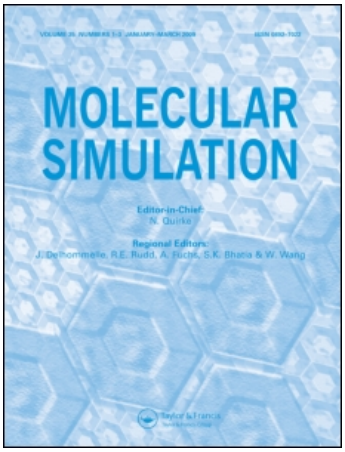

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A User's Guide to Polarisabilities and Dispersion Coefficients for Ions in Crystals

P. W. Fowler[a]
[a] Department of Chemistry, University of Exeter, Exeter, England

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A USER'S GUIDE TO POLARISABILITIES AND DISPERSION COEFFICIENTS FOR IONS IN CRYSTALS

P.W. FOWLER

Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, England

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The definition, calculation, modelling and physical interpretation of static polarisabilities and dispersion coefficients for ions in crystals are reviewed. *Ab initio* calculations on clusters of ions embedded in point-charge lattices show that anions are sensitive to electrostatic and overlap interactions which reduce their polarisabilities from the free-ion values, sometimes by factors of two or more. By contrast, cations of s^2 and p^6 configuration have almost constant polarisability. Models of optical and mechanical properties of ionic solids must take into account the variation of anion polarisability with lattice parameter. A semi-quantitative treatment of dispersion coefficients can be based on the Slater-Kirkwood formula which requires only the static polarisability and one adjustable parameter (fixed by reference to the isoelectronic inert gas).

KEY WORDS: Polarisability, dispersion energy, ion, crystal, *Ab initio*

1 INTRODUCTION

Polarisabilities and dispersion coefficients for ions are important parameters in the theoretical description of the optical and mechanical properties of ionic solids. The refractive index n and high-frequency dielectric constant ε of a cubic solid consisting of point-polarisable ions are both related to subunit polarisabilities by the Clausius-Mossotti equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3}\frac{\alpha_m}{3V_m} \tag{1}$$

where α_m and V_m are respectively the polarisability and volume of the formula unit. The quantity a_m can be broken up into a sum of ionic contributions so that e.g.

$$\alpha_m(\mathrm{LiF}) = \alpha^+(\mathrm{Li}^+ \text{ in LiF}) + \alpha^-(\mathrm{F}^- \text{ in LiF}) \tag{2}$$

where α^+ and α^- are positive quantities and the polarisability of an individual ion is constrained by the requirement that an infinite lattice of point ions interacting by the dipole induced-dipole mechanism shall reproduce the emprical n and ε. One further constraint is needed to fix both α^+ and α^-. In the case of LiF, for example, $\alpha(\mathrm{Li}^+)$ is small and can be neglected or set to a theoretical value. Of course the hope is that α^+ and α^- defined in this way will turn out to be transferable, much as one might hope for transferable ionic radii. Then, if a single polarisability were fixed, all others could be determined from experimental data. However, models based on strictly constant

ionic polarisabilities. [1] give only rough agreement with experiment and over the fifty years since Pauling's first calculations [2] a number of attempts to patch up the theory have been made. It is possible to find in the literature models which assume that both, either or neither of α^+ and α^- are independent of environment. This disarray led Pantelides to attack the validity of the concept of ionic polarisabilities ([3], but see[4]). Recent progress in *ab initio* calculation [5–8] shows that the model is sound enough, provided the physical difference between fluffy, diffuse anions and hard, tightly bound cations is taken properly into account. The present article reviews these calculations and the physical picture derived from them and makes an attempt to define the scope of transferable ionic polarisabilities.

The van der Waals/dispersion energy for the interaction of two spherical atoms A and B separated by a distance R has leading term

$$\Delta E_{vdW}^{AB} = -\frac{C_6^{AB}}{R^6} + \ldots \tag{3}$$

where the C_6 coefficient is related to the dynamic polarisabilities of the two species by

$$C_6^{AB} = \frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\alpha_B(i\omega)\, d\omega \tag{4}$$

When the interacting atoms are in fact ions in a crystal some care must be taken to damp the interaction because of the small value of R [9] but it remains true that a knowledge of C_6 is useful in discussing dispersion contributions to lattice energies. *Ab initio* calculation of C_6 is possible but perhaps more useful is the fact that a model for dispersion coefficients can be built on static polarisabilities [10], if certain approximations are made, and hence these parameters too come into the present review.

The contents of the article are as follows. §2 covers definitions and methods of calculation. §3 discusses choice of basis set. §4 the simulation of the crystal. Later sections present the physical picture of the in-crystal anion and models for α (§5) and C_6 (§6). Possible future directions are considered in the concluding section. The viewpoint adopted is that of a user who either wants to carry out further calculations on ions in solids (§§2-4) or who requires relable empirical parameters $\alpha^\pm$ and C_6 for construction of potential functions (§§5,6).

2 DEFINITIONS AND METHODS OF CALCULATION

(i) Definitions

The dipole polarisability [11] α is a symmetric 3×3 tensor whose components can be defined by the response of the energy of an atomic or molecular system to a uniform external electric field **F**:

$$\alpha_{\alpha\beta} = -(\partial^2 E/\partial F_\alpha \partial F_\beta)_{\mathbf{F}=0} \tag{5}$$

where Greek subscripts run over x,y,z. Equivalently, α can be defined in terms of the linear response of the system dipole moment to the applied field. For a system of electrons (charge -1. position r_i) and nuclei (charge $+Z_I$, position R_I) in a state ψ the dipole moment expectation value is the vector with components μ_a given by

$$\mu_\alpha = \langle\psi| - \sum_i r_{i\alpha} + \sum_I Z_I R_{I_\alpha} |\psi\rangle \tag{6}$$

and which is related to the energy in a field by

$$\mu_\alpha = -(\partial E/\partial F_\alpha)_{\mathbf{F}=0} \tag{7}$$

Thus an alternative expression for the polarisability is

$$\alpha_{\alpha\beta} = (\partial\mu_\alpha/\partial F_\beta)_{\mathbf{F}=0} \tag{8}$$

It is convenient to use atomic units in these equations, expressing distances in Bohr (a_0). energies in Hartree (E_h) and charges in multiples of the proton charge (ε). In this convention $\hbar$ and $4\pi\varepsilon_0$ take unit values, dipole moment is measured in $ea_0(\approx 8.4784 \times 10^{-30}\text{Cm} \approx 2.54177\,D)$, electric field in $e^{-1}a_0^{-1}E_h(\approx 5.1423 \times 10^{11}\text{Vm}^{-1})$ and polarisability in $e^2a_0^2E_h^{-1}$ ($\approx 1.6488 \times 10^{-41}\text{C}^2\text{m}^2\text{J}^{-1}$). Polarisability is often loosely described as a volume; the numerical value of α is the same in atomic units $e^2a_0^2E_h^{-1}$ and in a_0^3 ($1a_0^3 \approx 0.14815\,\text{Å}^3 = 0.148185 \times 10^{30}\text{m}^3$).

Of the nine components $\alpha_{\alpha\beta}$ at most six are independent since the definition (5) implies that $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$. This number is reduced if the molecule has non-trivial elements of symmetry. It is always possible to find an axis system in which $\alpha_{\alpha\beta}$ is diagonal. For a spherical atom or ion $\alpha_{xx} = \alpha_{yy} =$ so that $\alpha_{a\beta}$ can be specified by a single quantity

$$\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta} \tag{9}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta and

$$\alpha = \tfrac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{10}$$

is the mean polarisability. When the term 'polarisability' is used without qualification it is usually α that is implied.

Although the dipole moment of an ion has different values for different choices of coordinate origin, the polarisability is independent of this choice. α is positive for a system in its ground state, and can be qualitatively associated with the size and tightness of binding of the electron cloud. For example, the Kirkwood approximation [12] for α for a one-electron atom is proportional to the square of a radial expectation value

$$\alpha \sim \tfrac{4}{9}\langle\Psi|r^2|\Psi\rangle^2 \tag{11}$$

so that larger atoms are in general more polarisable. For the hydrogenic atom the value of α is inversely proportional to the fourth power of the nuclear charge

$$\alpha = \frac{9}{2Z^4} \tag{12}$$

so that, other things being equal, an anion will be more polarisable than a neutral or a cation.

Quantum-mechanical perturbation theory gives an expression for $\alpha_{\alpha\beta}$ as a sum over excited states (ψ_n, E_n) of the system

$$\alpha_{\alpha\beta} = \sum_{n\neq 0} \frac{2\langle\psi_0|\mu_\alpha|\psi_n\rangle\langle\psi_n|\mu_\beta|\psi_0\rangle}{E_n - E_0} \tag{11}$$

which shows that the polarisability is enhanced by the presence of low-lying dipole-

allowed excited states. Of more practical use than this infinite series (which is a sum over all discrete states and an integral over the ionisation continuum) is the integral formula

$$\alpha_{\alpha\beta} = 2\langle\psi_0|\mu_\alpha|\psi^1(F_\beta)\rangle \tag{14}$$

where $\psi^1(F_b)$ is the first derivative of the wavefunction with respect of the β component of the electric field. The so-called analytic methods for the calculation of α generally use (14) and are essentially ways of finding the first-order response of the election cloud either through ψ^1 or through the induced density change: $\Delta\rho^1 = 2|\psi_0\psi^1|$. Finite perturbation methods use either (5) or (7) implicitly by calculating the change in energy or dipole moment caused by an external field or set of charges.

(ii) Calculation

The various *ab initio* methods for evaluation of α differ in elegance and ultimate cost, but for the simplest problem — that the *static* dipole polarisability — they are all capable of producing equivalent results. The basic requirement for a calculation of α is a program that can evaluate the total electronic energy of a molecule at a given level of theory (SCF, CI, Møller-Plesset, etc.). Such programs (e.g. GAUSSIAN [13], CADPAC [14], SYSMO [15], MICROMOL [16]) generally also calculate the dipole moment at negligible extra cost in cpu time.

Given an energy program it is straightforward to obtain α by finite-perturbation methods e.g. FFT (the Finite Field Technique) [17]. When a system is subjected to a uniform electric field a term is added to the Hamiltonian

$$H^1 = -\mu_a F_\alpha = \sum_i r_{i\alpha} F_\alpha - \sum_I Z_i R_{I\alpha} F_\alpha \tag{15}$$

The first part of H^1 is a one-electron operator, the second an additive constant. The perturbation can be incorporated into a self-consistent treatment simply by adding a multiple of the matrices of cartesian integrals

$$\left\langle \chi_a \middle| \sum_i r_{i\alpha} \middle| \chi_b \right\rangle$$

(χ_a,χ_b are basis functions) to the matrix of the one-electron Hamiltonian. If the program is one that can calculate dipole moments, these integrals are already available. The new Hamiltonian can then be treated as usual to obtain the wavefunction,energy and dipole moment for the perturbed system. Since the two-electron integrals are unaffected by the field it is relatively cheap to repeat this calculation for different magnitudes and directions of **F**. If the program makes use of molecular symmetry, however, it is important to remember that these integrals must have been computed in the lower symmetry appropriate to the molecule + field system.

The polarisability can be calculated either from the energy change in the field or from the induced dipole moment. The Hellmann-Feynman theorem (HFT) for real eigenfunctions of a Hamiltonian with embedded paramters λ and v is

$$\left(\frac{\partial^2 E}{\partial v \partial \lambda}\right) = \left(\frac{\partial^2 E}{\partial \lambda \partial v}\right) = 2\left\langle \psi \middle| \frac{\partial H}{\partial \lambda} \middle| \frac{\partial \psi}{\partial v} \right\rangle = 2\left\langle \psi \middle| \frac{\partial H}{\partial v} \middle| \frac{\partial \psi}{\partial \lambda} \right\rangle \tag{16}$$

and guarantees the equivalence of the dipole and energy definitions of α. If the

wavefunction has been optimised with respect to all parameters then HFT holds. Thus, the two definitions of polarisability are equivalent for SCF, numerical Hartree-Fock and complete CI wavefunctions. They are *not* equivalent for Møller-Plesset and truncated correlated wavefunctions (e.g. singles-and-doubles CI).

Values of the applied field must be large enough to give a significant change in E or μ but should be small enough to avoid contamination by higher derivatives. For an atom

$$\Delta E = -\tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta + O(F^4) \tag{17}$$

$$\Delta\mu_\alpha = \alpha_{\alpha\beta}F_\beta + O(F^3) \tag{18}$$

and thus numerical differentiation of the dipole gives more significant figures. Fields of 0.0005 to 0.005 a.u. give reasonable accuracy in α, particularly if a differencing formula is used to extrapolate to zero field. Very large fields should be avoided as they can cause convergence problems. Finite-field calculation is a routine option in e.g. the CADPAC, SYSMO and MUNICH [18] progams.

An even simpler computational expedient is to use an array of point charges to supply the external field, thus avoiding any programming. This can be a useful way of producing non-uniform fields for evaluation of higher multipole polarisabilities but the bare charges can lead to difficulties with very diffuse basis sets. Bishop and coworkers [19] have used this method extensively and their papers give useful information on the choice and placing of charges. Again the effective symmetry to be used in the calculation of all integrals is that of the molecule + charge array. For calculation of dipole properties FFT is to be preferred.

Though easy to apply, the finite-field methods require multiple evaluations of the energy and wavefunction in reduced symmetry. Analytic techiniques in which polarisability is evaluated as a derivative property of *the unperturbed system* are potentially much more efficient. At the self-consistent field (SCF) level the most widely used technique is the coupled Hartree-Fock (CHF) [20] or Random-Phase Approximation (RPA) [21] where the first-order wavefunction $\psi^1(\mathbf{F})$ (or in RPA the set of transition amplitudes and energies) is evaluated exactly (within the finite basis). The time- and store-consuming step in such a calculation is the 4-index transformation of two-electron repulsion integrals from the atomic to the molecular orbital basis. The time for this step is roughly proportional to the fifth power of the number of basis functions. After the transformation the first-order equation for each perturbed molecular orbital can be solved self-consistently in the MO basis. The limitation of this method is that although the transformation can be shortened considerably by using Abelian point group symmetry, it is only with great difficulty that any higher symmetry can be used. Thus for molecules of moderate (e.g. C_{3v}) or high symmetry there is some loss of efficiency since the integral evaluation and energy calculation must be performed in the largest Abelian subgroup of the true molecular point group. Numerical problems with degenerate orbitals can occur when this non-degenerate subgroup is used. An advantage of the CHF/RPA approach is that many second-order properties are evaluated simultaneously. Dipole, quadrupole and mixed polarisabilities (α,C,A), nuclear magnetic and electric shieldings (σ^I,γ^I) and magnetisability (χ) can all be found at lettle extra expense once the main transformation has been done. The CHF procedure for these and other properties is a standard option in CADPAC, whilst SYSMO uses the equivalent RPA method to obtain them. A further advantage of the analytic approach is that it can be extended straightforwardly to embrace time-depen-

dent perturbations and hence dynamic polarisabilities for real and imaginary frequences — latter leading to *ab initio* values for C_6 dispersion coefficients.

Extension to correlated wavefunctions is more difficult but analytic calculations with Møller-Plesset (a perturbative treatment of correlation) [22]. Multi-configuration SCF [23] and CASSCF [24] (complete CI within a restricted active space) methods have been reported for atoms and small molecules. There are also higher-order propagator methods which correspond to correlated versions of RPA [25].

A different analytic approach avoids the bottleneck of the 4-index transformation by calculating the first-order density matrix iteratively in the AO basis; This is the McWeeny-Diercksen iterative SCF method [26], also known as Derivative Hartee-Fock (DHF) [27]. Its advantage is that it can utilise full molecular symmetry by taking into account the symmetry of the perturbation. Its disadvantage is that a separate, iterative calculation is required for each first-derivative wavefunction. Recursive extension to higher-order wavefunctions is relatively straightforward, and a time-dependent version of the algorithm has been described [28]. For very large, highly symmetric systems where the storage implications of a four-index transformation are prohibitive this will be the method of choice.

3 BASIS SETS

In some ways the most difficult part of a computation is the choice of a suitable basis. Any shortcomings introduced at this stage can produce hidden systematic errors. The counsel of perfection is to repeat every calculation varying the basis until stable results are obtained, but this is not always possible. However, much can be achieved by following a systematic approach to basis construction. For calculations of ionic polarisability the steps are: Take a good basis for the occupied orbitals of the neutral atom, modify it in the case of a negative ion, and polarise it to describe the response to an electric field.

Almost all calculations within the algebraic approximation now use basis sets of Gaussian-type functions (GTFs): $\chi \sim x^l y^m z^n exp(-\xi r^2)$. Because a GTF has an incorrect radial dependence at the nucleus and at large distances, for good polarisabilities it is necessary to use more functions than in, say, a typical basis of Slater orbitals ($\sim x^l y^m z^n exp(-\xi r)$). However, the ease of computing Gaussian integrals outweighs this disadvantage. Optimised exponents and contraction coefficients have been tabulated for most of the atoms in the Periodic Table, generally having been chosen to minimise the total energy of the neutral atom in its ground state. The family of basis sets built into the GAUSSIAN programs [13], for example, spans the range from minimal to split-valence + polarisation quality; polarisation in this sense is the loss of spherical symmetry by an atom in a molecular environment and is not directly linked to molecular dipole polarisation. These small sets are mainly of use in calculation of molecular energetics. Larger sets which are more suitable starting points for property calculations include those of van Duijneveldt [29] and Huzinaga [30] where each occupied orbital in the atom is represented by about six GTF primitives, usually contracted for the core orbitals.

In applications to cations it is usually to take the neutral-atom exponents without modification, or to scale them up by a few per cent to allow for the greater effective nuclear charge. With energy calculations on anions, however, it is essential to take into account the weaker binding of the electron cloud. This is done by adding diffuse

functions — extending the $s, p \ldots$ exponents in geometric progression down to very low values ($\xi < 0.01 a_0^{-2}$).

In a calculation of α it is necessary to represent both the unperturbed wavefunction ψ^0 and the first-order function ψ^1 which spans the representation $\Gamma(\mu) \times \Gamma(\psi^0)$. Thus, in spherical symmetry, if ψ^0 contains an occupied orbital of angular mometum l, ϕ_l, the basis for ψ^1 should include functions like $\phi_{l\pm1}$; first-row atoms require only s and p functions for an energy calculation but need a full *spd* basis for a calculation of α. The exponents for the polarisation functions can in principle be chosen by optimising the total energy in a small finite field, since for *the exact ground state wavefunction* the Hylleraas variation principle [31] guarantees that a will be a lower bound to the true value. In practice it is more usual to take as large a set of polarisation functions as can be afforded and to spread the exponents in a pattern determined by one of Werner and Meyer's magic sequences [32]. Thus, one polarisability basis [33] for F^- has $5d$ sets and the pattern of exponents is $(32\eta, 9\eta, 3\eta, \eta, \frac{1}{3}\eta)$ where η is the value of the eighth exponent in the diffuse p basis. In a molecular context (or in an ion cluster) the high exponents serve to improve the ground-state energy (polarisation in the 'other' sense) and the lower ones describe the response to the field. Some rather smaller sets that give extremely good results for first-row atoms have been published by Sadlej [34] but they would need to be augmented with diffuse functions for use with anions.

In the calculations reviewed here basis sets were found or constructed for the polarisability of the anions H^-, C^{4-}, O^{2-}, S^{2-},Cl^- and Br^-. Details are given in the original references [4–10,35,36]. Large sets for cations were also used (Li^+, Na^+, Mg^{2+}, K^+, Mg^{2+} K^+, Ca^{2+}, Ag^+, Rb^+) but a different type of cation basis was designed for the work on ion clusters. As will be described later, the small cations are almost unaffected by the crystalline environment; the rôle in our model is to help compress their softer anionic neighbours. In calculations on ion clusters (M^+) (x^-), therefore, an accurate and economical cation basis is found by taking the ground-state SCF orbitals of the free cation *as basis functions*. The SCF eigenvectors are interpreted as lists of contraction coefficients. This gives a *minimal* (highly contracted) basis which produces the same energy and charge density as the much larger parent set. For Li^+, for example [5], a $(10s) \rightarrow [1s]$ contraction is used. In a further refinement, the exact polarisability of the Li^+ in the large *sp* set can be recovered by taking the CHF first-order wavefunction as a contracted basis function, so that $(10s8p)$ reduces to $[1s1p]$. identification of basis functions with atomic orbitals in this way also has advantages for separation of basis-set-superposition error.

4 SIMULATION OF THE CRYSTALS

(i) Electrostatics

Inherent in the cluster treatment of ionic solids is the assumption that features of the *local* environment of an ion determine its properties. The most obvious fact about an ionic solid is that it consists of an infinite lattice of charge centres. If exchange of electrons between ions and the physical overlap of charge clouds can be ignored, the problem reduces to that of a single ion in a point-charge lattice. The potential energy of an electron belonging to this ion may be divided into a spherical term (attraction to its own nucleus, repulsion from other electrons on the same centre) and a term having the symmetry of the crystal site $- V^1$, the interaction with an infinite lattice of point-charge neighbours. The latter term acts as a (strong) perturbation of the

electronic structure and can be expanded in a series of spherical harmonics:

$$V^1(r) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} V_{lm}(r) Y_l(\theta,\phi) \tag{19}$$

as in crystal-field theory. For sites of cubic (O_h) symmetry the first non-vanishing terms are

$$V^1(r) = V_0(r) + V_4(r)K_4(\theta,\phi) + V_6(r)K_6(\theta,\phi) + \ldots . \tag{20}$$

and for tetrahedral site the anisotropy of lowest order is at $l = 3$ with a term in $K_3(\theta,\phi)$ i.e. $\sim xyz$. For ions which have s^2 or p^6 outer shell configurations the crystal potential is thus dominated by the isotropic spherically averaged potential $V_0(r)$. Splittings induced by anisotropic terms become significant only when d orbitals are occupied in the ground state.

As has been well documented [5–8,37], the spherical part of the crystal field potential provides extra stability for *anion* electrons by trapping them in a potential well with a flat bottom ($V_0(r)$ is constant out to R, the nearest-neighbour distance) and a steep wall at R. The precise details of well-depth, steepness of the wall and functional form of the oscillations in the potential for large r vary from structure to structure but the overall effect of V_0 is always to compress the anion charge cloud, and hence to decrease its polarisability.

In practical calculations of anionic properties the crystal-field perturbation can be included several ways. The easiest is to embed the ion of interest in a finite array of point charges. The Madelung sum in all but the simplest lattices has notoriously poor convergence properties but these can be overcome by scaling of the lattice charges — for example in a rocksalt fragment consisting of a cube of $(2N + 1) \times (2N + 1) \times (2N + 1)$ sites the outer charges are reduced by a factor of 2, 4 or 8 according as they lie on a face, edge or corner of the cube [5]. As Evjen has shown [38], this leads to a convergent Madelung potential. For properties of the central ion the convergence is even more rapid; the crystal-field polarisability of F^-, for example, reaches its limiting value in a lattice of only 125 centres [5] (Table 1). The physical interpretation of such stability is that the compression is a local effect occurring at the first steep change in $V_0(r)$. i.e. at the nearest-neighbour distance. Once the array of changes is sufficient to represent $V^1(r)$ within the first couple of shells, all the effect of the lattice on the polarisability is captured. Conversely, this implies that it is not necessary to go great lengths to reproduce the exact Madelung potential with the point charges; if the *change* in potential across the first shell boundary is correct, an overall shift in the zero of the potential is immaterial.

The point-charge method also implicitly includes the anisotropic terms $V_4(r)$ . . . . Comparison with simulated spherically symmetric arrays (actually concentric icosahedra) shows that V_4 has an influence of less than 1% on the CHF polarisability of F^- in an LiF point-charge lattice [7].

Table 1 Convergence of coupled Hartree-Fock polarisability for F^- in a fragment of the LiF point-charge lattice. Details of basis set and the method of calculation are given in [5]. Q is the absolute value of the mean second moment of the charge density of F^-. All quantities are quoted in a.u.

Lattice Size	$\alpha(F^-)$	$Q(F^-)$
5 × 5 × 5	7.300	5.014
7 × 7 × 7	7.299	5.014
9 × 9 × 9	7.299	5.014

The lattice interaction of an electron on a cation site is reversed in sign with respect to an anion site; the crystal potential stabilises positive charges at cation sites and therefore destabilises electrons. However, the electrons on cations are firmly held by the higher effective nuclear charge and the charge cloud is much less diffuse than for an anion. The consequence is that cation electrons sample only the constant plateau of the $-V_0(r)$ function, and for them the crystal-field does not cause internal rearrangement of the charge destribution of change in properties. For this reason, the increase in polarisability predicted for in-crystal cations by e.g. Ruffa's semiempirical model [39] is not found to occur in *ab initio* calculations on Li^+, Na^+, Mg^{2+} . . . . In this respect anions and cations are not symmetrically related in the theory of crystal refractive indices. Many empirical models have failed to incorporate this important fact.

Perhaps more elegant than the use of a point-charge lattice is the direct inclusion of partial-wave components $V_0(r)$, $V_4(r)$ . . . in the one-electron Hamiltonian [37]. The latter technique lends itself to the pseudopotential representation of overlap and exchange, but is less suitable for the full Hartree-Fock treatment of these effects. Simplified $V_0(r)$ functions have been derived by reducing the whole crystal to a single charged sphere — the Watson sphere [40]. This is quantitatively inaccurate, though qualitatively reasonable, for anions [7,41]. It can lead to misleading results for cations (see [42] and the discussion in [4]) and is not substantially cheaper than the explicit point-charge method.

(ii) Overlap compression

If the point-charge lattice expresses the most obvious factor in the crystalline environment, it neglects the second most obvious feature — that the neighbours of an ion are extended charge clouds. The full perturbation of a central ion has a classical electrostatic contribution from charge-overlap ('charge penetration'), and also an exchange repulsion term ('Pauli repulsion') caused by the orthogonalisation of orbitals on neighbouring ions. Both are relatively short-range effects and can be accounted for by explicit inclusion of the electrons and orbitals on the neighbours in a cluster supermolecule calculation. The effect of the cage on an anion is to compress it even more than the point-charge lattice alone [5]. An anion behaves as if compressed in a pseudo-potential well with a radus smaller than R. One could take this picture literally and attempt to represent the overlap compression by a local or non-local pseudopotential added to the perturbation Hamiltonian, though there is the perennial problem of parameterisation in such models [37]. It seems more direct to use the cluster approach.

Calculations on anions in clusters appropriate to alkali halides and chalcogenides [5–8] show several important trends; they give anionic polarisabilities in good agreement with experiment; they are generally insensitive to removal from the embedding point-charge lattice; correlation contributions to polarisability are reduced by comparison with the ion in a point-charge lattice, and especially strongly with respect to the free ion. These points are illustrated in Table 2. It is clear that the first shell is dominant and also that overlap is a vital factor in modifying the properties of the free anion.

For cation the extra effect of overlap will be small and opposed to the crystal-field tendency to expansion. Cluster calculations where the central ion has a positive charge are not therefore necessary. For cases where the cation is sensitive to its environment

Table 2 Comparison of *ab initio* (embedded cluster) and experimental polarisabilities for anions in crystals (all in a.u.). $\Delta\alpha_{MP}$ is the correlation correction to the CHF value. See the listed references for details of basis sets and method. Experimental values are derived from the tabulation of α_m in [4].

Anion	*ref.*	α_{CHF}	$+\Delta\alpha_{MP}$	$=\alpha(total)$	$\alpha(expt)$
F^- in LiF	[5]	5.39	0.79	6.18	5.98
F^- in NaF	[6]	6.37	(1.2)	7.57	6.95
Cl^- in LiCl	[6]	18.89	0.48	19.4	19.4
Cl^- in NaCl	[6]	20.23	(0.7)	20.9	21.2
O^{2-} in MgO	[7]	10.96	1.37	12.32	11.4
S^{2-} in MgS	[8]	29.25	(0.2)	29.4	31.0
Br^- in NaBr	[36]	27.5	1.0	28.5	28.8
C^{4-} in Be_2C	[35]	19.5	-	-	21.8

(e.g. Ag^+ [5]) it is not clear that a cluster calculation would be useful, since both the cation and its cage of anions would react to overlap and electrostatic factors, and it would not be easy to disentangle the results. By contrast, the situation for an anion in a cage of small, hard cations is relatively easy to understand.

It is possible to mimic the full in-crystal reduction of α for a diffuse anion by using a small basis (with an artifically low α) and only point charge neighbours [43] (or indeed a Watson sphere), but it is difficult to gauge the reliability of such calculations outside the example to which they are fitted, and they obscure the physics of the crystal. Furthermore, the aim of calculation is not primarily to reproduce experimental data, but by reproducing it to suggest or justify a physical interpretation. An *ab initio* calculation that failed to give an accurate result would be useless, just as an empirical calculation that *only* reproduces the observable would have little point.

(iii) Basis set superposition error

In calculations of intermolecular interaction energies it has been found that small basis sets often give spuriously high binding energies because of an effect known as basis set superposition error (BSSE) [44]. When systems *A* and *B* are in close proximity the basis functions assigned to *B* may improve the description of the monomer *A* and *vice versa*. This mathematical artefact lowers the monomer energies in the complex and may also affect other electrical properties. Though the cause is easy to describe, and the counterpoise method [44] for eliminating the error has been used for many years, there is still disagreement about the precise way to carry out the correction [45].

For ions in clusters a similar effect on the polarisability can arise when an anion is surrounded by a shell of minimal-basis cations. The polarisability of the cage is then formally zero but the cations may 'borrow' from the diffuse polarisation functions on the anion and thus achieve some fraction of their own total polarisability. A finite-field calculation on the whole cluster would give a total α contaminated to some extent by this spurious cation term. The ideal solution is to use a polarisable basis for the cations, as in the example of the [1*s*1*p*] basis for Li^+. A cation then has no need to borrow functions and the total cluster polarisability, apart from the small DID effects to be dealt with in the following subsection, reflects the sum of anion and cage terms. Where the error cannot be avoided, three different ways to correct for it have been used. A counterpoise correction can be made, in which the BSSE-generated cage polarisability is evaluated in the presence of a 'ghost' centre, consisting of a nuclear

charge equal to the norminal anionic charge and carrying the basis functions but not the electrons of the anion [5]. This may over-estimate the BSSE effect and is expensive. A second way is to freeze the cation electrons in the CHF procedure— i.e. to construct perturbed molecular orbitals for the occupied orbitals on the anion only and to eliminate cage MOs from the 4-index transformation [7]. Perhaps the most satisfactory way, and certainly the easiest to apply, is to partition the total polarisability into orbital contributions. The contributions from cage-localised MOs are then simply subtracted from the total property [35]. If there is good separation of anion and cage MOs this works well; if there is not, then the ion-cluster approach was probably inappropriate in the first place. This last method can be applied within the finite-field or analytic approaches if orbital contributions to the perturbed dipole moment or analytic polarisability are computed. These may be available as intermediate quantities in the computation, or may need to be evaluated from the final perturbed density matrix.

With properly chosen basis sets the BSSE in the reverse direction (anion → cage) should be insignificant. Again it can be calculated by the ghost orbital counterpoise method, though it is necessary to project out the cation core orbitals if spuriously high BSSE is not to be predicted through localisation of anion electrons on the bare point charges at the cation sites, unshielded by their cores. As mentioned earlier, the highly contracted minimal + polarisation basis sets for cations facilitate this projection — basis functions are simply dropped in the counterpoise calculation.

(iv) Dipole-induced-dipole correction

The effective polarisabilities α^+ and α^- derived *via* the Clausius-Mossotti relationship are corrected for the effects of induced local fields. Similar effects are present in a cluster calculation and can be removed by the same classical electrostatic procedure [46] — in the approximation of point ions — to yield *ab initio* quantities that are formally comparable with experiment.

In first order, the DID interaction between a central ion I and its cage of polarisable neighbours J leads to an enhancement of the total cluster polarisability of

$$\Delta\alpha_{\alpha\beta} = \alpha^I \alpha^J \sum_J T^{IJ}_{\alpha\beta} \tag{21}$$

where two ions at $\mathbf{R}_I$ and $\mathbf{R}_J$ interact by the dipole-dipole tensor

$$T^{IJ}_{\alpha\beta} = \frac{(3R^{IJ}_\alpha R^{IJ}_\beta - (R^{IJ})^2\delta_{\alpha\beta})}{(R^{IJ})^5} \tag{22}$$

For cubic site symmetries this first-order contribution vanishes. The most important term in second order is the one bilinear in α^I, given that α^J is small (as is usual for an anion in a cage of cations). It is

$$\Delta\alpha_{\alpha\beta} = (\alpha^I)^2(\alpha^J) \sum_{J,\gamma} T^{IJ}_{\alpha\gamma} T^{JI}_{\gamma\beta} \tag{23}$$

and accounts for the 'back-induction' i.e. reaction of the central ion to the dipoles which it has itself induced on the cage of cations. For cubic site symmetries this reduces to

$$\Delta\alpha_{\alpha\beta} = 2N(\alpha^I)^2(\alpha^J)\delta_{\alpha\beta}R^{-6} \tag{24}$$

where N is the number of ions at the nearest neighbour distance R. DID effects are typically of the order of 0.03 a_0^3 for lithium halide clusters [5].

(v) Charge Transfer

The partition of the refractive index of a solid into ionic contributions relies upon the concept of identifiable ions within the lattice, even if their properties are renormalised by the interaction with their neighbours. Formation of covalent bonds, or an appreciable transfer of charge compared with the fully ionic structure, would vitiate the ion-cluster approach. Within cluster calculations it is necessary to diagnose charge transfer (CT) if it occurs.

Charge transfer is often a contentious issue in the description of electronic structure, because its apparent magnitude is so model-dependent. If an interaction distorts the shape of an ion, for instance, then this may be described as polarisation or CT depending on where the boundary surfaces are drawn. Mulliken populations are often used to give an indication of CT, but these quantities are not totally reliable; they do not reproduce the overall dipole movement of a molecule, and they can be upset by imbalance in the basis. For example, the gas-phase NaCl pair could be described in a *complete* basis on one centre — this centre could move from Na to Cl or to the bond midpoint. The populations on Na and Cl would vary wildly in the process but the physical observables calculated in this infinite basis would be constant. Statements about CT in a calculation often assume that the description of electronic structure is 'balanced', i.e. that it is 'of equal quality' at all atomic centres. These imprecise notions are not testable.

For ionic solids we have taken a more pragmatic viewpoint. If a property calculated for a large anion basis does not change when virtual orbitals are added to the representation of the cation cage, then CT is unimportant. If the Mulliken and nominal charges are in agreement then this also is supporting evidence for ionic structure, though not proof of it.

Possible CT effects in LiF were investigated [5] by calculating the cluster polarisability for F^- in an $(Li^+)_6$ with (i) minimal, (ii) polarisable (iii) split-valence + polarisable cation basis sets. The cluster polarisability rises between steps (i) and (ii) as expected, but addition of '2s'-like orbitals on Li^+ causes hardly any change. Note that any appreciable movement of charge in the sense $F \rightarrow Li$ should have significant effects on α; Li^+ is almost unpolarisable, but a neutral lithium atom has a polarisability of over 150 a.u. because of the near degeneracy of $2s$ and $2p$ levels [47]. From these calculations it was concluded that CT is unimportant in α_m (LiF).

Similar numerical experiments on Be_2C [35] suggest a small transfer in the sense $C^{4-} \rightarrow Be^{2+}$, causing an increase in the calculated $\alpha_m(Be_2C)$ of 1–2%. The Mulliken charges in the same calculation show $\sim$ 3.8 excess electrons on the C centre. The ionic model, even in this extreme case, gives a quantitative account of the refractive index.

5 MODELS FOR IONIC POLARISABILITY

The physical picture of an anion in a crystal that emerges from the *ab initio* calculations is a simple one. The primary effect of the crystal is to compress the diffuse charge cloud of a free anion and to render it less polarisable. The combined and reinforcing effects of electrostatic and overlap compression create a spherical potential well, with

a characteristic radius of $\sim (R - r_+)$ where r is the nearest neighbour distance and r_+ is the cation radius, and thus anion polarisabilities become functions of lattice parameter, and to a lesser extent, of lattice type. Free anions are difficult objects to study, both physically and theoretically. Their polarisabilities are dominated by outer electrons which are bound weakly, if at all, and are highly correlated. By contrast, the anion in a solid is much more like a slightly diffuse inert gas atom. The crystalline environment stabilises (or binds) the polarisable electrons, quenches the raidal electron correlation and lowers the total polarisability. Cations of main-group metals are insensitive to their environment and have effectively constant polarisabilities.

Several empirical models for α^+ and α^- have been constructed before but they are unsatisfactory because they are too inflexible [1] (constant α^+ *and* α^-) and give poor results, or they are based on unobservable quantities [48] (e.g. the 'free-ion polarisability' for O^{2-}, an unbound system). or they include unphysical assumptions (e.g. cations that expand enormously in the crystal field [42]). A critique of models of these types has been made before [4] and need not be reproduced here. On our physical picture an empirical model can be expected to provide at most the following information; a constant value for α^+, usable in any crystal, and a functional form for $\alpha^-(R)$ from which α^- in particular crystals can be estimated. The model published by Fowler and Pyper [4] does this.

Starting from a set of reliable *ab initio* polarisabilities for small cations (Li^+, Na^+, Mg^{2+}, K^+, Ca^{2+}) and the experimental α_m for halides and chalcogenides, the variation of α^- for a set of anions (F^-, Cl^-, Br^-, I^-, O^{2-}, S^{2-}) was deduced and fitted to a simple function of nearest-neighbour distance:

$$\log_{10} \alpha^-(R) = BR^{-2} + CR^{-4} \ldots \tag{25}$$

Other functions such as [37]

$$\alpha^-(R) = A' + B'R^{-1} + C'R^{-2} \ldots \tag{26}$$

would be equally acceptable. The general form of the variation with R is expected from work on one-electron model problems [49] to be a smooth sigmoid curve for bound anions, and a more steeply rising monotonic curve for unbound anions. The function parameters appear to be roughly transferable between different structural types e.g. $\alpha^-(F^-$ in $CaF_2)$ differs by only $\sim 5\%$ from the value predicted for a hypothetical rocksalt fluoride with the same nearest-neighbour distance [4]. Using the anion curves it is possible to extract cation polarisabilities for Rb^+, Cs^+, Tl^+, Pb^{2+}. The model can be checked for self-consistency by the constancy or otherwise of the prediction for a given cation obtained in different salts. The variations lead to small error bars on each α^+. Table 3 gives the cation polarisabilities and a selection of anion polarisabilities derived in this way.

Some cations do not appear in Table 4 because they do not in fact have constant polarisabilities. Such are the d^{10} systems Ag^+ and Cd^{2+}. Use of the $\alpha^-(R)$ functions for F^- gives [4]

$$\alpha^+(Ag^+ \text{ in } AgF) = 11.8 \text{ a.u.} \tag{27}$$

$$\alpha^+(Cd^{2+} \text{ in } CdF_2) = 7.1 \text{ a.u.}, \tag{28}$$

both significantly larger than the CHF value free-ion values of 8.28 a.u. and 4.70 a.u., respectively, $\alpha^+(Ag^+)$ may also vary with the counterion. These effects arise essentially from the splitting of the polarisable d orbitals, though detailed calculations are

Table 3 Empirical values for ionic polarisabilities. Cation values are classified as either T (*ab initio*) or M (derived from α_m by substraction of the anion function $\alpha^-(R)$). Anion values are S (derived from α_m by direct subtraction of *ab initio* cation values). All polarisabilities are given in atomic units.

Ion	α	*source*
Li^+	0.192	T
Na^+	1.002	T
K^+	5.339	M
Rb^+	9.05 ± 0.15	M
Cs^+	15.28 ± 0.27	M
Mg^{2+}	0.486	T
Ca^{2+}	3.193	T
Sr^{2+}	5.20 ± 0.06	M
Ba^{2+}	10.1	M
Tl^+	28 ± 1	M
Pb^{2+}	17.9	M
F^- in LiF	5.98	S
F^- in NaF	6.95	S
F^- in KF	8.10	S
Cl^- in LiCl	19.60	S
Cl^- in NaCl	21.15	S
Cl^- in KCl	22.86	S
Br^- in LiBr	26.9	S
Br^- in NaBr	28.8	S
Br^- in KBr	30.6	S
I^- in LiI	39.6	S
I^- NaI	41.8	S
I^- in KI	44.9	S

necessary to apportion the polarisability enhancement between anisotropic electrostatic and overlap interactions. It is interesting that overlap repulsion can, through its anisotropic part, give rise to *increased* polarisability. Assigning a constant polarisability to a d^{10} cation would lead to incorrect results for the counterion in the decomposition of α_m.

An indication of how the tabulation could be extended is given by unpublished work on UO_2 by Fowler and Pyper. Taking the dielectric constant $\varepsilon(UO_2)$ to be 5.3 and a U–O distance of 2.3678 Å (in the fluorite structure), it is likely that the oxide ion has a polarisability of about 15.5 a.u. and therefore by subtraction $\alpha^+(U^{4+}$ in $UO_2)$ is about 8 a.u. – a very large value for a 4+ cation but perhaps explained by the open-shell electronic structure.

Table 4 Variation of the F^--F^- dispersion coefficient with environment. All values are computed by CHF theory and are in atomic units. (1 a.u. of $C_6 \equiv E_h \cdot a_0^6 \approx 9.5736 \times 10^{-80}$ Jm^6 $\approx$ 597.57 meV.Å^6) N is the effective number of electrons that the static polarisability (α) and C_6 obey the Slater-Kirkwood relationship.

Environment	$\alpha(F^-)$	$C_6(F^-\text{-}F^-)$	N_A
Free ion	10.65	40.5	2.41
CsF point charge	9.78	37.5	2.67
RbF point charge	9.49	36.4	2.76
KF point charge	9.20	35.4	2.85
NaF point charge	8.29	31.7	3.14
LiF point charge	7.30	27.6	3.47
LiF full cluster	5.41	19.4	4.24

This model can also make predictions about ions in less symmetrical situations. For example, at a surface site the anion charge density is less compressed by overlap but more strongly held by anisotropic fields so that α^- remains close to its bulk value even in 5-, 4- and 3-coordinate sites [50].

6 MODELS FOR DISPERSION COEFFICIENTS

C_6 dispersion coefficents are closely related to polarisabilities (see equation (4)) and are expected to show the same kind of sensitivity to the crystalline environment. *Ab initio* calculations by time-dependent coupled Hartree-Fock theory have been used to find a^+ and α^- as functions of imaginary frequency for several ions (Li^+, Na^+, F^-, Cl^-, O^{2-}) and to derive all the relevant pair C_6 coefficents [10]. Table 4 shows that $C_6(F^-,F^-)$ for example follows the trend in the static polarisability; both fall with R and both are reduced strongly by nearest-neighbour overlap. *Ab initio* values for various 2- and 3-body dispersion coefficents have been obtained in this way. They can be used directly, but also suggest an empirical model of much wider application.

The polarisability $\alpha(i\omega)$ is a monotonic function of imaginary frequency, without the poles of its real-frequency conterpart, and which falls smoothly from the static value to zero as $\omega \to \infty$. The simplest possible approximate functional form for this variation is the one-term Padé expression:

$$\alpha_A(i\omega) = \frac{\alpha_A \eta_A^2}{\eta_A^2 + \omega^2} = \frac{\alpha_A N_A}{N_A + \alpha_A \omega^2} \tag{29}$$

where

$$\eta_A = \left(\frac{N_A}{\alpha_A}\right) 1/2 \tag{30}$$

N_A is an effective number of electrons, and α_A is the static polarisability of species A. Substitution in the integral expression (4) for C_6 gives the Slater-Kirkwood approximations [51]

$$C_6(A,B) = \frac{3\alpha_A \alpha_B \eta_A \eta_B}{2(\eta_A + \eta_B)} \tag{31}$$

$$C_6(A,A) = \frac{3\alpha_A^2 \eta_A}{4} \tag{32}$$

From the experimental values of C_6 and α_A for inert-gas atoms a set of 'experimental' values of N_A can be found (see Table 5 and [10]), and these yield accurate off-diagonal dispersion coefficients $C_6(A,B)$. On analysis of the *ab initio* results for F^-, O^{2-} and Cl^- it is clear that the '*ab initio*' values of N_A for the fully compressed in-crystal anions are close to those for the isoelectonic inert gas atoms. Compare, for example, $N_A = 4.24$ for F^- and 4.46 for Ne, 5.64 for Cl^- and 6.11 for Ar.

A simple model for C_6 coefficients can be based on this observation. For an ion pair A,B

$$C_6(A,B) = \frac{3\alpha_A \alpha_B N_A^{1/2} N_B^{1/2}}{2[\alpha_B^{1/2} N_A^{1/2} + \alpha_A^{1/2} N_B^{1/2}]} \tag{33}$$

Table 5 Effective electron numbers for noble gas atoms, derived in [4] from the Slater-Kirkwood relationship.

X	N_v
He	1.430
Ne	4.455
Ar	6.106
Kr	7.305
Xe	7.901

where N_A and N_B are taken from the appropriate inert gas atom in Table 5, and α_A,α_B are taken from our polarisability model (Table 3). It follows that cation-cation coefficients will be constants but cation-anion and anion-anion dispersion coefficients will vary with environment. Results from this model are given in Table 6.

To apply these C_6 coefficients in practical calculations of interaction potentials a damped multipole series should be used to account for the effects of charge overlap on the long-range formula (3) for the energy. This problem has been discussed elsewhere [9]. Higher-order C_8 coefficients have also been calculated [52].

One application of this model is to the old problem of the non-rocksalt structure of CsCl. Cs^+–Cs^+ dispersion interactions would provide a driving force for the switch in structure, and some very large values for the C_6 coefficients have been proposed from time to time. Our model predicts $C_6(Cs^+ - Cs^+) = 125.9$ a.u. and rules out 2- or 3-body dispersion as the cause of the structural change [10].

7 CONCLUSION

It is now possible to calculate accurate in-crystal polarisabilities for a number of ions and to model the properties of many more. The model is physically based and leads to predictions for dispersion coefficents and for ions in low-symmetry environments. Polyatomic ions offer the next challenge to *ab initio* theory; for them properties may vary not only with counterion but also with orientation within the crystal lattice [53].

Table 6 Selected C_6 coefficients (in a.u.) for ions in crystals, obtained from static polarisabilities by the model described in the text.

A	B	C_6(A,B)
Li^+	Li^+	0.078
Na^+	Na^+	1.588
K^+	K^+	22.86
Rb^+	Rb^+	55.19
Cs^+	Cs^+	125.9
Mg^{2+}	Mg^{2+}	0.536
Li^+	F^- in LiF	1.130
F^-	F^- in LiF	23.17
Na^+	Cl^- in NaCl	13.61
Cl^-	Cl^- in NaCl	180.3
Mg^{2+}	O^{2-} in MgO	4.29
O^{2-}	O^{2-} in MgO	60.49
Cs^+	Cl^- in CsCl	164.9
Cl^-	Cl^- in CsCl	223.7

Solids with less markedly ionic bonding may be more difficult to treat by these methods, but also offer a rich field for future exploration and modelling on the basis of 'chemical' concepts.

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