF and NaCl, the results for the perpendicular polarizabilities are equally good, but now the parallel polarizabilities and dipoles are predicted to be too small. However, the polarizability of the sodium cation in the dimer basis set is more than 0.2 atomic units, and will be present in the supermolecule results but not the finite-field ones. This reduces the validity of the comparison. For KF and KCl the cation polarizability is much larger, and no useful comparison can be made. Results for KF are shown in Table 2; supermolecule calculations of the KCl polarizability were not considered to be worthwhile.

Symmetric linear trimers are considered next, with an anion placed between two cations at the crystal separation. In this case the dipole moment is zero, but the polarizability and the energy can be compared between finite-field $A[B_2]$ and supermolecule AB_2 calculations. With the same K values, the prediction of the polarizability improves markedly relative to the dimer (Table 3), even though dimer and not trimer properties are used for fitting K. For $B = Li^+$, both parallel and perpendicular polarizabilities agree to about 1%. The agreement is less good for $B = Na^+$ than for $B = Li^+$, but some of the disagreement may be due to the polarizability of the sodium ion. The 'interaction energy' in Table 3 is obtained for AB_2 by subtracting from the total SCF energy the monomer SCF energies and the (multipolar) Coulomb repulsion between the cations, leaving a quantity which is essentially the interaction energy due to the anion. For the finite-field calculations it is the difference between the SCF energy of

Table 2
Calculations on ion pairs

Ion pair	LiF	LiCl	NaF	NaCl	KF	KCl
R	3.7965	4.8566	4.3785	5.2390	5.0512	5.9451
K	8.70	9.08	4.88	4.35	6.76	7.18
α_{10} AB	8.78	30.08	9.90	31.21	10.36	
α_{10} A[B]	9.22	31.03	8.54	27.97	8.65	
α_{11} AB	8.50	25.92	9.14	26.93	10.19	
α_{11} A[B]	8.58	26.05	9.04	26.83	9.36	
$-\mu_e$ AB	0.392	0.919	0.338	0.800	0.231	
$-\mu_e$ A[B]	0.398	0.931	0.296	0.736	0.300	

The fitted parameter K is described in the text; R is the internuclear separation; α_{10} and α_{11} are polarizabilities parallel and perpendicular to the internuclear direction; μ_e is the electronic dipole moment of the polarised anion, as defined in the text; AB and A[B] denote the supermolecule and overlap model results. All quantities are in atomic units.

Table 3
Calculations on AB_2, AB_4 and AB_6

Ion pair	LiF	LiCl	NaF	NaCl	KF	KCl
α_{10} AB_2	7.68	27.71	8.83	28.38	10.93	
α_{10} $A[B_2]$	7.78	28.05	7.52	25.73	7.77	
α_{11} AB_2	7.04	22.06	7.94	23.36	10.19	
α_{11} $A[B_2]$	7.05	22.17	7.69	23.20	8.25	
$-V$ AB_2	0.5046	0.4005	0.4396	0.3673	0.3808	0.3214
$-V$ $A[B_2]$	0.5045	0.4001	0.4411	0.3678	0.3821	0.3227
α $A[B_6]$	5.30	18.82	5.78	19.08	6.33	19.68
α AB_6,PP	5.39	18.90	6.0, 6.4	19.5, 19.8		19.7, 24.3
α $A[B_4]$	5.99	20.62				
α AB_4,PP	6.08	20.70				
α $A[B_4]$,opt	5.44	18.41				
α AB_4,PP,opt	5.53	18.49				

V denotes the interaction energy for the trimer, excluding repulsion between the cations, see the text; the results of Pyper and Popelier [16] are indicated by PP; opt means that the calculations use the optimal internuclear separation for a 4:4 lattice ($R = 3.537$ for LiF and $R = 4.436$ for LiCl), instead of the separation in Table 2; other notation is defined in Tables 1 and 2.

the anion with, and without, the two cations present. Again, the prediction of the finite-field calculations is excellent for trimers involving the lithium ion and is also very good for $Na_2^+Cl^-$.

The most useful predictive power of the model is seen when considering the polarizabilities of anions in a crystal environment. Direct ab initio results on the octahedral AB_6 cluster, corrected for cation polarizability, are available in the SCF (and MP2) approximation for five of the six ion pairs [16], and finite-field $A[B_6]$ calculations are performed here for comparison. Table 3 shows that the prediction of the anion polarizabilities is remarkably good, especially for the lithium crystals, for which the published results are most reliable. The error in the polarizability in the sodium and potassium crystals is less than the discrepancy found by Pyper and Popelier [16] between their two different corrections for basis set superposition error. The current result for $K_6^+F^-$ is also included in Table 3 for information; on the basis of the other results, it is expected to be quite reliable.

In assessing the overlap model, it is useful to know how much effect the exchange term has on the polarizability. If it is removed completely, the increase in anion polarizability is over 2 atomic units for $Li_6^+F^-$. Doubling the exchange effect (using Eq. (5) with K for LiF doubled) reduces the polarizability from 5.30 to 4.61. Similar results are found for the other ion pairs. Evidently the value of K is important. The effect of changing geometry is also investigated, since all calculations up to this point have been performed with the same ionic separation and it might be argued that the value of K will not transfer well from one geometry to another. Pyper and Popelier [16] give anion polarizabilities for LiF and LiCl in a tetrahedral structure with two different bond lengths. Finite-field calculations on the anions surrounded by four cations not only give excellent polarizabilities at both bond lengths (Table 3), but the derivatives with respect to bond length are reproduced exactly, as is the change from sixfold to fourfold coordination. This gives confidence in the ability of the overlap model to adapt to different crystal environments.

3. Discussion

A new method for including intermolecular exchange effects in finite-field calculations has been introduced. It can be applied to the polarisation of a reference molecule by a neighbour molecule which is assumed to be largely unaffected by the interaction. This is directly relevant to the interaction of large, polarisable anions with small, rigid cations in ionic solids, and may also be relevant to molecular modelling studies which treat one molecule quantum mechanically and the surrounding molecules semiclassically.

Formally, the charge density overlap model replaces the exchange of electrons between A and B by an effective term in the interaction Hamiltonian which may be written as $\Sigma_{ab} K \delta(\boldsymbol{r}_a - \boldsymbol{r}_b)$, where a is an electron of A, b is an electron of B, and intermolecular overlap is neglected. The model has been applied previously to the ground states of the interacting molecules: this could be regarded as the first term in a perturbation expansion and it gives as the first-order exchange energy a term proportional to the charge density overlap integral between the monomers. In the current work the theory is extended to infinite order in the wavefunction of one molecule. It thus incorporates the effect of exchange on polarisation, even when considering the very strong electric fields and large overlap integrals typical of ionic interactions.

The theory requires an adjustable parameter, K, to be fitted to experimental or theoretical data. It is interesting to compare the values obtained in this work and in other work. Table 1 shows that the parameter apparently depends markedly on the cation, but very little on the anion. This may be useful in estimating values of K for other interactions between ions where accurate data are not available. Previously, K has been fitted to experimental data in obtaining a model for the exchange energy between water and lithium [17] and sodium [18] ions. Although previous work used only the unperturbed charge densities, employed different data for fitting, and considered interactions of a quite different nature, nevertheless the K parameters obtained (10.95 ± 1 for Li^+H_2O and 3.93 ± 0.8 for Na^+H_2O) are relatively constant for the same cation. It seems significant that K depends mainly on the cation, but the reason is not known.

It is also noted that the finite-field calculations described here could also be used to obtain dispersion energy coefficients for anion pairs in solids, with the effect of exchange compression included, which is an important part of the total lattice energy for the ionic solid.

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